STUDIES IN REGULAR SOLUTION THEORY

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ABSTRACT

The development of Regular Solution theory for binary and ternary mixtures is discussed and the reasons for its failure are noted.

The thermodynamic properties of ternary nonpolar mixtures have been predicted using a modified version of the solubility parameters for the mixed solvents. Excellent agreement between theoretical and experimental properties is observed for dilute ternary mixtures. The theory has also been extended to the concentrated solutions but not with much success, and the probable reasons for this failure are also noted.

The "scaled particle" theory of fluids is used in calculating the partial molal entropy of solution of solid solutes and has been found to be in excellent agreement with the experimental results from different sources.

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INTRODUCTION

The properties of nonelectrolyte solutions are of great interest to chemical engineers for whom they represent design data and to chemists for whom they represent a source of information about intermolecular forces and the thermodynamic behaviour of molecules in solutions. From either point of view the aim is to develop methods that will be able to predict the properties of solutions either from the results of a few measurements on solutions or more hopefully from the properties of pure components.

Since the early twentieth century, many attempts have been made to develop theories of the solutions of nonelectrolytes but the most widely used and the most successful theory in its limited field is the Regular Solution theory. This theory was first developed by Hildebrand to calculate the thermodynamic properties of solutions of nonelectrolytes. It is one of the simplest theories proposed on this subject and over the decades it has been the basis of many discussions and many improvements on the theories of solutions. In Chapter I we shall discuss the different aspects of Regular Solution theory and its limitations.

The most attractive systems for studying on the basis of Regular Solution theory are the three component systems whose components have almost similar molar volumes. In such cases the effects of molar volume disparities of the components on the free energy of mixing would be negligible. The extension of the Regular Solution theory, which was originally developed for binary systems, to ternary systems assumes that the ternary systems may be considered as a pseudo-binary system of one solute and one mixed solvent whose solubility parameter is given by the volume fraction average of the solubility parameters of the components of the mixed solvent. Although the resultant solubility equation is a very simple one, unfortunately it has been observed from solubility studies of solid solutes in mixed solvents (all three components are nonelectrolytes) that the experimental saturation solubility is always greater than the predicted value. In earlier studies of the partial molal volumes of Br_2 in CCl_4 - n-C_7F_{16} and in CCl_4 - c-$C_4Cl_2F_6$ mixed solvents, it was shown that the partial molal volume of Br_2 is less than the calculated values derived from the assumption that the solubility parameter of the mixed solvents is given by the volume fraction average of the solubility parameters of the components of the mixed solvent. Such an assumption about the solubility parameter of the mixed solvents implies that the distribution of components of the mixed solvents around the solute molecule depends upon the volume fraction of the components and not on the interactions of the solute molecules with the individual components. In this thesis it is proposed to study the effect of solute - pure solvent interactions on the solubility studies of solid solutes in the mixed solvents. A detailed account of the studies of iodine, stannic iodide and other solid solutes in mixed solvents will be presented, and a theory developed which allows the ratio of the "nearest neighbours" mixed solvent component molecules around the solute molecules to be calculated. This new term, denoted as the "effective volume fraction," is introduced to represent the nearest environment of the solute molecule in the mixed solvents.

This "effective" volume fraction essentially implies a preferential solvation of the solute molecules by one solvent partner in the mixed solvent. By making allowances for this preferential solvation of the solute molecule, it will be shown that the Regular Solution theory can be successfully applied to explain all the available data on the solutions of the nonpolar solid solutes in nonpolar mixed solvents.

In Chapter II of this thesis we shall discuss the different aspects of the three component systems.

The other interesting phenomenon to study is the effect of solvent-solute volume disparity in the binary systems because it is well known that if the solvent-solute volume disparity is too large, the entropy of mixing of supercooled liquid (the assumed standard state of the solids in the Regular Solution theory) solute and the liquid solvents are no longer zero and Regular Solution theory can not be applied successfully in these cases. It is difficult to calculate the magnitude of the excess entropy because it has been observed that for spherical solid solute molecules such as tetraphenyl tin the usually used "Flory-Huggins" entropy of mixing to take account of the volume disparity between solute and solvent are usually unreliable. To examine the effect of the solvent-solute volume disparity on the solubilities of the solids, we have carried out the solubility studies along with the experimental determination of the partial molal volume of tetra perfluoro phenyl tin ($Sn(C_6F_5)_4$) whose molar volume is 404.4 cc in different organic solvents of molar volumes around 100 cc.

In this thesis we shall also present a method to calculate partial molal entropy of mixing solid solutes in liquid solvents. This method will be developed from the scaled particle theory of dense fluids and it will also be shown that this method can successfully be applied in predicting the partial molal entropies of iodine, stannic iodide, tetraphenyl tin, along with tetra perfluorophenyl tin. We developed this method to calculate partial molal entropy because, as mentioned earlier, the Regular Solution theory usually can not cope with systems such as ours and the Flory-Huggins entropy term is unreliable.

In Chapter III we shall discuss the scaled particle theory and its application in deriving the properties of pure liquid and binary liquid mixtures.

Chapter - I

Regular Solution Theory

Any complete understanding of mixtures of nonelectrolytes must need a clear solution of the problems involving intermolecular forces in the theory of the liquid state. To date there exist only approximate treatments but it is surprising that these theories can be applied more successfully in formulating the theory of solutions than one would expect from the drastic approximations involved in them. Or conversely it could be said that the empirical success of the theories of the solutions may not be used to justify the theories of the liquid state or of intermolecular forces from which the postulated theory has been derived. Under these circumstances we shall discuss the theories on the liquid state and intermolecular forces very briefly and the main topic of our discussion in this chapter will be the Regular Solution theory which, as Scott[1] wrote in 1956, "...offers a useful initial approach to a very wide area of solution like a small-scale map for a very broad long distance air view of the subcontinent."

The success of Regular Solution theory lies in its ability to predict the excess free energy of mixing and hence the saturation solubilities within a few percent of the experimental values. However the theory is not accurate in predicting many other thermodynamic properties such as the heat of solution or the volume change upon mixing.

Intermolecular Forces

The properties of solutions depend upon the nature of the interactions between the various types of molecules, both like and unlike, in the solution. Two commonly used potential functions for the interactions of spherical molecules are Lennard-Jones (L-J) potential,[2] i.e. 12-6 potential and exp-6 potential. The Lennard-Jones potential is defined as

$$U(r) = \epsilon[(r_o/r)^{12} - 2(r_o/r)^6] \tag{1a}$$

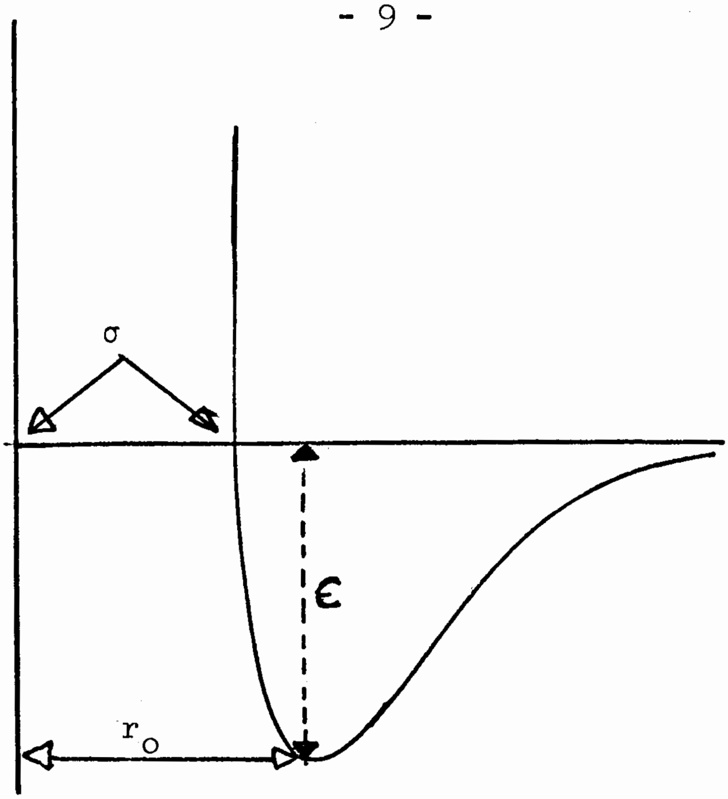
or as

$$U(r) = \epsilon[(\sigma/r)^{12} - 2(\sigma/r)^6] \tag{1b}$$

The exp-6 potential is defined as

$$U(r) = \frac{\epsilon\alpha}{\alpha-6}\left\{\frac{6}{\alpha}\exp[-\alpha(r - r_o)/r_o] - (r_o/r)^6\right\} \tag{2}$$

In both of these expressions ϵ represents the depth of the potential well, r is the distance and r_o is the separation at which the minimum in the potential occurs. The σ in the equation (1b) is the distance at which the potential is zero (see Figure 1). The α in the equation (2) is the steepness of the exponential repulsion and is usually about 13.5.



FigureI.1 The parameters used in expressing the pair potentials.

The 12-6 potential has only two adjustable parameters whereas the exp-6 potential has three. One modification of the L-J potential is the Kihara core potential in which the point center of the L-J potential is replaced by a hard core. The potential is given by

$$U(r) = \epsilon[(r_o/\sigma)^{12} - 2(r_o/\sigma)^6] \tag{3}$$

where σ is the shortest distance between hard cores and r_o is its value at the potential minimum. The net effect of the Kihara core potential is to make the attractive energy a mildly steeper function of r and the repulsive energy a much steeper function in comparison to L-J potential.

For interactions between unlike molecules, the following commonly used rules are available: the geometric mean rule for the energy parameters is

$$\epsilon_{ij} = (\epsilon_{ii}\,\epsilon_{jj})^{\frac{1}{2}} \tag{4}$$

and the arithmetic combining rule for the distance parameters is

$$r_{ij} = \frac{r_{ii} + r_{jj}}{2} \quad \text{or} \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{5}$$

In using these "combination rules" one must remember that in the cases where the potential functions for the components of a solution have different shapes, the relations of this kind cannot give full information on the interactions between the unlike molecules.[4]

Recent publications[4-9] along with earlier reviews by London,[10] Margenau,[11] and Rowlinson[12] summarise our present knowledge about the intermolecular forces. As more kinds of information on intermolecular forces become available, it seems that the simple analytical potential expressions as discussed above are not adequate in describing the intermolecular interaction, even for the spherical molecules.[13,14]

Another important aspect of the intermolecular potential is the nonadditivity of the intermolecular forces (which has been known for a long time) yet the most usual method of describing the intermolecular energy of a group of molecules is to assume that the intermolecular energy may be represented by the sum of the pair energies, i.e.

$$U = \frac{1}{2} \sum_{i} \sum_{j} U(r_{ij}) \tag{6}$$

or in other words the contribution of the triplet interaction term in the total intermolecular energy is very small. There has been a recent revival of interest concerning the contribution of the triplet interaction energies (in excess over the sum of the pair energies in equation (6)) to the total interaction of a group of molecules. The main problem with the triplet interaction term is the uncertainty about the magnitude of this contribution to the total energy: the estimate for argon may vary from less that 1% to as high as 15%.[14,15] For liquids there is no definite way of deciding whether the contribution of the triplet interaction term will be negligible or not. But from the physical pictures it seems, as mentioned by Hildebrand et al.,[19] that the different orientations in the liquid state "largely eliminates this factor for large number of atoms as closely packed as in a liquid," and throughout all our discussion we shall assume that the contribution due to the triplet interaction term is negligible.

Information about intermolecular forces can be obtained from quantum mechanical calculations, from molecular beam scattering experiments, from the measurement of transport properties in the gaseous state and the measurement of the equilibrium thermodynamic properties of liquids and gases. Information about intermolecular forces can also be obtained from the heat of vaporisation data and from the measurement of the $\left(\frac{\partial P}{\partial T}\right)_V$ of normal liquids.[21,22] The last two sources of information will be discussed because of the use of these properties in Regular Solution theory.

Heat of Vaporisation

Hildebrand and Wood[23] showed that the potential energy of liquid can be expressed in terms of its molecular pair potential and its distribution function as

$$E = \frac{2\pi N_o^2}{V}\int U(r)\ g(r)\ r^2\ dr \tag{7}$$

where N_o is Avogadro's number when the equation (7) is written for one mole of liquid, E is the total potential energy per mole of liquid, V is the molar volume, and $g(r)$ is the radial distribution function of the liquid.

They expressed $U(r)$ in terms of an n-6 potential defined as

$$U(r) = \frac{j}{r^n} - \frac{k}{r^6} \tag{8}$$

Substituting the equation (8) in the equation (7) one obtains

$$E = \frac{2\pi N_o^2}{V} \left\{ j\int \frac{g(r)}{r^{n-2}} - k\int \frac{g(r)}{r^4} \right\} dr \qquad (9)$$

Hildebrand, Wakeham and Boyd [21] evaluated k, j and n for mercury by setting $E = -\Delta E^{Vap}$, the heat of vaporisation, and by using the experimentally determined value for g(r), they obtained the values for k, j and n which are in remarkably good agreement with these values determined from the other sources. This agreement has a considerable significance in formulation of the Regular Solution theory because in this theory the interaction terms are described in terms of the cohesive energy density, where the cohesive energy density is defined as the heat of vaporisation divided by the molar volume at the same (extrapolated) temperature.

Measurements of the $\left(\frac{\partial P}{\partial T}\right)_V$ of normal liquids

Further evidence about the intermolecular potential energies are obtained from the behaviour of a van der Waals liquid, for which

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2} \qquad (10)$$

Comparing equation (10) with the thermodynamic equation of state

$$P + \frac{a}{V^2} = \frac{RT}{V - b} \qquad (11)$$

one obtains

$$P + \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad (12)$$

Smith and Hildebrand[22] determined $\left(\frac{\partial P}{\partial T}\right)_V$ for different liquids and they observed that $V^2\left(\frac{\partial E}{\partial V}\right)_T$ decreases for $c\text{-}C_6F_{11}CF_3$ with increasing temperature. Similar phenomenon was also observed by Scott et al.[25] for CCl_4. This drifting was correlated by Frank[26] by writing $E = \frac{a}{V^n}$ for dilute vapors. This allows one to write

$$V^{n+1}\left(\frac{\partial E}{\partial V}\right)_T = n\ V^n\ \Delta E^{Vap} = \text{constant} \qquad (13)$$

for dilute vapors.

From the equation (13) a definition of n can also be found as n is the ratio of $\left(\frac{\partial E}{\partial V}\right)_T$ to $\left(\frac{\Delta E^{Vap}}{V}\right)$ of the liquid. Smith and Hildebrand found that n has value larger than unity for the liquids they studied.

Potential energies between unlike molecules

The van der Waals constant a for one mole of binary mixture and the constants for the pure components are related by

$$a = x_1a_1{}^2 + 2x_1x_2a_{12} + a_2{}^2 \qquad (14)$$

where a_{12} is the interaction between the unlike molecules and the x's are the mole fractions.

Writing

$$a_{12} = (a_1a_2)^{\frac{1}{2}} \qquad (15)$$

and then substituting equation (15) in equation (14) one obtains

$$a = (x_1a_1{}^{\frac{1}{2}} + x_2a_2{}^{\frac{1}{2}})^2 \qquad (16)$$

The validity of the geometric mean assumption in the equation (15) was tested by Hildebrand and Carter[27] by measuring the $\left(\frac{\partial P}{\partial T}\right)_V$ of the three pure liquids and of their binary liquid mixtures. The calculated values for a_{12} from the equation (15) were within 1% of the experimental values for a_{12}. (Another interesting discussion about the geometric mean assumption is given by Barker[4]) The potential energies between the unlike molecules will be considered in the latter part of this chapter. In this section we discussed the importance of the thermodynamic measurements in relation to the intermolecular forces.

Liquid State

In the beginning of this chapter we mentioned the two approximations that are involved in formulating any theory of solutions: one involves use of a formal expression for the intermolecular potential function (as has been discussed above) and the other involves the approximations in the liquid state theory used.

Detailed discussion and the extensive review of the theories of liquids and dense gases which will be beyond the scope of this chapter may be found elsewhere,[28-30] but there are mainly two approaches to the formulation of the liquid state. One approach is the formal approach used by Mayer, Kirkwood and others. This approach is based on the use of a radial distribution function. At present the most promising and interesting theories based on this approach are the Scaled Particle theory and the perturbation theory of Barker and Henderson[29]. The Scaled Particle theory will be discussed in a later chapter.

The other approach is to use theories based on empirical mathematical models. The most commonly used model theories are cell theory[33] and the significant structure theory.[32] Both these theories have been widely used in calculating the properties of liquids.[29,31,32]

But as our main topic of discussion is the Regular Solution theory and its applications, and as the Regular Solution theory is based on the assumption of "maximum randomness," the whole idea of a model approach is unacceptable because all the theories based on the model approach assume some sort of "quasi-lattice" order in the liquid state.

The controversy over the properties and the "structure" of liquids has been best summarised in an article written by Eyring, Hildebrand and Rice[33] in 1963. Hildebrand[34] in the book named Regular Solutions also discussed the experimental evidence in favour of the "maximum randomness" in the liquids. Considering that our interest is to apply the Regular Solution theory in the studies of solutions of nonelectrolytes, we shall accept the formal approach in the following discussion.

Regular Solutions

The name "Regular Solution" was first proposed by Hildebrand[36] in 1929 in describing the solubilities of iodine in different nonpolar solvents. In 1931, G. Scatchard[37] put forward a theory to explain the behavior of such regular solutions. This theory of Scatchard is known as the Regular Solution theory. A regular solution may be defined as

> ...one involving no entropy change when a small amount of its component is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged.[38]

Some Important Thermodynamic Relations

Before discussing the different aspects of the Regular Solution theory it seems important to specify some of the notation and thermodynamic relations which will be used frequently in this thesis.

The following superscripts will be used to distinguish the state and the kind of process:

g = gas

l = liquid

o = standard state (in this discussion the standard state is always pure liquid)

i = ideal

e = excess over ideal solutions

m = mixing or in mixed solvent

r = regular

The following notations will be used for the thermodynamic functions:

F = Gibbs free energy

A = Helmholtz free energy

E = energy

H = enthalpy

S = entropy

P = pressure

V = volume

f = fugacity

T = temperature in degrees absolute

The thermodynamic relations which will be needed frequently are:

$$F = H - TS, \quad A = E - TS = F - PV, \quad E = H - PV.$$

The other important thermodynamic relations are given in Appendix A1.1.

Ideal Solution

The concept of ideal solution serves the same purpose in the studies of real solutions as the concept of ideal gas does in the studies of real gases. Perhaps very few solutions are ideal, which is not surprising, but the advantage of introducing the concept of ideal solution in thermodynamic studies of solutions is that it is thermodynamically well-defined. An ideal solution[39] is defined as one in which the fugacity of each component is proportional to the mole fraction of that component in the solution and this proportionality is obeyed over the complete composition range of the solution. So according to this definition the fugacity of component 1, f_1^i, of an ideal solution is given by

$$f_1^i = f_1^o x_1 \tag{20}$$

where f_1^o is the proportionality constant for a given temperature and pressure. If we can proceed over the whole range of concentration to $x_1 = 1$, f_1^o appears as the fugacity of the pure component 1.

From the definition of activity, a , we obtain

$$a_1^i = \frac{f_1^i}{f_1^o} \tag{21}$$

If the fugacities can be replaced by vapor pressures then we may write equation (21) as

$$\frac{p_1^i}{p_1^o} = x_1 \tag{22}$$

which is Raoult's Law for solutions.

The free energy change for an ideal solution can be derived from equation (21) as

$$\overline{F}_1^i - F_1^o = RT \ln x_1 \tag{23a}$$

$$\overline{F}_2^i - F_2^o = RT \ln x_2 \tag{23b}$$

$$\Delta F^M = n_1(\overline{F}_1^i - F_1^o) + n_2(\overline{F}_2^i - F_2^o)$$

$$= n_1 RT \ln x_1 + n_2 RT \ln x_2 \tag{23c}$$

If the equations (23a) and (23b) hold over a range of temperature and pressure, the following occurs:

$$\overline{S}_1^i - S_1^o = -\left\{\frac{\partial(\overline{F}_1^i - F_1^o)}{\partial T}\right\}_{P,x} = -R \ln x_1 \tag{24a}$$

$$\overline{S}_2^i - S_2^o = -\left\{\frac{\partial(\overline{F}_2^i - F_2^o)}{\partial T}\right\}_{P,x} = -R \ln x_2 \tag{24b}$$

$$\Delta S^M = -\left(\frac{\partial \Delta F^M}{\partial T}\right)_{P,x}$$

$$= -R(n_1 \ln x_1 + n_2 \ln x_2) \tag{25}$$

From the thermodynamic relation

$$H = F + TS \tag{26}$$

we obtain

$$\Delta\overline{H}_1^i = \Delta\overline{H}_2^i = \Delta H^M = 0 \tag{27}$$

Similarly for the volume change on mixing we find

$$\overline{V}_1^i - V_1^o = \left\{\frac{\partial(\overline{F}_1^i - F_1^o)}{\partial P}\right\}_{T,x} = 0 \tag{28a}$$

$$\overline{V}_2^i - V_2^o = \left\{\frac{\partial(F_2^i - F_2^o)}{\partial P}\right\}_{T,x} = 0 \tag{28b}$$

$$\Delta V^M = \left\{\frac{\partial \Delta F^M}{\partial P}\right\}_{T,x} = 0 \tag{29}$$

Thus the thermodynamic properties of an ideal solution formed from liquid components can be stipulated as follows:

(1) There is no volume change on mixing for an ideal solution;

(2) there is no heat of mixing for an ideal solution;

(3) the entropy of mixing for a binary ideal solution is given by

$$\Delta S^M = -R(n_1R \ln x_1 + n_2R \ln x_2)$$

In this section we have defined the ideal solution from the thermodynamic point of view and we will use this definition for the ideal solution throughout this

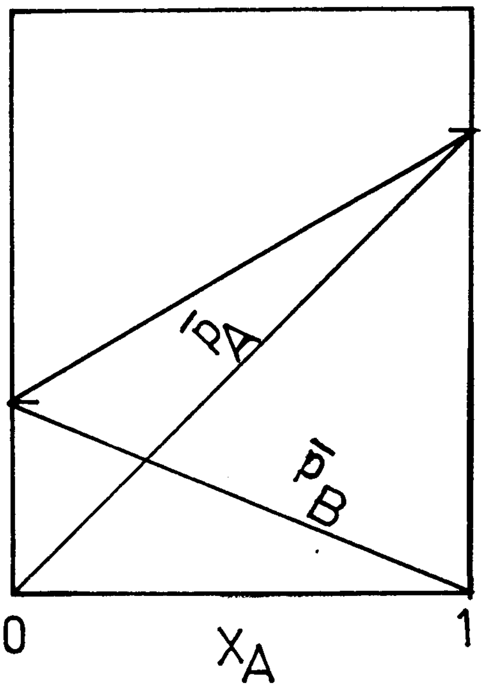


Fig.I.2.

Mole fraction of A in a hypothetical ideal mixture of A and B - partial and total pressure of A and B.

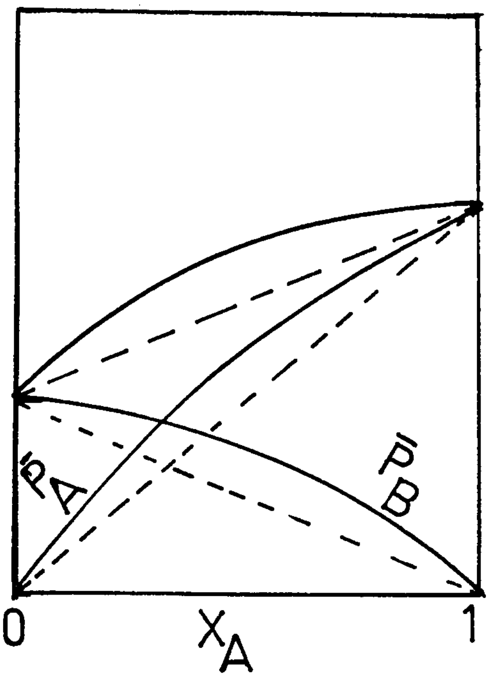


Fig.I.3.

Partial and total pressure for a nonideal mixture of A and B with $\gamma > 1$.

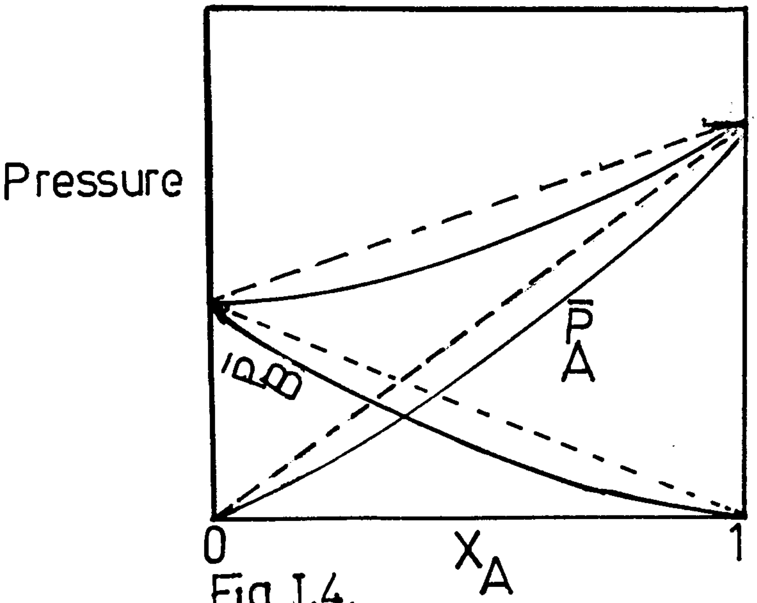


Fig.I.4.

Partial and total pressure of a nonideal solution of A and B with $\gamma < 1$.

discussion.

Nonideal or Real Solution

In the earlier section we defined an ideal solution as a solution for which the activity of a component in the solution is equal to the mole fraction of that component in the solution such that

$$a_2 = x_2^i$$

But for most of the solutions, this is not the case, and for convenience we define a term called activity coefficient (see Appendix A1.1) as

$$\gamma_1 = \frac{a_1}{x_1} \qquad \text{and} \qquad \gamma_2 = \frac{a_2}{x_2} \tag{30}$$

So for an ideal solution,

$$\gamma_1 = 1 \qquad \text{and} \qquad \gamma_2 = 1 \tag{31}$$

Again from the equation the partial molal free energy of mixing may be written as

$$\Delta\overline{F}_1 = \overline{F}_1 - F_1^o = RT \ln a_1 = RT \ln x_1 + RT \ln \gamma_1 \tag{32a}$$

$$\Delta\overline{F}_2 = \overline{F}_2 - F_2^o = RT \ln a_2 = RT \ln x_2 + RT \ln \gamma_2 \tag{32b}$$

$$\Delta F_M = RT(x_1 \ln a_1 + x_2 \ln a_2)$$

$$= RT(x_1 \ln x_1 + x_2 \ln x_2) + RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \tag{33}$$

In equations (32a), (32b) and (33) we see that the first terms in the right hand side are ideal free energies of mixing so the second terms are the excess over the ideal free energies of mixing and they are known as the "excess" free energies of mixing. So the excess free energy of mixing is defined as

$$\overline{F}_1^E = RT \ln \gamma_1 \tag{34a}$$

$$\overline{F}_2^E = RT \ln \gamma_2 \tag{34b}$$

$$F^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{35}$$

Similarly other excess properties may be defined with reference to the ideal solutions.

The positive value of the excess free energy of mixing, i.e. γ, is greater than unity, and is known as a positive deviation from Raoult's Law. Similarly the negative value of the excess free energy of mixing, i.e. γ, is less than unity, and is known as a negative deviation from Raoult's Law.

In Figures 2-4 we show the different thermodynamic properties of ideal and non-ideal solutions for mixtures of hypothetical liquids A and B.

Solubility of Nonelectrolytes and Regular Solution Theory

In this section we limit our discussion to the solubilities of nonelectrolytes because the long-range nature of the electrostatic forces yields problems which are beyond the scope of this thesis.

Primary consideration will be given to mixtures of two or more liquids. For mixtures with a solid as the solute we shall assume that the standard state of the solids is the hypothetical supercooled liquid of the solid at that temperature.

As mentioned earlier, Hildebrand in 1929 drew attention to the very significant similarity in behavior of a class of nonideal solutions which he named regular solutions. The absence of any specific interactions is the most important feature of these solutions. The pure components of a regular solution have the properties of simple fluids or liquids.

The difference between a regular solution and an ideal solution is that for a regular solution the heat of mixing has a positive value whereas for ideal solution the heat of mixing is zero. As mentioned earlier the entropy of mixing forararegular solution is equal to the ideal entropy of mixing.

Heat of Mixing and Hildebrand-Scatchard Equation

The first attempt to calculate the change in entropy or enthalpy when two liquids are mixed, was made by van Laar in 1906 but it was not very successful.

In 1931, G. Scatchard[37] published a paper where he derived an equation to calculate ΔE_V^M or energy change on mixing two liquids at constant volume. To do so he assumed

(1) The mutual energy of two molecules depends only upon the distance between them and their relative orientation and not at all on the nature of the other molecules between or around them, or on temperature;

(2) the distirbution of the molecules in position and in orientation is random, i.e. it is not dependent on the temperature or on the nature of other molecules present;

(3) the change of volume on mixing is zero.

These assumptions allowed him to write the "cohesive energy" of a mole of liquid mixture,

$$-E_M = \frac{C_{11}V_1^2X_1^2 + 2C_{12}X_1X_2V_1V_2 + C_{22}X_2^2V_2^2}{x_1V_1 + x_2V_2} \qquad (36)$$

For pure liquids $-E = C_{11}V_1$, etc. For liquids the vapor is nearly ideal at ordinary temperature so $-E$ can be identified with the energy of vaporization ΔE^{Vap} or $C_{11} = \frac{\Delta E_{11}^{Vap}}{V}$. In terms of the volume fractions equation (36) becomes

$$-E_M = (x_1V_1 + x_2V_2)(C_{11}\Phi_1{}^2 + 2C_{12}\Phi_1\Phi_2 + C_{22}\Phi_2{}^2) \qquad (37)$$

where $\Phi_1 = \frac{N_1V_1}{N_1V_1 + N_2V_2}$ and so on.

So the energy of mixing is given by

$$\Delta E^M = E_m - x_1E_1 - x_2E_2$$

$$= A_{12}(x_1V_1 + x_2V_2)\Phi_1\Phi_2 \qquad (38)$$

where $A_{12} = C_{11} + C_{22} - 2C_{12}$.

Then it is assumed that

$$C_{12} = (C_{11}C_{22})^{\frac{1}{2}} \qquad (39)$$

or

$$A_{12} = (C_{11} - C_{22})^{\frac{1}{2}} \qquad (40)$$

and substituting $C_{ii} = \frac{\Delta E_i^V}{V_i}$ in equation (38) the energy change on mixing becomes

$$\Delta E^M = (x_1V_1 + x_2V_2)\left\{\left(\frac{\Delta E_1^V}{V_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_2^V}{V_2}\right)^{\frac{1}{2}}\right\}\Phi_1\Phi_2 \qquad (41)$$

The square root of the "cohesive energy" density, i.e. $\left(\frac{\Delta E_i^V}{V_i}\right)^{\frac{1}{2}}$ is called the "solubility parameter" and is denoted by δ. So equation (24) may be written as

$$\Delta E^M = (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)\Phi_1\Phi_2 \qquad (42)$$

As equation (42) was derived from the assumption that the volume change on mixing is zero, ΔE^m in equation (42) is actually ΔE_V^m.

Since ΔV^M is very small, then

$$F^E = A_V^E = E_V^E - TS_V^E \qquad (43)$$

By definition $\Delta S^E = 0$ for regular solution, so

$$F^E = E_V^E = \Delta E_V^M \qquad (44)$$

Combining equation (41) with equation (44), one obtains

$$F^E = (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2\Phi_1\Phi_2 \qquad (45)$$

The corresponding partial molal free energy for a solute is

$$\overline{F}_2^E = RT \ln \gamma_2 = V_2^o \Phi_1^2(\delta_1 - \delta_2)^2 \qquad (46)$$

where γ_2 is the activity coefficient of solute 2, or

$$\Delta\overline{F}_2 = RT \ln a_2 = RT \ln x_2 + V_2^o \Phi_1^2(\delta_1 - \delta_2)^2 \qquad (47)$$

Rearranging equation (47), one obtains

$$\ln a_2 = \ln x_2 + \frac{V_2^o}{RT} \Phi_1^2(\delta_1 - \delta_2)^2 \qquad (48)$$

where a_2 is the activity for solute 2.

Hildebrand and Wood derived the same equation by integrating the intermolecular potential between pairs throughout the liquid with the aid of a continuous distribution function.[23]

In equation (48), we see that the Scatchard-Hildebrand equation is valid only for the solutions for which the excess free energies are positive, i.e. those solutions which show positive deviations from Raoult's Law. This is the direct consequence of the geometric mean assumption in equation (39).

Hildebrand and Wood[23] derived an equation similar to equation (41) for heat of mixing by integrating the intermolecular pair potentials throughout the liquid using a continious distribution function.

In a pure liquid of spherically symmetrical molecules, a spherical shell of radius r around a designated central molecule and thickness dr will contain $\frac{N}{V}4\pi r^2 g(r)dr$ molecules where $g(r)$ is the radial distribution function. The potential energy, E, of pure liquid of N molecules in volume V is given by

$$E = \frac{2\pi N^2}{V} \int_0^\infty U(r)\ g(r)\ r^2\ dr$$

$$= n\ \frac{2\pi N_o^2}{V} \int_0^\infty U(r)\ g(r)\ r^2\ dr \quad . \qquad (49)$$

where $U(r)$ is the pair potential at a distance r, N_o is Avogadro's number, and n is the number of moles.

Similarly for a binary mixture of liquids containing n_1 moles of type 1 and n_2 moles of type 2, the potential energy of the mixture of total volume

$$V_m = n_1V_1 + n_2V_2 = (n_1 + n_2)\ (x_1V_1 + x_2V_2) \qquad (50)$$

is given by

$$E_m = (n_1V_1 + n_2V_2)\ 2\pi N_o \left\{ \frac{\Phi_1^2}{V_1^2} \int U_{11}g_{11}\ r^2\ dr \right.$$

$$\left. + \frac{2\Phi_1\Phi_2}{V_1V_2} \int U_{12}g_{12}\ r^2\ dr + \frac{\Phi_2^2}{V_2^2} \int U_{22}g_{22}\ r^2\ dr \right\} \qquad (51)$$

The energy of two unmixed components is given by

$$E_1 + E_2 = 2\pi N_o^2 (n_1V_1 + n_2V_2) \left\{ \frac{\Phi_1^2}{V_1^2} \int U_{11}g_{11}^o\ r^2\ dr \right.$$

$$\left. + \frac{\Phi_2^2}{V_2^2} \int U_{22}g_{22}^o\ r\ \ dr \right\} \qquad (52)$$

Therefore the energy of mixing is

$$\Delta E^{M} = E_{m} - E_{1} - E_{2}$$

$$= (n_1V_1 + n_2V_2)2\pi N_o^{2} \left\{ \frac{\Phi_1^2}{V_1^2} \int U_{11}(g_{11} - g_{11}^{o})\, r^2\, dr + \frac{\Phi_2^2}{V_2^2} \int U_{22}(g_{22} - g_{22}^{o}) r^2 dr + \Phi_1\Phi_2 \left(\frac{2}{V_1V_2} \int U_{12}g_{12}r^2 dr - \frac{1}{V_1^2} \int U_{11}g_{11}^{o}r^2 dr + \frac{1}{V_2^2} \int U_{22}g_{22}^{o}r^2 dr \right) \right\} \quad (53)$$

The ΔE^{M} in equation (53) is the energy of mixing at constant volume and the terms in the brackets in equation (53) can be identified with Scatchard's $(C_{11} + C_{22} - 2C_{12})$ term in equation (38).

Next Hildebrand et al. wrote the intermolecular pair potential as

$$\int U(r)g(r)r^2 dr = -k \int \frac{g(r)}{r^4}\, dr + j \int \frac{g(r)}{r^{n-2}}\, dr \quad (54)$$

From the discussion of the intermolecular forces given earlier j, the coefficient of the repulsive interaction can be expressed in terms of k and the equilibrium distance, (see Appendix A1.2) as

$$j = \frac{6}{n}\, (r_o)^{n-6}\, k \quad (55)$$

(where r_o is the equilibrium distance)

Substituting equation (55) in equation (54), one obtains

$$\int U(r)g(r)r^2dr = -k\left\{ -\int \frac{g(r)}{r^4}\, dr + \frac{6}{n}(r_o)^{n-6}\int \frac{g(r)}{r^{n-2}}\, dr \right\} \qquad (56)$$

It was then assumed[40] that g's are functions of $\frac{r}{\sigma}$ or $\frac{r}{r_o}$ where σ is the collision diameter of molecules. This assumption can be justified from the observation by Hildebrand et al. that the distribution functions of different species can be superimposed when compared at equal degree of expansion by plotting $g(r)$ versus $\frac{r}{r_{max}}$, where r_{max} is the position of the first maximum. As σ and r_o are proportional to r_{max} and if the substances have same type of potential, then

$$g(r) = g(r/\sigma) = g(y); \qquad y = \frac{r}{\sigma} \qquad (57)$$

Substituting equation (57) in equation (56) one obtains

$$\int U(r)g(r)r^2dr = k\left\{ \frac{-1}{\sigma^3}\int \frac{g(y)}{y^4}\, dy + \frac{6(r_o)^{n-6}}{n(\sigma)^{n-3}}\int \frac{g(y)}{y^{n-2}}\, dy \right\} \qquad (58)$$

Assuming

$$r_o = \sigma \qquad (59)$$

and then substituting σ for r_o in equation (58) one obtains

$$\int U(r)g(r)r\,dr = \frac{k}{\sigma^3}\left\{-\int \frac{g(y)}{y^4}\,dy + \frac{6}{n}\int \frac{g(y)}{y^{n-2}}\,dy\right\} \tag{60}$$

Substituting equation (60) into equation (53) and then assuming that each radial distribution function is independent of composition of the solution, i.e.

$$g_{11}^{o}(r) = g_{11}(r); \qquad g_{22}^{o}(r) = g_{22}(r) \tag{61}$$

the expression for the energy of mixing, ΔE^M , of a regular solution may be rewritten as

$$\Delta E^M = 2\pi N_o\,(n_1V_1 + n_2V_2)\Phi_1\Phi_2\left\{\frac{2k_{12}}{V_1V_2(\sigma_{11}+\sigma_{22})^3} - \frac{k_1}{V_1^2(2\sigma_{11})^3} - \frac{k_2}{V_2^2(2\sigma_{22})^3}\right\}\left\{-\int\frac{g(y)}{y^4}dy + \frac{6}{n}\int\frac{g(y)}{y^{n-2}}dy\right\} \tag{62}$$

Equation (61) is the mathematical statement of Scatchard's assumption that "...the distribution of the molecules in position and in orientation is random, i.e. it is not dependent on...the nature of other molecules present (in a regular solution)."

Returning to equation (62), the values for k_{12} can be found in London's relation[4]

$$k_{12} = \frac{2I_1^{\frac{1}{2}}I_2^{\frac{1}{2}}}{I_1 + I_2}\,k_1^{\frac{1}{2}}k_2^{\frac{1}{2}} \tag{63a}$$

where I's are the ionization potentials.

Substituting equation (63a) into equation (62),

$$\Delta E^M = 2\pi N_o^2 \, (n_1 V_1 + n_2 V_2) \, \Phi_1 \Phi_2 \left\{ \frac{1}{V_1^2} \frac{k_1}{(2\sigma_{11})^3} - \frac{4 I_1^{\frac{1}{2}} I_2^{\frac{1}{2}} k_1^{\frac{1}{2}} k_2^{\frac{1}{2}}}{V_1 V_2 (I_1 + I_2)(\sigma_{11} + \sigma_{22})^3} + \frac{1}{V_2^2} \frac{k_2}{(2\sigma_{22})^3} \right\} \int \left\{ \frac{1}{y^4} - \frac{6}{n y^{n-2}} \right\} g(y) \, dy \qquad (63b)$$

The equation (63b) will reduce to Scatchard's equation if one assumes "cohesive energy densities", C's, as

$$C_{11} = \Delta E_1^{Vap} / V_1$$

$$= \frac{2\pi N_o^2}{8\sigma_{11}^3 V_1^2} \int \left\{ \frac{1}{y^4} - \frac{6}{n y^{n-2}} \right\} g(y) \, dy \qquad (64a)$$

$$C_{22} = \Delta E_2^{Vap} / V_2$$

$$= \frac{2\pi N_o^2}{8\sigma_{22}^3 V_2^2} \int \left\{ \frac{1}{y^4} - \frac{6}{n y^{n-2}} \right\} g(y) \, dy \qquad (64b)$$

$$C_{12} = \frac{\quad}{8 V_1 V_2 (\sigma_{11} + \sigma_{22})^3} \frac{2 I_1^{\frac{1}{2}} I_2^{\frac{1}{2}}}{(I_1 + I_2)} \, k_1^{\frac{1}{2}} k_2^{\frac{1}{2}} \int \left\{ \frac{1}{y^4} - \frac{6}{n y^{n-2}} \right\} dy \qquad (64c)$$

Geometric Mean Assumption

Before discussing the other aspects of the Regular Solution theory, it is important to consider the reliability of the geometric mean assumption given in equation (39), i.e.

$$C_{12} = \sqrt{C_{11}C_{22}}$$

and its effect on the magnitude of the interaction constant, A_{12}, in equation (39).

From equation (64c) we see that

$$C_{12}^{2} = \left\{ \frac{2\pi N_0^{2}}{8V_1V_2} \frac{2I_1^{\frac{1}{2}}I_2^{\frac{1}{2}}}{(I_1 + I_2)} \frac{k_1^{\frac{1}{2}}k_2^{\frac{1}{2}}}{(\sigma_{11} + \sigma_{22})^{3}} \right.$$

$$\left. \int \left\{ \frac{1}{y^4} - \frac{6}{ny^{n-2}} \right\} dy \right\}^{2}$$

or $$C_{12}^{2} = \frac{I_1I_2}{[(I_1 + I_2)/2]^{2}} \frac{}{[(\sigma_{11} + \sigma_{22})/2]^{6}} C_{11}C_{22} \qquad (65)$$

From equation (65) we see that if

$$I_1 = I_2 \qquad \text{and} \qquad \sigma_{11} = \sigma_{22} \qquad (66)$$

then only

$$C_{12} = \sqrt{C_{11}C_{22}}$$

For a number of systems these conditions are not satisfied. For example, hydrocarbons and fluorocarbons have ionization potentials about 10 ev and 16 ev respectively and it is now generally accepted[41] that systems such as hydrocarbon-fluorocarbon mixtures do not obey geometric mean assumptions. Reed,[42] in an attempt to account for the large excess free energies which have been observed for hydrocarbon-fluorocarbon mixtures, reexamined the role of the differences in ionization potentials and the collision diameters of the components in the geometric assumptions. He wrote

$$A_{12} = C_{11}+C_{22}-2C_{12} = (\delta_1-\delta_2)^2+2\delta_1\delta_2(1-f_I f_\sigma) \qquad (67)$$

where

$$f_I = \frac{2\, I_1^{\frac{1}{2}}\, I_1^{\frac{1}{2}}}{I_1+I_2}$$

and

$$f_\sigma = \left\{ \frac{2\sigma_{11}^{\frac{1}{2}}\sigma_{22}^{\frac{1}{2}}}{\sigma_{11}+\sigma_{22}} \right\}^3$$

Reed estimated that, for hydrocarbon-fluorocarbon mixtures, f_I is about 0.97 and f_σ is about 0.995. So for $\delta_1 = 7.5$ and $\delta_2 = 6.0$ cal$^{1/2}$cm$^{-3/2}$, the second term in equation (67) becomes about 3 cal cm^{-3} which when coupled with molar volume from 100 to 200 cm^3 can produce an energy of mixing at constant volume as much as 150 cal mole^{-1} in excess of that predicted from equation (38).

The consideration of the difference in ionization potentials offers a satisfactory explanation for the anomalously large heat of mixing and excess free energy of mixing observed for hydrocarbon-fluorocarbon mixtures. It would predict for other solutions similar anomalies which are not observed experimentally, eg. CCl_4 and I_2 have ionization potentials of 11.0 and 9.7 ev respectively but their mixtures with fluorocarbons show excess free energy in good agreement with equation (38) with no need for a correction term. On the other hand it has also been reported[43] that for a benzene-toluene mixture, where the differences in ionization potential of the components are not very large, the values of C_{12} calculated from experimentally determined ΔE_V^M are consistently lower than values calculated from δ_1 and δ_2. Recent measurements[44] of activity coefficients of hydrocarbon solutes in alkane solvents such as $n\text{-}C_{24}H_{50}$, $n\text{-}C_{30}H_{62}$ and $n\text{-}C_{36}H_{74}$, by gas-liquid partition chromatography, also indicate that for aromatic hydrocarbons, the δ value of the solvent $n\text{-}C_{30}H_{62}$ has to be changed from 7.730 to 6.850 to fit the experimental values for activity coefficients whereas for alkane hydrocarbons no such adjustment is needed.

Hudson and McCoubrey[55] examined the effect of the differences in the collision diameters of molecules on the geometric mean assumption. Assuming that $I_1 = I_2$ they rewrote the equation (65) as

$$C_{12}^2 = \frac{\sigma_{11}^3 \sigma_{22}^3}{(\sigma_{11} + \sigma_{22}/2)^6} \qquad (68)$$

They used the equation (68) to calculate the critical temperature for the binary liquid mixture of $c\text{-}C_6H_{12}$ - $c\text{-}C_6F_{12}$ and obtained a better agreement with the experimental values.

Vitoria and Walkley[53] looked into the effects of the differences of the molar volumes upon C_{12}'s of tetraphenyl tin - organic solvents mixtures. They wrote equation (68) as

$$C_{12} = k_\sigma C_{11} C_{22} \tag{69}$$

where

$$k_\sigma = \left\{ 2^6 \frac{V_1 V_2}{(V_1^{\frac{1}{2}} + V_2^{\frac{1}{2}})^6} \right\}^{\frac{1}{2}}$$

and then they rewrote the experimentally determined $(\delta_1 - \delta_2)^2$ as

$$(\delta_1 - \delta_2)^2 = \delta_1^2 - \delta_2^2 - 2b\delta_1\delta_2$$

or,

$$b = \frac{\delta_1^2 + \delta_2^2 - (\delta_1 - \delta_2)^2}{2\delta_1\delta_2} \tag{70}$$

where b, in the left hand side of the equation, was calculated from the saturation solubilities. They found that for tetraphenyl tin k_σ is much smaller than unity but b is nearly equal to unity if excess entropy of mixing is included in writing the saturation solubility equation. Or in other words the experimentally determined b indicates that the effects of solvent-solute molar volume disparity on the geometric mean assumption is much smaller for the systems containing tetraphenyl tin as solute than one would have expected from equations such as the equation (69).

In conclusion, though the geometric mean assumption is based on a narrow theoretical basis, this assumption when used in the form of solubility parameters has been proven to be quite useful in calculating the thermodynamic properties of the solutions of nonelectrolytes.

Determination of "Solubility Parameter"

The Regular solution theory requires δ to be a self-consistent parameter. The δ value has been calculated for a large number of substance, either

(1) from the relation $\delta = \left\{\frac{\Delta E^V}{V^\ell}\right\}^{\frac{1}{2}}$, which is usually used for substances which are liquid at room temperature, or

(2) by determining saturation solubility, i.e. x_2 and then substituting x_2 in the equation (48), provided δ_1 is known.

The δ_2 value for SnI_4 was determined by E. B. Smith and J. Walkley [45] from its solubility in a large number of organic solvents. In Table 1 δ_2 value for SnI_4 is given to show that there exist a reasonable consistency in δ_2 when determined from saturation solubility.

The "solubility parameter" can also be calculated from the calorimetric heat of vaporization. At low vapour pressure, the vapour in equilibrium with liquid is essentially ideal and $-E$ can be replaced by ΔE^V, the energy of vaporization, which in turn can be replaced by $\Delta H^V - RT$ where ΔH^V is the heat of vaporization.

Table I.1; Solubility parameter for SnI_4 - calculated from saturation solubility data.[45]

Solvent	Solubility $100x_2$	δ_1 for solvent	δ_2 for SnI_4
CCl_4	1.459	8.6	11.6
$SiCl_4$	0.382	7.6	11.4
$CCl_2F.CF_2Cl$	0,128	7.5	11.8
C_6H_6	2.181	9.2	11.8
$c\text{-}C_4Cl_4F_6$	0.0337	7.1	11.9
$n\text{-}C_7F_{16}$	0.001	5.9	12.0
$C_6H_5CH_3$ (toluene)	2.507	8.9	11.6

δ's are expressed in $cal.^{\frac{1}{2}}\ c\bar{m}.^{\frac{2}{3}}$

So

$$\delta = (\Delta H^V - RT / V^l)^{\frac{1}{2}} \tag{71}$$

R. L. Scott proposed an empirical rule for heat of vaporization at 298° K and at boiling point of the liquid which is given below.

$$\Delta H^V_{298}\ (\text{cal/ mole}) = -2950 + 23.7T_B + 0.02T_B^{\ 2} \tag{72}$$

$$\Delta H^V_B\ (\text{cal/ mole}) = 17.0T_B + 0.009T_B^{\ 2} \tag{73}$$

T_B is the boiling point of the liquid. It should be mentioned here that δ calculated from equation (71) may not be appropriate for solids because of the long extrapolation involved in such cases.

Volume Change on Mixing

It has been assumed before that the volume change on mixing is zero for regular solution, or in other words the heat of mixing can be identified with the energy of mixing. So x_2^{max} or mole fraction of component 2 at which the heat of mixing will be maximum can be calculated from equation (11).

The experimental and the predicted values for x_2^{max} are given in Table 2. These values are taken from reference [46]. It is clear from Table 2 that the calculated value of x_2^{max} quite often does not agree with the experimental value. One of the reasons, as suggested by G. Scatchard,[47] is that the ΔV^m or the volume

Table I.2: Observed and predicted values for x_2^{max} (i.e., mole fraction of component 2 at which the heat of mixing is maximum).

System	V_1 cc	V_2 cc	H^M_{max} cal/mole	T^oA	x_2^{max} obs.	x_2^{max} calc'd
n-C_6H_{14} + c-C_6H_{12}	132	109	53	293	0.63	0.53
iso-C_8H_{18} + hexadecane	166	294	55	293	0.42	0.43
n-C_6F_{14} + n-C_6H_{14}	205	131	516	298	0.52	0.55
C_6H_6 + c-C_6H_{12}	89	109	182	298	0.53	0.47
CCl_4 + c-C_6H_{12}	97	109	40	298	0.47	0.48

change on mixing is never zero for a regular solution. So it becomes necessary to convert the experimental numbers which are usually determined at constant pressure to the constant volume numbers.

The method of making these thermodynamic corrections was first outlined by G. Scatchard.[47] His equations were derived from a two-step process, a mixing of two components at constant volume followed by an expansion or contraction of the mixture (as the case may be) to recover the pressure, i.e. the initial pressure. He obtained the constant volume functions ΔA_V^M, ΔS_V^M and ΔE_V^M by expanding the constant pressure functions ΔA_P^M, ΔS_P^M and ΔE_P^M in the form of a Taylor series expansion around $V^M = V^o + \Delta V^E$ as

$$\Delta A_P^M = \Delta A_V^M - \left(\frac{\partial A}{\partial V}\right)_{V=V_o+V^E} V^E - \frac{1}{2}\left(\frac{\partial^2 A}{\partial V^2}\right)_{V=V_o+V^E} (V^E)^2 \tag{74}$$

$$\Delta S_V^M = \Delta S_P^M - \left(\frac{\partial P}{\partial T}\right)_V V^E \tag{75}$$

$$\Delta E_P^M = \Delta E_V^M + \left\{ T\left(\frac{\partial P}{\partial T}\right)_V - P \right\} V^E \tag{76}$$

ΔF_P^M and ΔH_P^M are obtained by adding ΔPV to equation (74) and equation (76) respectively. As the initial and final pressures are the same, ΔPV is merely $P\Delta V^M$, or

$$\Delta F_P^M = \Delta A_P^M + P\Delta V^M = \Delta A_V^M - \frac{1}{2\beta V}(\Delta V^M)^2 \tag{77}$$

$$\Delta H_P^M = \Delta E_P^M - PV^E = \Delta E_V^M - T \left(\frac{\partial P}{\partial T}\right)_V V^E$$

$$= \Delta E_V^M - T \left(\frac{\alpha}{\beta}\right) V^E \tag{78}$$

The α and β in equation (78) are the coefficients of thermal expansion and isothermal compressibility of the mixture, respectively.

Rearranging the equation (78), one obtains

$$\Delta E_V^M = \Delta H_P^M - T \left(\frac{\alpha}{\beta}\right) V^E \tag{79}$$

So the knowledge of α and β allows one to compare experimentally determined ΔH_P^M with calculated ΔE_V^M.

From equation (77) we also see that the difference between ΔF_P^M and ΔA_V^M is dependent on $(V^E)^2$ and not on V^E or as long as V^E is small, the difference between ΔF_P^M and ΔA_V^M is small. It has been observed that Regular Solution theory predicts free energy of mixing within a few percent of the experimental values whereas for the heat and the entropy of mixing the agreement between the experimental and the predicted values is not very good.[1,19,43]

Magnitude of Volume Change at Constant Pressure

V^E, the excess volume of mixing, is given by an exact thermodynamic relation as

$$V^E = \left(\frac{\partial F^E}{\partial P}\right)_T$$

and writing
$$F^E = A^E_V(T,V) + \frac{1}{2(V\beta)_m}(V^E)^2$$

and if V^E is small $(V^E)^2$ can be neglected to make $F^E = A^E_V(T,V)$, or

$$V^E = \left(\frac{\partial F^E}{\partial P}\right)_T = \left(\frac{\partial A^E}{\partial P}\right)_T = \left(\frac{\partial E^E_V}{\partial P}\right)_T - T\left(\frac{\partial S^E_V}{\partial P}\right)_T \qquad (80)$$

For regular solutions $S^E_V = 0$, and it is independent of pressure. So equation (80) becomes

$$V^E = \left(\frac{\partial E^E_V}{\partial P_u}\right)_T = \left(\frac{\partial E^E_V}{\partial V_u}\right)\left(\frac{\partial V_u}{\partial P_u}\right)_T = (\beta V)_u\left(\frac{\partial E^E_V}{\partial V_u}\right)_T \qquad (81)$$

u in equation (81) corresponds to the pressure, volume, compressibility, etc. of the unmixed initial state of the system. Now if $E^E_V = E_m - E_u$ where E_m is the energy of the mixture and $\left(\frac{\partial E}{\partial V}\right)$ is replaced by $n\left(\frac{-E}{V}\right)$ where n is the ratio of internal pressure to cohesive energy density, equation (81) becomes

$$V^E = -(\beta V)_u\left\{\left(\frac{\partial E_m}{\partial V_u}\right)_T - \left(\frac{\partial E_u}{\partial V_u}\right)_T\right\} = (\beta V)_u\left\{\frac{n_m E_m - n_u E_u}{V_u}\right\} \qquad (82)$$

Assuming n_m and n_u are the same for the mixtures and the unmixed components and then invoking the condition that $S^E_V = 0$ and $\Delta E_V = F^E$, V^E can be written as

$$V^E = n\,\frac{(\beta V)_u(E^{\cdot\cdot}_m - E_u)}{V_u} = n\beta\Delta E^E_V = n\beta F^E \qquad (83a)$$

Partial molal volume in dilute solutions

Of special interest are the partial molal volumes of solutes in the highly dilute solutions. Differentiation of equation (83a) in the limit as $x_2 \to 0$ yields the equation

$$V^E_2 = \overline{V}_2 - V^o_2 = n_1\beta_1\overline{F}^E_2 = \frac{\alpha_1 T}{\delta_1^{\;2}}\,\overline{F}^E_2 \qquad (83b)$$

Recalling equation (46)

$$\overline{V}^E_2 = n_1\beta_1 RT\ \ln\gamma_2 = n_1\beta_1 V^o_2\Phi_1^{\;2}(\delta_1 - \delta_2)^2 \qquad (83c)$$

In Table 3 a comparison between experimental and predicted values for the partial molal volumes are given.

TableI.3

Solute	Solvent	V^o_2	$\overline{V}_2$(obs)	$\overline{V}^E_2$(obs)	$\overline{V}^E_2$(calc'd)
I_2	n-C_7F_{16}	59	100 cc	41	60 [49]
Br_2	"	51	73 cc	21	24.7 [50]

V_2(calc'd) in Table 3 was calculated from equation (82c). It should be mentioned here that though for Br_2 the agreement between the calculated value and experimental value is not bad, the equations (83a,b,c) are very approximate equations. But these equations can explain the results qualitatively.

Entropy of mixing molecules of unequal size [84-91]

So far we have assumed that a solution is ideal if the heat of mixing is zero (see equation (47)). But it has been known since 1933 that the entropy of mixing unequal molecules may not be ideal even if the heat of solution and the volume change on mixing are zero.

J. H. Hildebrand[51] derived the expression for the entropy of mixing of unequal molecules from the "free volume theory" point of view as

$$\Delta S^M = -R \left\{ x_1 \ln \frac{x_1 V_1^f}{x_1 V_1^f + x_2 V_2^f} + x_2 \ln \frac{x_2 V_2^f}{x_1 V_1^f + x_2 V_2^f} \right\} \qquad (84)$$

for one mole of solution formed at constant pressure. By differentiating equation (84),

$$\Delta \overline{S}_1 = -R \left\{ \ln \frac{x_1 V_1^f}{x_1 V_1^f + x_2 V_2^f} + \frac{x_2 (V_2^f - V_1^f)}{x_1 V_1^f + x_2 V_2^f} \right\} \qquad (85)$$

Then he assumed that $\frac{V_1}{V_2} = \frac{V_1^f}{V_2^f}$. So equation (85) becomes

$$\Delta \overline{S}_1 = -R[\ln \Phi_1 + \Phi_2 (1 - \frac{V_1}{V_2})] \qquad (86a)$$

Similarly, $$\Delta \overline{S}_2 = -R[\ln \Phi_2 + \Phi_1 (1 - \frac{V_2}{V_1})] \qquad (86b)$$

When $V_1 \approx V_2$, the equation (86b) becomes

$$\Delta\overline{S}_2 = -R \ln x_2 \tag{87}$$

Adding equation (87) to the heat of mixing term as derived previously, the equation (47) becomes

$$\Delta\overline{F}_2 = RT\ln a_2 = RT[\ln\Phi_2 + \Phi_1(1-\frac{V_2}{V_1})] + V_2^o\Phi_1{}^2(\delta_1 - \delta_2)^2 \tag{88}$$

If $x_2 \ll x_1$ such that $x_1 \rightarrow 1$, then

$$\Phi_1 = \frac{x_1V_1}{x_1V_1 + x_2V_2} \approx 1 \tag{89}$$

$$\Phi_2 = \frac{x_2V_2}{x_1V_1 + x_2V_2} = \frac{x_2V_2}{V_1} \tag{90a}$$

$$\ln \Phi_2 = \ln x_2 + \ln \frac{V_2}{V_1} \tag{90b}$$

So equation (88) can be written as

$$\ln a_2^i = \ln x_2 + \ln \frac{V_2}{V_1} + (1 - \frac{V_2}{V_1}) + \frac{V_2^o}{RT}(\delta_1 - \delta_2)^2 \tag{91}$$

Entropy of solution of a solid

In deriving the Regular Solution theory, it has been assumed that the mixing is "random." It is possible to determine the partial molal entropy change of solid solute for a very dilute solution from the temperature dependence of the saturation solubility and can be compared with the predicted values. It is related to the temperature coefficient of the solubility by means of the thermodynamic equation

$$\overline{S}_2 - S_2^s = - \left\{ \frac{\partial(\overline{F}_2 - F_2^s)}{\partial T} \right\}_{P,x}$$

$$= \left\{ \frac{\partial(\overline{F}_2 - F_2^s)}{\partial \ln x_2} \right\}_{P,T} \left\{ \frac{\partial \ln x_2}{\partial T} \right\}_{\overline{F}_2 - F_2^s, P} \qquad (92)$$

The second factor on the right hand side of the equation (92) is just the change of solubility with temperature at constant pressure if $F_2 - F_2^s = 0$, in the first factor, $F_2 - F_2^s = RT \ln(\frac{f_2}{f_2^s})$, where f_2 is the fugacity of the solute in the solution and f_2^s is that in the solid state. If the solid state is the pure solute (i.e. if no solid solution is formed), f_2^s is independent of x_2 and so it can be written as

$$\left\{ \frac{\partial(\overline{F}_2 - F_2^s)}{\partial \ln x_2} \right\}_{P,T} = RT \left\{ \frac{\partial \ln f_2}{\partial \ln x_2} \right\}_{P,T} = RT \left\{ \frac{\partial \ln a_2}{\partial \ln x_2} \right\}_{P,T} \qquad (93)$$

or

$$\overline{S}_2 - \overline{S}_2^s = R \left\{ \frac{\partial \ln x_2}{\partial \ln T} \right\}_{Sat.p} \left\{ \frac{\partial \ln a_2}{\partial \ln x_2} \right\}_{P,T} \qquad (94)$$

$\left\{ \frac{\partial \ln a_2}{\partial \ln x_2} \right\}_{P,T}$ is the Henry's Law correction factor; it is close to unity for a dilute solution of solids. Since at saturation solubility, $F_2 = F_2^s$ the heat of solution may be written as

$$\overline{H}_2 - H_2^s = T(\overline{S}_2 - S_2^s) = RT \left\{ \frac{\partial \ln x_2}{\partial \ln T} \right\}_{Sat.p} \qquad (95a)$$

The alternate form of equation (95a),

$$\left\{ \frac{\partial \ln x_2}{\partial T} \right\} = \frac{\overline{H}_2 - H_2^S}{RT^2} \qquad (95b)$$

is the "van't Hoff equation" and is extensively used to calculate the heat of solution of a dilute solute.

Equation (94) gives the entropy of solution at constant pressure but Regular Solution theory is mainly concerned with constant volume quantities. So equation (95) has to be converted to the constant volume entropy change. From equation (75),

$$(\overline{S}_2 - S_2^S)_V = (\overline{S}_2 - S_2^S)_P - \left(\frac{\partial P}{\partial T}\right)_V V^E \qquad (96)$$

at $x_2 \to 0$ where α and β of the mixture approach the values of the pure solvent.

Discussion

From the Regular Solution theory, it is expected that when ΔS_2^V , i.e. $(\overline{S}_2 - S_2^S)_V$ is plotted against $-R \ln x_2$, a straight line should be obtained whose slope is expected to be equal to unity and the intercept to be equal to the entropy of fusion of the solid solute at that temperature.

E. B. Smith and J. Walkley[52] plotted $(\overline{S}_2 - S_2^S)_P$ and $(\overline{S}_2 - S_2^S)_V$ against $-R \ln x_2$ for SnI_4 and they obtained a straight line which had a unit slope and a correct intercept. J. H. Hildebrand plotted $(\overline{S}_2 - S_2^s)_V$ versus $-R \ln x_2$ for iodine. He obtained a straight line but the slope was 1.10 and the intercept was different from the expected value. It should be mentioned here that there are uncertainties involved regarding the determination of V_2^o of a solid with high melting point. V_2^o of a solid at any temperature is the volume of the hypothetical liquid supercooled below melting point. Usually it involves a long extrapolation.

In the case of non-violet solution of iodine, the entropy of solution should not be expected to be ideal as it has been suggested that the change of colour of the iodine solution from the violet to the non-violet is due to the formation of "charge-transfer" complex.

As expected, the agreement between the calculated $(\overline{S}_2 - S_2^s)_V$ from $-R \ln x_2$ and experimental $(\overline{S}_2 - S_2^s)_V$ becomes worse when the difference between the molar volume becomes larger as in the case of tetraphenyl tin in ordinary nonpolar solvents [53,54] or bromine in $n\text{-}C_7F_{16}$.[50]

Regarding $\overline{V}_2$, as predicted by equation (83), it has been mentioned before that this is only an approximate equation and is only qualitative in nature. It predicts the increase of $\overline{V}_2$ of solute with the increase of $(\delta_1 - \delta_2)^2$ value which has been verified by E. B. Smith and J. Walkley [52] and M. Vitoria and J. Walkley [53,54] by plotting $\overline{V}_2$ against δ_1 of the solvent.

The application of the simple Regular Solution theory to mixtures of unequal molecules raises a few yet-unsolved problems, particularly when the entropy of mixing unequal molecules is almost invariably non-ideal, even if the molecules are spherical and have their bonds highly covalent. Equation (86b) which is known as the "Flory-Huggins term" is often used to calculate $(\overline{S}_2 - S_2^s)_V$ but there are doubts about its reliability.[53,54]

This problem will be discussed in more detail in later chapters.

Chapter - II

Solubility Studies in Mixed Solvents

Hildebrand and Scott[56] calculated the heat of mixing for three component systems following the similar procedure used by Scatchard[37] for binary nonelectrolyte systems. They wrote the cohesive energy per mole of a ternary mixture as

$$-E_m = (x_1V_1 + x_2V_2 + x_3V_3)(C_{11}\Phi_1^2 + C_{22}\Phi_2^2 + C_{33}\Phi_3^2 + 2C_{12}\Phi_1\Phi_2 + 2C_{13}\Phi_1\Phi_3 + 2C_{23}\Phi_2\Phi_3) \qquad (1)$$

where x's, Φ's, and V's have the meaning of mole fraction, volume fractions and volumes, and C's are the cohesive energy densities.

In equation (1), C's are the constants of binary systems and there are not constants depending on all three components simultaneously. This is the direct consequence of the assumption that the energy of three sets of molecules can be represented by the sum of the three pairs taken independently.

Recalling that $-E_{11} = C_{11}V_1$ etc., the heat of mixing, ΔH^M, may be written as

$$\begin{aligned}\Delta H^M &= E_m - x_1E_1 - x_2E_2 - x_3E_3\\ &= (x_1V_1 + x_2V_2 + x_3V_3)\\ &\quad \times (A_{12}\Phi_1\Phi_2 + A_{13}\Phi_1\Phi_3 + A_{23}\Phi_1\Phi_3) \qquad (2)\end{aligned}$$

where

$$A_{12} = C_{11} + C_{22} - 2C_{12} \tag{3a}$$

$$A_{23} = C_{22} + C_{33} - 2C_{23} \tag{3b}$$

$$A_{31} = C_{33} + C_{11} - 2C_{31} \tag{3c}$$

The A's are the interaction constants of three separate binary systems; so the ternary systems may be completely described if all three two-component systems are known.

Differentiating equation (2), one obtains partial molal heats of mixing:

$$\Delta\overline{H}_1 = V_1[\ A_{12}\Phi_2^2 + A_{13}\Phi_3^2 + (\ A_{12} + A_{31} - A_{23})\ ] \tag{4a}$$

$$\Delta\overline{H}_2 = V_2[\ A_{12}\Phi_1^2 + A_{23}\Phi_3^2 + (\ A_{12} + A_{23} - A_{13})\ ] \tag{4b}$$

$$\Delta\overline{H}_3 = V_3[\ A_{13}\Phi_1^2 + A_{23}\Phi_2^2 + (\ A_{13} + A_{23} - A_{12})\ ] \tag{4c}$$

If the assumption that the interaction energy between the unlike pair is the geometric mean of that between the like pairs, then

$$A_{ij} = (\ \delta_i - \delta_j)^2 \tag{5}$$

and the equations (4a,b,c) reduce to

$$\Delta\overline{H}_1 = V_1\ [\ (\ \delta_1 - \delta_2)\Phi_2 + (\delta_1 - \delta_3)\Phi_3\ ]^2 \tag{6a}$$

$$\Delta\overline{H}_2 = V_2\ [\ (\ \delta_2 - \delta_1)\Phi_1 + (\delta_2 - \delta_3)\Phi_3]^2 \tag{6b}$$

$$\Delta\overline{H}_3 = V_3\ [\ (\ \delta_3 - \delta_1)\Phi_1 + (\delta_3 - \delta_1)\Phi_3]^2 \tag{6c}$$

The equations (6a,b,c) can be rearranged in different ways:

(i) Each of the equations may be rearranged in such a way as to show that the heat of mixing of liquid 2 with liquids 1 and 3 is equivalent to the heat of mixing of liquid 2 with a hypothetical liquid whose δ is the volume fraction average of 1 and 3.

$$\Delta\overline{H}_2 = V_2(\delta_2 - \delta_m)^2 \, \Phi_m^2 \tag{7}$$

where
$$\delta_o = \frac{\Phi_1^s\delta_1 + \Phi_3^s\delta_3}{\Phi_1^s + \Phi_3^s} \tag{8}$$

and
$$\Phi_m = \Phi_1^s + \Phi_3^s \tag{9}$$

The equations (7), (8), and (9) can be rearranged further in terms of the volume fractions Φ_i^o of component 1 and 3 in pure mixed solvents when component 2 has not yet been added, such that

$$\Phi_1^o + \Phi_3^o = 1 \tag{10}$$

whereas analysis of the equations (7), (8), and (9) yields

$$\Phi_m + \Phi_2 = 1$$

or
$$\Phi_1^s + \Phi_2^s + \Phi_3^s = 1 \tag{11}$$

The transformation of the equations (7), (8), and (9) in terms of equation (10) can be done in a much simpler manner in the following way:

From equation (7),

$$\Delta\overline{H}_2 = V_2(\Phi_m\delta_2 - \Phi_m\delta_m)^2$$

or

$$\Phi_m\delta_m = \Phi_m \frac{\Phi_1^s\delta_1 + \Phi_3^s\delta_3}{\Phi_m}$$

$$= \Phi_1^s\delta_1 + \Phi_3^s\delta_3 \qquad (12)$$

Now there exists a relationship between the Φ_i^o's in pure mixed solvents and Φ_i's in three component systems such that

$$\frac{\Phi_1}{\Phi_1^o} = \frac{\Phi_3}{\Phi_3^o} = 1 - \Phi_2 \qquad (13)$$

or

$$\Phi_1 = \Phi_1^o(1 - \Phi_2^s) \qquad (14)$$

$$\Phi_3 = \Phi_3^o(1 - \Phi_3^s) \qquad (15)$$

Substituting Φ_1 and Φ_3's from the equations (14) and (15) in equation (12) one obtains

$$\Phi_m\delta_m = \Phi_1^o(1 - \Phi_2)\delta_1 + \Phi_3^o(1 - \Phi_2)\delta_3$$

$$= \Phi_1^o\delta_1 - \Phi_2^s\delta_1 + \Phi_3^o\delta_3 - \Phi_2^s\delta_3$$

$$= \Phi_1^o\delta_1 + \Phi_3^o\delta_3 - \Phi_1^o\Phi_2^s\delta_1 - \Phi_3^o\Phi_2^s\delta_3 \qquad (16)$$

Again if one defines δ_m in terms of Φ_1^o and Φ_3^o then

$$\Phi_m\delta_m(1) = \Phi_m(\Phi_1^o\delta_1 + \Phi_3^o\delta_3)$$

$$= (1 - \Phi_2^s)(\Phi_1^o\delta_1 + \Phi_3^o\delta_3)$$

$$= \Phi_1^o\delta_1 + \Phi_3^o\delta_3 - \Phi_1^o\Phi_2^s\delta_1 - \Phi_3^o\Phi_2^s\delta_3 \qquad (17)$$

As equations (16) and (17) are identical and Φ_m 's in both the equations are the same, $\delta_m(1) = \delta_m$ or δ_m for a mixed solvent can be defined in terms of the volume fractions of component 1 and 3 in pure mixed solvent such that

$$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3 \qquad (18)$$

such that

$$\Phi_1^o + \Phi_3^o = 1$$

(ii) An alternate transformation of the equations (6a,b,c) leads to the partial molal heat of mixing as a function of the δ of the pure substance and the average δ of the ternary mixture:

$$\Delta\overline{H}_2 = V_2[\ \delta_2(1 - \Phi_2^s) - \Phi_1^s\delta_1 - \Phi_3^s\delta_3\ ]^2$$

$$= V_2[\ \delta_2 - \Phi_2^s\delta_2 - \Phi_1^s\delta_1 - \Phi_3^s\delta_3\ ]^2$$

$$= V_2[\ \delta_2 - \overline{\delta}\ ]^2 \qquad (19)$$

where

$$\overline{\delta} = \Phi_1^s\delta_1 + \Phi_2^s\delta_2 + \Phi_3^s\delta_3$$

Activity Coefficient in Regular Ternary Systems

For regular solutions, the entropy is ideal and the activity coefficients are directly related to the partial molal heats of mixing. Hence for the equations (7) and (19), one may write,

$$\ln \gamma_2 = \frac{\Delta \overline{H}_2}{RT} = \frac{V_2}{RT} \Phi_m^{\ 2} (\delta_2 - \delta_m)^2$$

$$= \frac{V_2}{RT} (\delta_2 - \overline{\delta}\ )^2 \qquad (20)$$

or the saturation solubility of the solute 2 can be formulated as

$$\ln a_2^i = \ln x_2^m + \frac{V_2}{RT} \Phi_m^{\ 2} (\delta_2 - \delta_m)^2 \qquad (21)$$

where a_2^i is the ideal solubility of component 2.

In this chapter we investigate the relationship $\delta_m = \Phi_1^o \delta_1 + \Phi_3^o \delta_3$ and other excess thermodynamic properties of component 2 in mixed solvents. Our investigation suggests that such a relationship of δ_m can only be assumed if we are allowed to define an "effective volume fraction" term. This re-definition arises due to the fact that the solvent molecule environment around a solute molecule is not adequately described by the simple volume fractions, so that one has to take account of the possibility that the solute may be preferentially solvated by a particular solvent partner. In order to emphasize this preferential solvation, we first chose benzene as a mixed solvent partner in the benzene-iodine-cyclohexane system. Later we determined the solubility of stannic iodide in benzene - c-C_6H_{12} mixtures. We selected I_2 and SnI_4 as solutes and C_6H_6 - c-C_6H_{12} as the solvents because of the fact that all necessary thermodynamic data for these systems are available and the binary systems of each solute in each solvent are well studied.[69,70,71-73]

Experimental

Temperature Control

The temperature of the bath in which the saturated solutions were prepared was controlled by means of a contact thermoregulator and an electronic relay box - both supplied by Fisher Scientific Co. Ltd.

A Beckmann thermometer was inserted in the bath to determine any temperature fluctuations.

The thermoregulator was connected to an electronic relay box as was a heating coil. In addition to the heating coil and thermoregulator, one pump for circulating water and a cooling coil were immersed in the bath. The cooling coil was connected to the cold water supply in the laboratory, which is sufficiently cold to keep temperature of the bath at 20°C (the lowest temperature used in this experiment). The temperature of the bath was held within $\pm$ 0.01°C of the desired value.

For the determination of the partial molal volume of the solute a toluene regulator instead of thermoregulator was used. No fluctuation of the liquid level in the stem of the dilatometer was observed using a cathetometer.

Determination of the solubility:

The method used in determining the saturation solubility was a simple and quick one. The procedure can be described in the following way:

The solvent and excess solute were placed in 50 ml flask along with a small teflon-coated magnet bar. The flask was placed at the side wall of the thermostated bath. A Fisher "Thermix" magnetic stirrer was placed outside the bath in contact with the side wall. With such an arrangement the solution can be stirred as long as needed. Usually the solution was stirred for 24 hours and the solution allowed to settle for further 12 hours. Then the flask was opened and the required amount of solution was taken out by means of a volumetric pipet. Two test solutions were pipetted out. Then the flask was closed again and the whole procedure was repeated. This procedure was repeated for each solvent-solute system at one temperature, until three consecutive self-consistent pairs of values were found.

The amoung of solute in the solution was measured spectroscopically at an appripriate absorption peak of the solute (I_2 : 520 mμ; SnI_4 : 320 mμ; and $Sn(C_6F_5)_4$: 267 mμ). A Beer's law calibration plot was constructed for each solute, using known quantities solute in different solvent mixtures.

The saturated solution of solute pipetted out (1-2 ml) was too concentrated for direct spectroscopic studies. Each sample removed from the dissolution cell was diluted (usually 1 : 250 for I_2 and 1 : 500 for SnI_4 and $Sn(C_6F_5)_4$) with c-C_6H_{12} and then the optical density of the diluted solution was measured at the absorption peak of the solute using a Cary - 14 spectrometer.

The accuracy of this technique was verified by comparing the solubility data obtained by this method with available solubility data obtained by other means. A comparison of the solubility of I_2 determined spectroscopically with the solubility of I_2 determined by means of chemical analysis (titration) is given below.

Solvent	Temperature	x_2 (spectroscopic method)	x_2 (titration)
C_6H_6	25°C	0.0481	0.0480 0.430[75]
n-heptane	25°C	0.00676	0.00679[75]

The general consistency of the final results also confirmed the accuracy of this technique (the percentage average error in the saturation solubility is ± 1%).

The spectroscopic analysis is simpler in technique and quicker in determining the amount of solute in solution than any other method of chemical analysis.

The solvents were spectroscopic grade (supplied by Fisher Scientific Co. Ltd.) and were used without further purification.

A typical experimental result: - Saturation solubility of I_2 in a benzene - cyclohexane mixed solvent at 25°C.

Volume fraction of benzene in solute-free mixed solvent = 0.7604

Number of observation	Saturation solubility of I_2 in gms/liter of solvent.
1	110.2
2	109.5
3	107.5
4	107.5
5	109.5
6	109.0
Average =	108.9
Average error =	± 0.9%

or, the saturation solubility of I_2 = 108.9 ± 0.9 gms/liter of solvent.

Effect of average error on δ_m

(a) Effect of positive error on δ_m

Saturation solubility of I_2 = 108.0 + 0.9 gms/liter of solvent or, $x_2 = 0.0392$

Writing the saturation solubility as

$$\ln a_2^i = \ln x_2^m + (V_2/RT)\ (\delta_1 - \delta_2)^2$$

we obtain,

$$\delta_m = \delta_2 + [(V_2/RT)\ (\ln a_2^i - \ln x_2^m)]^{1/2}$$

(where $\delta_2 = 14.1$, $V_2 = 59$ cc and $\ln a_2^i = -1.355$)[110]

or, $\delta_m = 9.75$

(b) Effect of negative deviation on δ_m

Saturation solubility of I_2 in gms/liter of solvent

$= 108.9 - 0.9$

or, $x_2 = 0.0385$

or, $\delta_m = 9.73$

δ_m determined from the average saturation solubility $= 9.74$. So, we see that a 1% average error affects δ_m for the benzene - I_2 - cyclohexane system by one in second decimal place, so that the effect is one in thousand.

The effect of ± 1% error on δ_m for the benzene - SnI_4 - cyclohexane system will be much smaller because for SnI_4, $(V_2/RT)^{1/2} = 1.98$ in comparison to $(V_2/RT)^{1/2} = 3.168$ for I_2.

Determination of partial molal volume

The common method of determining partial molal volume, by determining the density of solution of known composition, requires that the density be measured with an accuracy difficult to obtain with volatile compounds; moreover the method is inaccurate if the solution is dilute[95]. We, therefore, adopted a simple dilatometric method, which has been applied successfully previously for measuring the partial molal volume of iodine, [95] stannic iodide[52] and tetraphenyl tin[54]. The two dilatometers which were built by Dr. M. Vitoria[54] consisted of cylindrical glass bulbs -- one being of 150 ml capacity, the other of 10 ml capacity to conserve solvent. The stem of the dilatometer is calibrated capillary of uniform internal diameter of 0.2 cm[54].

The dilatometer bulb was placed in the thermostated water bath whose temperature was kept constant at 25 ± 0.01°C. A weighed amount of solute was sealed into a long thin-walled capillary, narrow enough to slip down through the stem into the bulb. This was broken under the solvent by a glass ball sealed in the dilatometer and the solute was dissolved by carefully shaking the glass ball. The rise of the liquid level in the capillary was determined by using a cathetometer, after equilibrium of the solution was reached. A correction was made for the amount of glass added and the partial molal volume of the solute was calculated from the expression

$$\overline{V}_2 = (\pi r^2 \Delta \ell M_2)\ /W_2$$

where r is the radius of the capillary, $\Delta \ell$ is the corrected rise in the liquid level, W_2 is the weight of the solute and M_2 is the molecular weight of the solute. A typical experimental result along with error analysis is given below[71].

A typical experimental result:

Composition of mixed solvent:

$$\Phi_{\text{Benzene}} = \Phi_1^0 = 0.6927$$
$$\Phi_{c-C_6H_{12}} = \Phi_3^0 = 0.3073$$

Wt. of glass = 0.0324 gm

Wt. of glass + I_2 = 0.0456 ± 0.0001 gms

so, wt. of I_2 = 0.0141 ± 0.0001 gms.

Total rise of liquid level = 0.565 ± 0.001 cm.

Rise due to glass = 0.453 ± 0.002 cm.

(Density of glass was taken as 2.26 ± 0.01 gm/cc[72].)

Rise due to I_2 in solution = 0.112 ± 0.003 cm.

Partial molal volume of I_2 = $\overline{V}_2$

= 63.3 ± 1.7 cc.

Results

Saturation solubility, entropy of solution ($\Delta\overline{S}_2^P$), partial molal volumes and other relevant data for I_2 in C_6H_6 - c-C_6H_{12} are given in Table II.1. In Figure II.1 we give $-R \ln x_2$ versus $^0_1$ (volume fractions of benzene) plots at 20°, 25° and 30°C. In Figure II.2 we plot the excess quantities

$$R(\Delta \ln x_2^m) = R[\ln x_2^m - (\Phi_1 \ln x_2^1 + \Phi_3 \ln x_2^3)]$$

and

$$\overline{V}_2^m(\text{excess}) = \overline{V}_2^m - (\Phi_1 \overline{V}_2^1 + \Phi_3 \overline{V}_2^3)$$

Assymetry of both the excess curves was noted.

In Table II.5 we give the saturation solubility and other relevant data for SnI_4 in benzene - c-C_6H_{12}.

In Figure III9 we plot $-R \ln x_2^m$ (for SnI_4) against Φ_1^0 (volume fraction of benzene) at 25°C.

The saturation solubility of naphthalene in CH_2I_2 - c-C_6H_{12} mixed solvent determined spectroscopically is given in Table II.10. The saturation solubility of $Sn(C_6F_5)_4$ determined spectroscopically is given in Table III.4 and the partial molal volumes of $Sn(C_6F_5)_4$ in different organic solvents are given in Table III.5.

Discussion

In terms of Regular Solution theory, the saturation solubility of iodine in the mixed solvent and iodine in pure $c\text{-}C_6H_{12}$ solvent are given by

$$\ln a_2^i = \frac{V_2}{RT} \Phi_m^2 (\delta_2 - \delta_m)^2 + \ln x_2^m \qquad (22)$$

$$\ln a_2^i = \frac{V_2}{RT} \Phi_3^2 (\delta_2 - \delta_3)^2 + \ln x_2^3 \qquad (23)$$

where subscript m refers to the particular property or quantity of the mixed solvent for I_2 in C_6H_6 - $c\text{-}C_6H_{12}$ system, subscript 1 always refers to benzene, 2 to iodine and 3 to $c\text{-}C_6H_{12}$.

$$\delta_m = \Phi_1^o \delta_1 + \Phi_3^o \delta_3$$

x_2^m is the saturation mole fraction solubility of 2 in the mixed solvent; similarly x_2^3 is the saturation mole fraction solubility of 3 in pure solvent 3 (here $c\text{-}C_6H_{12}$). For a dilute solution as in the case of I_2 in $c\text{-}C_6H_{12}$ or I_2 in C_6H_6 - $c\text{-}C_6H_{12}$ mixed solvent, the iodine mole fraction solubilities are of the order of 10^{-2}, and Φ_3^2 and Φ_m^2 can be assumed to be equal to 1. So equations (22) and (23) can be rewritten as

$$\left\{ \frac{RT}{V_2}(\ln a_2^i - \ln x_2^m) \right\}^{\frac{1}{2}} = \delta_2 - \delta_m$$

$$= \delta_2 - (\Phi_1^o \delta_1 + \Phi_3^o \delta_3)$$

$$= (\delta_2 - \delta_3) - \Phi_1^o(\delta_1 - \delta_3) \qquad (24)$$

Similarly for iodine in the pure solvent 3,

$$\left\{ \frac{RT}{V_2} (\ln a_2^i - \ln x_2^3)^{\frac{1}{2}} \right\} = \delta_2 - \delta_3 \qquad (25)$$

Dividing equation (24) by equation (25) and then rearranging, one obtains

$$(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} = (\ln a_2^i - \ln x_2^3)^{\frac{1}{2}}$$

$$- (\ln a_2^i - \ln x_2^3)^{\frac{1}{2}} \Phi_1^o \left\{ \frac{\delta_1 - \delta_3}{\delta_2 - \delta_3} \right\} \qquad (26)$$

Equation (26) implies that a linear relationship exists between the $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^o for which the intercept value at $\Phi_1 = 0$ can be compared to an experimental quantity and for which the ratio of the slope:intercept may be compared with δ_i's.

The relationship between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^o for iodine in C_6H_6 - c-C_6H_{12} is shown in Figure II.3 and $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^o i.e. volume fraction of benzene for SnI_4 in C_6H_6 - c-C_6H_{12} is shown in Figure II.10. Assuming that an expected linear proportionality exists, the best intercept value for iodine in C_6H_6 - c-C_6H_{12} mixed solvent obtained by drawing the best line is 1.755 which compares badly with the experimental value of 1.835 for $(\ln a_2^i - \ln x_2^3)^{\frac{1}{2}}$. An analysis of the plot in Figure II.3 suggests that the relationship is not in fact linear. On the contrary, if a smooth curve is drawn through the experimental points, then the intercept of the plot compares favourably with the expected value. The above analysis rests on the validity of the assumption that $\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$ but not on any assumption of the actual δ values. In Table II.2 δ_m for C_6H_6 - c-C_6H_{12} mixed solvent in C_6H_6 - I_2 - c-C_6H_{12} system calculated from the solubility relationship, equation (22), and those calculated according to the relationship $\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$ for $\delta_3 = 8.2$ and δ_1 (for benzene) of both 9.2 and 9.99, are compared. The former δ_1 value being the thermodynamic $(\frac{\Delta E}{V})^{\frac{1}{2}}$ value, the latter being derived from the experimental saturation solubility of iodine in pure benzene. The first set of the calculated δ_m values are quite incompatible with the δ_m(experimental) and the latter are only in moderate agreement. The disagreement between the calculated δ_m's and the experimental δ_m values suggests either that a pairwise additivity approximation does not hold, or that the nearest solute neighbours of solute in the mixed solvent are probably not reflected by the volume fractions composition of the bulk solvent mixture.

In analysing the first assumption, we see that in the absence of dipole interactions and molar volume difference of the solute and solvents, this assumption is similar to the one that is usually made in formulating the additivity rule for dispersion or van der Waals forces in calculating intermolecular forces. Although it has been shown by Axilord and Teller[59,60] (and later by Jansen and co-workers[61-63]) that the additivity rule for van der Waals or dispersion forces are only approximate but the magnitude of the contribution of the nonadditivity to the total intermolecular forces and their importance are not very clear at present. Anyway it seems that at room temperature, the contribution due to the nonadditivity is negligible provided no dipole and steric interactions are present. A similar conclusion was drawn by Hildebrand et al.[19]

The second assumption originates from the earlier assumption that the partial heat of mixing of liquid 2 with liquids 1 and 3 is equivalent to the heat of mixing of liquid 2 with a hypothetical new liquid whose δ is the volume fraction average of 1 and 3 in solute free pure mixed solvents. In a previous work [64] concerning the partial molal volume of bromine in CCl_4 - $c\text{-}C_4Cl_2F_6$ a preferential contact between bromine and CCl_4 was needed to explain the experimental results. Christian et al.[65,66] in their studies of the effect of the solvents on the formation of electron donor-acceptor complexes, proposed a "distribution coefficient" of the acceptor and donor in the solvents. This idea was introduced in order to correlate the variation of equilibrium constant of donor acceptor complexes with solvents. In other words for a given donor and acceptor, the number of donor molecules around the acceptor molecules depends upon the ability of solvent to solvate the acceptor, provided the number of the nearest neighbour of the acceptor does not change. The distribution coefficient, $K_{A,i}$ of acceptor A in a solvent i with respect to a reference solvent, ref , was written[66] as

$$K_{A,i} = \frac{\gamma_D^{ref} \quad V^{ref}}{\gamma_D^{i} \quad V_i} \tag{27}$$

where γ_D 's are the activity coefficients of component of acceptor in reference solvent and the solvent i, V^{ref} is the molar volume of reference solvent, and V_i is the molar volume of solvent i .

Christian defined γ's of the solute (here acceptor) from Regular Solution theory as

$$\gamma_2^{ref} = \frac{V_D}{RT} (\delta_{ref} - \delta_A)^2 \tag{28}$$

where V_D is the molar volume of D , and δ's are the solubility parameters.

Defining the distribution coefficients of the donor in terms of the equations (27) and (28), Christian was able to correlate K_{eq} for pyridine-iodine in various nonpolar solvents with the distribution coefficient K_{D2i} .

Murrell et al.[67,68] introduced the idea of a "well defined solvation shell" which is supposed to form around the acceptor molecule in the solution. The formation of an electron donor acceptor complex in solution results in the elimination of the solvent molecules of the so-called "well defined solvation shell."

These experimental results definitely indicate that in three component systems there is a preferential solvation around the solute by one of the solvents, or in other words the volume fractions of components 1 and 3 in pure mixed solvent do not adequately define the environment around the solute molecules in the mixed solvent. Considering the possibility that there may be some preferential solvation effect around the solute molecule, we selected benzene as one of the components of the mixed solvent, because of the well-known "likeness" of iodine for benzene (due to the formation of electron donor acceptor complex between benzene and iodine.[69,70])

The relative number of nearest neighbour molecules of a particular solvent around a solute molecule in the three component system can be calculated from the experimental δ_m from the equations

$$\delta_m(\text{expt}) = \Phi_1^*\delta_1 + \Phi_3^*\delta_3 \tag{30}$$

and

$$\Phi_1^* + \Phi_3^* = 1$$

where Φ^*'s are now defined as the effective volume fractions, which are the measure of the relative number of benzene and cyclohexane molecules around the iodine solute molecule.

We may also define the "effective volume fractions" Φ^* in terms of the relative number of solvent molecules around the solute molecule as

$$\frac{\Phi_1^*}{\Phi_3^*} = \frac{N_1^*V_1}{N_3^*V_3} = \frac{N_1}{N_3}\frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2}\frac{V_1}{V_3}$$

$$= \frac{\Phi_1^o}{\Phi_3^o}\frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2} \qquad (31)$$

when

$$\Phi_1^o + \Phi_3^o = 1$$

and

$$\Phi_1^* + \Phi_3^* = 1 \qquad (32)$$

Although we have not been able to justify this type of definition for Φ^* from the complete mathematical derivations, it can be clearly seen that equations (31) and (32) are based upon the interaction constants for 1-3 and 2-3 systems given in the saturation solubility equation for two component systems. These equations say that the ratio of the 1 and 3 types of the nearest neighbour molecules is the bulk solvent mixture ratio weighted by the respective heats of mixing of iodine in pure solvents. The total effect of the "effective volume fraction" Φ^* defined by equations (31) and (32) is the minimization of partial molal excess free energy of component 2 in the three component systems. As we are unable to justify these equations from the mathematical derivations of an established equation, these equations can be justified from experimental results from different sources and from the effects of these equations on other thermodynamic properties of three component systems. From the physical significance of the "preferred environment around the solute molecule" (i.e. 2) we expect that the numbers of the preferred molecules, in this case benzene, in the solution must be greater than the number of molecules of component 2 in the solution. As in this section we are dealing with very dilute solutions of component 2, where the composition of three component are such that the number of "preferred molecules" are always greater than the solute molecules, we need not mention these restrictions. But for nondilute solutions, as will be discussed later, this restriction will play a very important role in determining the thermodynamic properties.

Using δ_2, δ_1 and δ_3 values of 14.1, 9.99 and 8.2 respectively for iodine in benzene-cyclohexane mixed solvent, we calculated δ_m^* from the relationship

$$\delta_m^* = \Phi_1^*\delta_1 + \Phi_3^*\delta_3 \tag{33}$$

These are given in Table II.2. Clearly δ_m^*'s are in excellent agreement with δ_m(experimental). In Figure II.3 the $(\ln \frac{a_2^i}{x_2^m})^{\frac{1}{2}}$ versus Φ_1^* is also plotted. An excellent linear relationship is seen to exist, the intercept of 1.85 agreeing well with the experimental value 1.835 and from the ratio of the slope to intercept, δ_1 iscalculated as 9.9, in exact self-consistent agreement with the value previously used.

In Figure II.4 and II.5 we plotted both $-R \ln x_2^m$ and partial molal volume against Φ_1^*. These plots are in sharp contrast with the dependence of $-R \ln x_2$ and $\overline{V}_2^M$ on Φ_1. The Figures II.4 and II.5 suggest almost linear dependence of $-R \ln x_2^m$ and $\overline{V}_2^M$ on Φ_1^* values, such that

$$R \ln x_2^m = \Phi_1^* R \ln x_2^1 + \Phi_3^* R \ln x_2^3 \tag{34}$$

and

$$\overline{V}_2^M = \Phi_1^* \overline{V}_2^1 + \Phi_3^* \overline{V}_2^3 \tag{35}$$

Although Figures II.4 and II.5 suggest a linear relationship between Φ_1^* and $-R \ln x_2^m$ and $\overline{V}_2^M$, we will see in a later section of this chapter that equations (34) and (35) are merely limiting cases of more rigorous equations.

It is useful to examine the Φ_1^* term for other systems. We consider data for the solubility of iodine in a mixed benzene - carbon tetrachloride solvent reported by S. E. Wood et al.[73] The $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_1^* plot is given in Figure II.6. The linearity is seen to be excellent and the intercept $(\ln a_2^i - \ln x_2^3)$ $= 1.785$ is in good agreement with experimental value 1.80. In this calculation superscript and subscript 1 stand for benzene, 2 for iodine and 3 for CCl_4. (x_2^3 i.e. mole fraction saturation solubility of iodine in CCl_4 was taken from Wood's data.) δ_3 (for CCl_4) was calculated from x_2^3 . From the slope we again find that for iodine solute the "best" δ parameter for benzene is of value 9.99. In Table II.3 we compare the experimental δ_m value with those values calculated using both volume fraction and effective volume fraction terms. The latter data show an excellent agreement with the experimental value. In Figure II.7 we plot $\ln x_2^m$ against Φ and Φ_1^* and using Φ_1^* , the experimental data appears to be additive in terms of the saturation solubility of iodine in two pure solvents. Clearly this linear dependence of both $\ln x_2^m$ and $\overline{V}_2^m$ upon Φ_1^* , with the inference of "zero excess property of mixing term" is a special case of a more generalized formulation of Regular Solution theory, which will be discussed later. In this section we are more interested in examining the validity of the definition of Φ^*'s. As mentioned above, we chose benzene as one component of our solvent mixture because of the electron donor acceptor interaction between benzene and iodine. The enhancement of the δ_1 parameter for benzene from 9.2 to 9.99 reflects this.

So far, we have limited our discussion to systems where the solute has a special liking for one solvent, thus enlarging the effect of preferential solvation. Now we examine the cases where no such special interactions such as the electron donor acceptor interaction exist. This is the case with iodine in a mixed CCl_4 - n-C_7F_{16} solvent[74]-- only two data points exist for this system. The agreement between equation (26) and the above data is examined by recognizing that the $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ relationship can be predicted knowing the saturation solubility of the solute in the pure solvent, the ideal saturation solubility and the three δ_i values. In Figure II.8 this relationship is plotted for the iodine - CCl_4 -n-C_7F_{16} system and it is seen that data points lie on the observed line only if they are plotted against Φ_1^* value.

From the above discussions, it is clear that if δ_1 and δ_3 are adjusted with respect to a constant δ_2 value from the saturation solubility for 2 in 1 and 2 in 3, no forther adjustment of δ parameters is needed for three component systems. Besides we also showed the importance of Φ^* in calculating the saturation solubility and $\overline{V}_2^m$ of 2 in a mixed solvent. To verify these statements we changed the solute from iodine to stannic iodide -- but we keep the mixed solvents as benzene - c-C_6H_{12} mixture. The reason for this can be found in the fact that for SnI_4 , δ_1 i.e. solubility parameter of benzene, calculated from the saturation solubility data, assuming δ_2 (solubility parameter of stannic iodide) equal to 11.8, was found to be 9.24 in $(cal/cm^3)^{\frac{1}{2}}$, an excellent agreement with the δ_1 value 9.2, calculated from the heat of vaporization

$\ln x_2^m)^{\frac{1}{2}}$ versus Φ_1^*) is found to be 0.38 which is in good agreement with the value 0.376, calculated for the slope from equation (26) with $\delta_1 = 9.24$, $\delta_2 = 11.8$ and $\delta_3 = 8.5\ (\mathrm{cal/cm^3})^{\frac{1}{2}}$. In the case of SnI_4 in C_6H_6 - c-C_6H_{12} mixed solvent, we see that we definitely need a preferential solvation around the SnI_4 molecule by one of the solvents, i.e. benzene, even though there are no specific interactions between SnI_4 and benzene molecules. But because of the close proximity of δ_1 and δ_3 values, the actual preferential solubility is much less than that in the case of I_2 in benzene - c-C_6H_{12} or I_2 in benzene - CCl_4 mixed solvents.

In Figure II.11 we plot $\ln x_2^m$ versus Φ_1^* for SnI_4 in benzene - c-C_6H_{12} . Unlike I_2 in benzene - c-C_6H_{12} or I_2 in benzene - CCl_4 , the experimental $\ln x_2^m$ is not linearly dependent on Φ_1^* , which indicates that the "excess property of mixing" is no longer zero for this system.

Finally we test the validity of the definition of Φ^* 's from the expected linearity of δ_m(experimental) and Φ or Φ_1^* because if

$$\begin{aligned} \delta_m(\mathrm{expt}) &= \Phi_1^o\delta_1 + \Phi_3^o\delta_3 \\ &= \Phi_1^o\delta_1 + (1 - \Phi_1^o)\delta_3 \\ &= \Phi_1^o(\delta_1 - \delta_3) + \delta_3 \qquad (36) \end{aligned}$$

data. Whereas for iodine-benzene system, as mentioned earlier, δ_1 for benzene had to be shifted to 9.99 (assuming that the solubility parameter of iodine is equal to 14.1) to take account of the electron donor acceptor interaction between benzene and iodine. From the saturation solubility of stannic iodide in cyclohexane, δ_3 (i.e. the solubility parameter of cyclohexane) was found to be 8.50 in comparison to 8.2 calculated from the heat of vaporization data.

In Table II.5 we have given the saturation solubility along with the values for $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ of SnI_4 in five mixed solvents at 25° C. In Table II.6 we compare δ_m(experimental) calculated from the saturation solubilities of SnI_4 in the mixed solvents assuming $\delta_2 = 11.8$ with δ_m(calc'd) calculated from the relationship

$$\delta_m = \Phi_1^o \delta_1 + \Phi_3^o \delta_3$$

and

$$\delta_m^* = \Phi_1^{o*} \delta_1 + \Phi_3^{o*} \delta_3$$

Clearly δ_m^* values are in much better agreement with the experimental δ_m values than δ_m calculated from the simple volume fractions. In Figure II.10 $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ for SnI_4 in C_6H_6 - c-C_6H_{12} is plotted against both Φ_1 and Φ_1^*. Again we see that an excellent linear relationship exists between the $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^* rather than Φ_1. The slope line ($(\ln a_2^i$ -

or if

$$\delta_m(\text{expt}) = \Phi_1^{o*}\delta_1 + \Phi_3^{o*}\delta_3$$

$$= \Phi_1^{o*}(\delta_1 + \delta_3) + \delta_3 \qquad (37)$$

then one should expect a straight line when δ_m (experimental) is plotted either against Φ_1^{o*} or Φ_1^{o} , with an intercept equal to δ_3 and a slope equal to $(\delta_1 - \delta_3)$. In Figure II.12 we plot δ_m (experimental) against Φ_1^{o} (volume fraction of benzene) and Φ_1^{o*} , for I_2 in benzene - c-C_6H_{12} system. Clearly δ_m(experimental) when plotted against Φ_1^{*} is in much better agreement with the expected line than when plotted against Φ_1 .

In Figure II.13 δ_m(experimental) for C_6H_6 - CCl_4 mixed solvent in C_6H_6 - I_2 - CCl_4 system is plotted against Φ_1^{o} and Φ_1^{o*} (volume fraction of benzene),and in Figure II.14 δ_m(experimental) for C_6H_6 - c-C_6H_{12} mixed solvent in C_6H_6 - SnI_4 - c-C_6H_{12} is plotted against Φ_1^{o} and Φ_1^{o*} (volume fraction of benzene). From both of the figures, it is clear that δ_m(experimental) is better described in terms of Φ^{*}'s rather than Φ_1, or in other words, an assumption of preferential solvation of solute by one solvent is definitely needed to describe the different properties of solutes in mixed solvents. By"describing" we mean to correlate the solubility and thermodynamic properties of solute with those properties of solute and solvents in two component systems containing solute 2 and solvent 1, and solute 2 and solvent 3.

Excess Properties of Mixing for Dilute Solutions

Introduction

In previous sections, we have attempted to show that Regular Solution theory may be usefully employed to interpret the solubility properties of a dilute solute in mixed solvents. We also tried to show that there is needed a term called the "effective volume fraction," Φ_i^* , to define the immediate environment of solute molecules in a mixed solvent. We also showed that in some cases there exist linear relationships between $\ln x_2^m$, V_2^m , and Φ_i^* such as

$$\ln x_2^m = \Phi_1^* \ln x_2^1 + \Phi_3^* \ln x_2^3$$

and

$$\overline{V}_2^m = \Phi_1^* \overline{V}_2^1 + \Phi_3^* \overline{V}_2^3$$

(the notations are the same as in previous section).

The relationship between δ_m and Φ^* satisfies the condition that a mixed solvent may be considered as a hypothetical solvent whose solubility parameter (here δ_m) is the volume fraction average of the two pure components. The other two relationships, although very attractive at first glance, do have a very limited applicability because, as suggested earlier, these two relationships hold because of the "zero excess property of mixing." In this section we will derive the excess properties with respect to the binary systems, and from the Regular Solution theory we will try to predict these excess quantities. We shall also try to show that Φ_i^* is needed to define the excess properties and the volume fraction of the mixture, where the maximum of the "excess properties" would be observed.

The main purpose of this chapter is to generalize the solubility relationships for three component systems and so derive the limiting conditions where the saturation solubilities of the solute in mixed solvents can depend linearly on, say, Φ_1^* . In the first part of this section we limit our discussions to very dilute solutions such that

$$\ln a_2^i = \ln x_2^m + \frac{V_2}{RT} (\delta_1 - \delta_2)^2$$

i.e. the Φ_2 (ie the volume fraction of the solute)in the solution approaches zero.

Theory

Excess Saturation Solubility

Having established the definition of Φ_i^* and the importance of this term in three component systems, we now turn to the generalized properties of solubility relationships for three component systems. In all the discussions in the previous section we limited ourselves to the case where $\delta_1 < \delta_2 > \delta_3$. For those cases where

$\delta_1 > \delta_2 > \delta_3$, at certain volume fraction of Φ_1^*, the δ_m value becomes equal to the δ_2 value (of the solute) and the partial molal heat of solution of component 2 then becomes zero and the saturation solubility of the solute (x_2) is equal to the ideal solubility (a_2^i) of the solute. All the derivations discussed in the previous section are applicable where $\delta_1 > \delta_2 > \delta_3$ as long as the solubility of component 2 is very small, i.e. where $\Phi_1^S + \Phi_3^S \rightarrow 1$.

We shall accept that the saturation solubility of some dilute solute 2 in a solvent S may be written with the usual Regular Solution notations as

$$\ln x_2 = \ln a_2^i - A(\delta_2 - \delta_s)^2 \tag{38}$$

where

$$A = \frac{V_2 \Phi_S{}^2}{RT}$$

$$= \frac{V_2}{RT} \quad \text{(for a dilute solution)} \tag{39}$$

For the cases where the solvent is a binary mixture of components 1 and 3, we then assume

$$\delta_S = \Phi_1^o \delta_1 + \Phi_3^o \delta_3 = \delta_m \tag{40}$$

If one writes the saturation solubility of component 2 in mixed solvent in terms of the saturation solubility of the solute in pure solvents 1 and 3, as done in equation (34), then

$$\ln x_2^m(i) = \Phi_1^o \ln x_2^1 + \Phi_3^o \ln x_2^3 \qquad (41)$$

Substituting equation (38) into equation (41) for the case for which $\delta_S = \delta_1$ or δ_3 then

$$\ln x_2^m(i) = \ln a_2^i - A[\ \delta_2{}^2 - 2\delta_2(\Phi_1^o\delta_1 + \Phi_3\delta_3) + \Phi_1^o\delta_1^2 + \Phi_3^o\delta_3^2\ ] \qquad (42)$$

Again substituting equation (40) into equation (38) we find

$$\ln x_2^m = \ln a_2^i - A(\delta_2 - \delta_m)^2$$

$$= \ln a_2^i - A(\delta_2{}^2 - 2\delta_2\delta_m + \delta_m{}^2) \qquad (43)$$

Again substituting equation (40) into equation (42) and then comparing equation (42) with equation (43) we see that

$$\delta_m{}^2 = \Phi_1^o\delta_1{}^2 + \Phi_3^o\delta_3{}^2 \qquad (45)$$

a requirement which is obviously in contradiction with the condition given in equation (40) for δ_m.

In equation (41) we used the notation $\ln x_2^m(i)$ to identify this as the "thermodynamic" saturation solubility in mixed solvent, relative to the saturation solubilities of a solute in two pure solvents.

The thermodynamic justification of this notation is based on the fact that the partial molar excess free energy is also zero with respect to that of the solute in the pure solvents. (Note that $\ln x_2^m(i)$ is not

$\ln a_2^i$ which is the ideal solubility of solute irrespective of solvents.) So we can define the excess saturation solubility as

$$\Delta(\ln x_2^m) = \ln x_2^m(i) - \ln x_2^m \tag{46}$$

Using equation (41), we see that $\Delta(\ln x_2^m)$ can be evaluated from the experimentally determined quantities $\ln x_2^1$, $\ln x_2^3$ and $\ln x_2^m$. It can also be determined from the Regular Solution theory. Equation (38) is defined in terms of the pure solvents 1 and 3, and the mixed solvents, m , as

$$\begin{aligned}\Delta(\ln x_2^m) &= \Phi_1^o A(\ln x_2^1) + \Phi_3^o A(\ln x_2^3) \\ &\quad - A(\delta_2 - \delta_m)^2 \\ &= A(\Phi_1\delta_1{}^2 + \Phi_3\delta_3{}^2 - \delta_m{}^2)\end{aligned} \tag{47}$$

i.e.

$$\frac{1}{A}\,\Delta(\ln x_2^m) = \Phi_1\Phi_3(\delta_1 - \delta_3)^2 \tag{48}$$

So far we have not used the effective volume fractions, but if one writes the $\ln x_2^m(i)$ in terms of the effective volume fraction, then

$$\frac{1}{A}\,\Delta^*(\ln x_2^m) = \Phi_1^*\Phi_3^*(\delta_1 - \delta_3)^2 \tag{49}$$

To be rigorous, even if we allow ourselves to use the "effective volume fraction" terms in defining the δ_m , and if we recognize that the effective volume fraction describes only the immediate solvent environment of the solute molecule, we must still define the $\ln x_2^m(i)$ in terms of Φ^o's and not Φ^*'s because the "ideal" term must refer to the composition of the bulk solvent, as in equation (41). So, writing δ_m as

$$\delta_m = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$$

in the expression for $\Delta \ln x_2^m$,

$$\Delta(\ln x_2^m) = A(\Phi_1 \ln x_2^1 + \Phi_3 \ln x_2^3) - A(\delta_2 - \delta_m)^2$$

one obtains the excess saturation solubility as

$$\frac{1}{A}\Delta(\ln x_{2*}^m) = [\ \Phi_1\delta_1^2 + \Phi_3\delta_3^2 - \delta_m^2 - 2\delta_2(\Phi_1\delta_1 + \Phi_3\delta_3 - \delta_m)\ ] \qquad (50)$$

In equation (50) one can clearly see that we have made

$$\delta_m = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$$

and not

$$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$$

The notation of subscript $2*$ has been used to denote that the possibility of the immediate solute 2 environment is different from the "average" bulk solvent environment.

Excess Volume of Mixing

For a very dilute solution of non-electrolytes one may calculate the partial molal volume of solute from Regular Solution theory.[78] We may write for a very dilute solution

$$\bar{V}_2^E = \bar{V}_2 - V_2^o = n_1 \beta_1 \bar{F}_2^E$$

where $\bar{V}_2$ is the partial molal volume of the solute in solution, V_2^o is the reference volume of the solute, n_i is the ratio of the internal pressure of the solvent to its cohesive energy density, and β_i is the coefficient of isothermal compressibility of the pure solvent, i .

From the Regular Solution theory,

$$\bar{F}_2^E = V_2^o(\delta_2 - \delta_i)^2$$

or we may obtain a very useful equation such as

$$\bar{V}_2 - V_2^o = n_i \beta_i V_2^o(\delta_2 - \delta_i)^2 \tag{51}$$

or[78]

$$\bar{V}_2 - V_2^o = \frac{\alpha_i T V_2^o}{\delta_i^2}(\delta_2 - \delta_i)^2 \tag{52}$$

where α_i is the coefficient of thermal expansion.

As mentioned earlier, equations (51) and (52) were derived as approximate equations and their applicability is far less than the applicability of Regular Solution theory in predicting the excess free energy of mixing. Remembering the limitations of these equations, we now define a term Δ_V^i as

$$\Delta_V^i = \frac{\bar{V}_2^i - V_2^o}{V_2^o}$$

or

$$\Delta_V^i = n_i\beta_i(\delta_2 - \delta_i)^2 \tag{53}$$

So far the expressions for $\overline{V}_2^E$ have been written for binary systems. For the mixed solvents, the partial molal volume of solute, $\overline{V}_2$, is given by

$$\overline{V}_2^M - \overline{V}_2^o = V_2^o n_m\beta_m(\delta_2 - \delta_m)^2$$

or,

$$\Delta_V^M = \frac{\overline{V}_2^M - V_2^o}{V_2^o} = n_m\beta_m(\delta_2 - \delta_m)^2 \tag{54}$$

In the following derivations, we will assume that only Φ^*'s describe δ_m correctly rather than Φ's.

Now we define another term $\Delta_V^{M,1,3}$ in terms of the properties of the solute in each of the pure solvents as

$$\Delta_V^{M,1,3} = \Phi_1\Delta_V^1 + \Phi_3\Delta_V^3 \tag{55}$$

or we may define the excess partial molal volume of mixing for solute 2 in a mixed solvent system with respect for the excess partial molal volume of solute (2) in pure solvents, i.e.

$$\overline{V}^{E,M} = -V_2^o(\Delta_V^M - \Delta_V^{M,1,3}) \tag{56}$$

Substituting the respective equations in equation (55) we obtain

$$\Delta_V^{M,1,3} = \Phi_1[n_1\beta_1(\delta_1 - \delta_2)^2] + \Phi_3[n_3\beta_3(\delta_1 - \delta_3)^2] \tag{57}$$

or using the assumption that

$$n_i\beta_i = \frac{\alpha_i T}{\delta_i^2}$$

or

$$n_i\beta_i\delta_i^2 = \alpha_i T \qquad (58)$$

we obtain

$$\Delta_V^{M,1,3} = (\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_2^2 - 2\delta_2[\Phi_1(\frac{\alpha_1}{\delta_1}) + \Phi_3(\frac{\alpha_3}{\delta_3})]T + (\Phi_1\alpha_1 + \Phi_3\alpha_3)T \qquad (59)$$

We may similarly rewrite the equation (56) as

$$\Delta V^{E,M} = n_m\beta_m\delta_2^2 - 2\delta_2(\frac{\alpha_m}{\delta_m})T + \alpha_m T \qquad (60)$$

We may further assume that the mechanical properties of the mixed solvent may be expressed in terms of those of the pure solvents by *

$$n_m\beta_m = \Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3 \qquad (61)$$

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* Probably a more reasonable approximation would be to write $n_m\beta_m$ in the following manner:

$$n_m\beta_m = (\Phi_1\beta_1 + \Phi_3\beta_3)(\Phi_1 n_1 + \Phi_3 n_3)$$

$$= \Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3 - (\Phi_3^2 n_3\beta_1 + \Phi_1^2 n_1\beta_3)$$

Neglecting the higher terms in Φ's we obtain equation (61).

and

$$\alpha_m = \Phi_1\alpha_1 + \Phi_3\alpha_3 \qquad (62)$$

Besides equation (61) and (62), we also assume that

$$n_m\beta_m\delta_m^{\,2} = \Phi_1 n_1\beta_1\delta_1^{\,2} + \Phi_3 n_3\beta_3\delta_3^{\,2} \qquad (63)$$

Substituting equations (61), (62) and (63) in equation (56), the excess terms, i.e. $\Delta\overline{V}_2^{E,M}$, becomes

$$\Delta\overline{V}_2^{E,M} = 2\delta_2 T V_2^o\left[\frac{\alpha_m}{\delta_m} - \left(\Phi_1\frac{\alpha_1}{\delta_1} + \Phi_3\frac{\alpha_3}{\delta_3}\right)\right] \qquad (64)$$

If we do not choose to use α_i's, then the excess volume, $\Delta\overline{V}_2^{E,M}$ becomes more complex (see Appendix AII.1 for derivations) and is given by

$$\begin{aligned}\Delta\overline{V}_2^{E,M} = V_2^o \Big\{ & 2\delta_2[(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_m \\ & -(\Phi_1 n_1\beta_1\delta_1 + \Phi_3 n_3\beta_3\delta_3)] \\ & + (\Phi_1 n_1\beta_1\delta_1^{\,2} + \Phi_3 n_3\beta_3\delta_3^{\,2}) \\ & - (\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_m^{\,2} \Big\} \qquad (65)\end{aligned}$$

As seen in equation (65) we have not assumed that

$$n_m\beta_m\delta_m^{\,2} = \Phi_1 n_1\beta_1\delta_1^{\,2} + \Phi_3 n_3\beta_3\delta_3^{\,2}$$

(as in equation (63)) which is probably an incorrect assumption.

The expression $\Delta_V^{E,M}$(expt) can be written as

$$\Delta_V^{E,M}(\text{expt}) = \overline{V}_2^{E,M} - (\Phi_1\overline{V}_2^1 - \Phi_3\overline{V}_2^3) \qquad (66)$$

In the following discussion we will refer to $\Delta\overline{V}_2^{E,M}$ (calc'd) as it is given in equation (65) and not as in equation (64).

In our above discussion of the volume of mixing term we have developed both equation (64) and (65) without defining δ_m, i.e. these equations are independent of the definition of δ_m. In these equations, any derivation of δ_m can be substituted as long as the solution is dilute in solute. But, as we have mentioned earlier, δ_m's are better described by Φ^* values. In further discussions on excess volumes we will use only δ_m's calculated from Φ^*'s.

Discussion

We shall first discuss those systems in which the solute solubility parameters are greater than those of either component mixtures, i.e. $\delta_1 < \delta_2 > \delta_3$. We see from the equation (48) that the magnitude of the excess term, i.e. $\frac{1}{A}\Delta(\ln x_2^m)$, is governed by the square of the difference of the solubility parameters of the components of the mixed solvents. The maximum value for the excess term will occur at

$$\frac{\partial[\frac{1}{A}\Delta(\ln x_2^m)]}{\partial\Phi_1^o} = 0 = (1 - 2\Phi_1) \quad \text{at} \quad \Phi_1^o = \Phi_1^o(\max)$$

or

$$\Phi_1^o(\max) = 0.5 \qquad (67)$$

Similarly, the excess term $\frac{1}{A}\Delta^*(\ln x_2^m)$ in equation (44) will have its maximum value displaced from $\Phi_1 = 0.5$ by the relative $(\delta_2 - \delta_3)^2$ and $(\delta_2 - \delta_1)^2$ values. (See the definition of Φ^* values.) It can be shown that the position of this maximum, given by

$$\frac{\partial[\frac{1}{A}\Delta^*(\ln x_2^m)]}{\partial \Phi_1^o} = 0 \quad \text{at} \quad \Phi_1^o = \Phi_1^o(\max) \qquad (68)$$

can be formulated as a simple analytical expression, viz.

$$\Phi_1(\max) = \left\{ \frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2} + 1 \right\}^{-1} \qquad (69)$$

(See Appendix AII.2 for the derivation.)

From the equation (69) we see that in those cases where $|\delta_2 - \delta_3| = |\delta_2 - \delta_1|$, (i.e. for which $\Phi_1^* = \Phi_1$ with the implication that there is no preferential solvation of the solute molecules by either of the solvent molecules) the equation reduces to $\Phi(\max) = 0.5$ in agreement with the position of miximum for the $\frac{1}{A}\Delta(\ln x_2^m)$ term. We also see from equation (69) that for a solute in a mixed solvent whose omponents are of widely disparate δ such that $|\delta_2 - \delta_3| \gg |\delta_2 - \delta_1|$, a considerable shift in $\Phi(\max)$ will occur for these equations. In Figure II.15, we illustrate the three excess functions, equation (48), equation (49) and equation (50) for hypothetical systems with a solute of $\delta_2 = 14$ in a mixed solvent of components $\delta_1 = 12$ and $\delta_3 = 6$.

We ignore the possibility of the likely immiscibility of the solvent mixtures. From the equation (69), the position of the maximum of the $\frac{1}{A}\Delta^*(\ln x_2^m)$ curve will be shifted to $\Phi_1(\max) \approx 0.5$. The position of the maximum of the excess $\frac{1}{A}\Delta(\ln x_2^m)$ does not appear capable of any simple formulation but it is seen to be at a position $\Phi \cong 0.1$. We further see from Figure II.15 the considerably larger value of the excess function for the $\frac{1}{A}\Delta(\ln x_{2*}^m)$ formulation over the whole range of solvent composition.

In Figure II.16, we present the excess saturation solubility terms $\Delta(\ln x_2^m)$ and $\Delta(\ln x_{2*}^m)$ for the system of solute iodine in mixed benzene-cyclohexane solvent. In Figure II.17 we present similar plots of excess properties of iodine in benzene - CCl_4 mixed solvents. Both these systems were discussed earlier, particularly with respect to equation (22). As commented earlier, this equation depends quite critically on the use of Φ_1 or Φ_1^* in the expression for δ_m . The agreement between the experimental curves and the calculated excess curves $\Delta(\ln x_{2*}^m)$ rather than $\Delta(\ln x_2^m)$ curve observed in Figures II.16 and II.17 again argues well for the use of the effective volume fractions in the description of δ_m . It is obvious from the data presented in Figure II.15 that $\Delta^*(\ln x_2^m)$ curve will fit the experimental data no better than does $\Delta(\ln x_2^m)$ curve, because for both these curves the maximum value of the excess properties is the same even if $\Phi(\max)$'s are different.

Earlier it was shown that for both these systems, the experimental data obey the relationship

$$\ln x_2^m = \Phi_1^* \ln x_2^1 + \Phi_3^* \ln x_2^3$$

rather than

$$\ln x_2^m = \Phi_1^o \ln x_2^1 + \Phi_3^o \ln x_2^3$$

Recognizing that the saturation solubility in the mixed solvent is given by

$$\ln a_2^i = \ln x_2^m + \frac{V_2^o}{RT} (\delta_2 - \delta_m)^2$$

if δ_m is written as $\delta_m = \Phi_1^* \delta_1 + \Phi_3^* \delta_3$ we see that the magnitude of any divergence from the $\ln x_2^m$ versus Φ_1 linearity will be equal to the excess saturation solubility term, $\Delta(\ln x_{2*}^m)$ and not $\Delta(\ln x_2^m)$ because the δ_m(experimental) is not described by $\Phi_1^o \delta_1 + \Phi_3^o \delta_3$. Similarly, the nonlinearity of $\ln x_2^m$ versus Φ_1^* plot will be of the magnitude of the excess $\Delta^*(\ln x_2^m)$ term. The excess term $\Delta^*(\ln x_2^m)$ seems to be very small for the two systems with iodine as solute. Hence the linearity observed in $\ln x_2^m$ versus Φ_1^* plots (Figures II.4 and II.6) for iodine in benzene-cyclohexane and iodine in benzene - carbon tetrachloride mixed solvents, is due to the negligible magnitude of the excess term, as concluded earlier. (See equation (45).) In these cases, $\delta_m{}^2 = \Phi_1^o\delta_1{}^2 + \Phi_3^o\delta_3{}^2$ is a fair assumption. In Figure II.18 we plot $\Delta(\ln x_2^m)$, $\Delta^*(\ln x_2^m)$ and $\Delta(\ln x_{2*}^m)$ for SnI_4 in benzene - c-C_6H_{12} mixtures. For SnI_4, although $(\delta_3 - \delta_1)^2$ is smaller than that for iodine, the V_2^o of SnI_4 is almost three times bigger than V_2^o of iodine (cf. 151 cc for SnI_4 to 59 cc for iodine). This makes the magnitude of excess terms bigger for SnI_4 in benzene - c-C_6H_{12} systems than for iodine in benzene - c-C_6H_{12} system. This explains the nonlinearity of $\ln x_2^m$ (for SnI_4) on Φ_1^*. In the case of SnI_4, we tried to demonstrate the effect of V_2^o of solute on the excess property -- because at the same temperature, the excess of solubility of two solutes in mixed solvents depends simultaneously on the V_2^o of the solute and the square of the difference of the solubility parameters of the solvents.

Next we consider the system iodine ($\delta_2 = 14.1$) in the mixed solvent CCl_4 ($\delta_1 = 8.6$) plus n-C_7F_{16} ($\delta_3 = 5.6$) which offers a greater test for the proposed theory. This system has a large miscibility gap and only two data points exist for the mixtures. It has been shown earlier that this system was best expressed by the Φ^* formulation for δ_m. In Figure II.19 we show the excess saturation solubility curves $\Delta(\ln x_2^m)$, $\Delta^*(\ln x_2^m)$ and $\Delta(\ln x_{2*}^m)$ and in Figure II.20 we plot the $\ln x_2^m$ against Φ_1 and Φ_1^*, where $\ln x_2^1$ and $\ln x_2^3$ are the actual experimental values. It is seen in Figure II.19 that the available experimental data points lie well on the $\Delta(\ln x^m_{2*})$ curve. Again the $\Delta^*(\ln x^m_2)$ curve for this system is of small magnitude and consequently the two data points lie on a linear $\ln x^m_2$ versus Φ^*_1 plot as seen in Figure II.5.

From the saturation solubility equation

$$\ln a^i_2 = \ln x^m_2 - \frac{V^o_2}{RT}(\delta_2 - \delta_m)^2$$

with the assumption that $\delta_m = \Phi^o_1\delta_1 + \Phi^o_3\delta_3$ it is easily shown that (see Appendix AII.3)

$$\frac{\partial \ln x^m_2}{\partial \Phi^o_1} = 0 \quad \text{where} \quad \Phi_1 = \Phi^{max}_1 = \left(\frac{\delta_2 - \delta_3}{\delta_1 - \delta_3}\right) \tag{70}$$

This latter relation is seen to predict a maximum value of Φ_1 which is meaningful (i.e. $0 < \Phi_1 < 1$) only if $\delta_i > \delta_2 > \delta_j$ ($i,j = 1,3$ $i \neq j$). In other words, in the cases where $\delta_i > \delta_2 > \delta_j$ and $\delta_m = \Phi^o_i\delta_i + \Phi^o_j\delta_j$, at certain volume fractions of the ith and jth component of mixed solvent, δ_m will be equal to δ_2 and consequently $x^m_2 = a^i_2$; i.e. in that mixture, $\ln x^m_2$ will be a maximum. Or the volume fraction of component 1 of mixed solvent at which $\delta_m = \delta_2$, is the Φ^{max}_1 in equation (70).

Similarly if one defined δ_m in terms of "effective volume" fractions, the position of the maximum is given by

$$\frac{\partial \ln x_2^m}{\partial \Phi_1^*} = 0 \quad \text{where} \quad \Phi_1^{*max} = \frac{\delta_2 - \delta_3}{\delta_1 - \delta_3} \tag{71}$$

or converting Φ_1^{*max} to Φ_1^o values, i.e. $\Phi_1^o(max,*)$, one obtains (see Appendix AII.3 for derivation)

$$\Phi_1^o(max,*) = \frac{\delta_2 - \delta_1}{\delta_3 - \delta_1} \tag{72}$$

The equations (71) and (72) are again <u>only</u> valid if $\delta_i > \delta_2 > \delta_j$. Comparing equation (70) with (72) we also see

$$\Phi_1^o(max,*) + \Phi_1^{o,max} = 1 \tag{73}$$

For the systems where $|\delta_2 - \delta_1| = |\delta_2 - \delta_3|$, $\Phi_1(max) = \Phi_1(max,*) = 0.5$. Such a behavior pattern is shown in Figure II.21 for naphthalene ($\delta_2 = 10$) in hypothetical solvent mixtures (i) $\delta_1 = 12$, $\delta_3 = 8$ and (ii) $\delta_1 = 14$, $\delta_3 = 6$. In this plot we only give $\frac{1}{A}\Delta(\ln x_2^m)$ term because $|\delta_2 - \delta_1| = |\delta_2 - \delta_3|$, and Φ_1 and Φ_1^* are equal over the complete range of composition. All three excess solubility equations reduce to $\frac{1}{A}\Delta(\ln x_2^m)$ form. In Figure II.22, we plot $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ against Φ_1^* . It is seen that at $a_2^i = x_2^m$ (i.e. the maximum solubility) $\Phi_1^* = \frac{(\delta_2 - \delta_3)}{(\delta_1 - \delta_3)} = \Phi_1^{o,max}$ which is in agreement with the discussion given above. Furthermore, we can see from the relationship

$$(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} = (\ln a_2^i - \ln x_2^3)^{\frac{1}{2}}$$

$$+ \Phi_1^*(\ln a_2^i - \ln x_2^3)(\frac{\delta_1 - \delta_3}{\delta_2 - \delta_3})$$

that this relationship is valid only over the range $\Phi_1^* = 0$ to $\Phi_1^* \leq \Phi_1^{*,max}$. The range $\Phi_1^{*,max} \leq \Phi_1^* \leq 1$ can be determined if the reference state is changed from the saturation solubility of solute 2 in pure solvent 3, (i.e. x_2^3) to saturation solubility of solute 2 in pure solvent 1 (i.e. x_2^1). The relationship then can be rewritten as

$$(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} = (\ln a_2^i - \ln x_2^1)^{\frac{1}{2}}$$

$$- \Phi_3^*(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}(\frac{\delta_3 - \delta_1}{\delta_2 - \delta_1})$$

The appropriate plots for naphthalene in two hypothetical solvent mixtures are given in Figure II.23. As $|\delta_2 - \delta_1| = |\delta_2 - \delta_3|$, the symmetry of these plots is retained.

In Figure II.23 we examine the three excess saturation solubility terms $\Delta(\ln x_2^m)$, $\Delta^*(\ln x_2^m)$ and $\Delta(\ln x_{2*}^m)$ for another hypothetical system for which $\delta_2 = 11.7$ (e.g. SnI_4) in mixed solvents whose components have $\delta_1 = 5.6$ and $\delta_3 = 14.0$. The considerable asymmetry due to the large difference in the $|\delta_2 - \delta_1|$ and $|\delta_2 - \delta_3|$ term is also shown in Figure

II.24 where $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ is plotted against both Φ_1^* and Φ_1^o ; only the plot of $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ against Φ_1^* is linear. The purpose of these hypothetical systems and the plots is to show the effect of the difference between $|\delta_2 - \delta_1|$ and $|\delta_2 - \delta_3|$ on the different properties of mixed solvents.

So far we have only discussed the excess saturation solubilities. In the remaining part of this discussion we will consider the excess volume of mixing, ΔV^E , and the effect of the "effective" volume fractions on this quantity.

In the derivation of the equations describing the excess volume of mixing, we mentioned that basic equations as derived from the Regular Solution theory are only approximate. In general for single component solvent systems both equation (51) and equation (52) are found to predict $\overline{V}_2$ values in good agreement with the experimental data. But our calculations on excess volume of mixing are completely dependent on the ability of these basic equations to predict the partial molal volume of solute in a one-component solvent.

Earlier, we have shown (see Figure II.5) that the partial molal volume data for iodine, i.e. $\overline{V}_2^M$, in C_6H_6 - c-C_6H_{12} mixed solvent system was a good linear function of the "effective" volume fractions of the mixed solvent (cf. equation (35)). In Figure II.25 we plot $\overline{V}_2^M$ for bromine in mixed CCl_4 - c-C_6H_{12} system. Althoughthe experimental scatter for this system is large, it would appear that there occurs a large deviation from the linearity for $\overline{V}_2^M$ even as a function Φ_1^* (i.e. the effective volume fraction of CCl_4). In Figure II.26 we plot the excess function $\Delta V^{E,M}$ for iodine in C_6H_6 - c-C_6H_{12} mixture and compare it with the experimental values, $\Delta V^{E,M}$(expt) in equation (66). The experimental data compare extremely well with the calculated line which has been calculated writing $\delta_m = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$. We plot the excess volume of mixing terms for bromine - CCl_4 - c-$C_4Cl_2F_6$ mixed solvent in Figure II.27. The theoretical expression appears to underestimate the magnitude of the excess term. For bromine in mixed CCl_4 - n-C_7F_{16} solvent the theoretical ΔV^E term is of a magnitude far greater than that found from the experimental data. We give data for all these systems in Table II.7 . It is worth noting that $\Delta V_2^{E,M}$ (expt) value is very dependent upon the accuracy of the $\overline{V}_2$ values of the solute in each pure solvent and $\Delta V_2^{E,M}$ (calc'd) value is very dependent upon the accuracy of equation (51) in predicting the partial molal volume of the solute. In deriving the excess term (calculated) we used equation (51) to describe $\overline{V}_2^1$ and $\overline{V}_2^3$ where for experimental $\Delta\overline{V}_2^{E,M}$ we used experimentally determined $\overline{V}_2^1$ and $\overline{V}_2^3$. In Table II.8 we compare the calculated and experimental $\overline{V}_2$'s in different solvents.

From Table II.8 we see that for Br_2 in n-C_7F_{16}, the calculated $\overline{V}_2$ is equal to 77.08 cc/mole in comparison to the experimental value 71.8 cc/mole, whereas for Br_2 in CCl_4, the calculated and experimental values are in good agreement. As equation (51) predicts bigger $\overline{V}_2^3$ than the experimental $\overline{V}_2^3$ for bromine in n-C_7F_{16}, this error will be manifested in all quantities derived from equation (51) for this system; for Br_2 in c-$C_4Cl_2F_6$, the $\overline{V}_2^3$(calc'd) = 60.69 cc in comparison to the $\overline{V}_2^3$(expt) = 64.3 cc, i.e. the equation (51) predicts a lower value for $\overline{V}_2^3$ for Br_2 in c-$C_4Cl_2F_6$ whereas for Br_2 in n-C_7F_{16}, it predicts a higher value. Or in other words errors introduced in $\Delta V_2^{E,M}$ (equation (65)) because of the inadequacy of equation (51) will have the opposite sign (which has been observed) for Br_2 in CCl_4 - c-$C_4Cl_2F_6$ and Br_2 in CCl_4 - n-C_7F_{16}. In one case equation (65) overestimates the excess term whereas in the other case it underestimates.

As the basic theoretical expression (viz. equation (51)) is inadequate in predicting the partial molal volume of solute in pure solvent, any extensive comparison of the calculated and experimental excess term, $\Delta V_2^{E,M}$, is not worth while.

Concentrated Solution

So far we have limited our discussion to the dilute solution such that $\Phi_2^m \rightarrow 0$, i.e. the solubility of the solute is so small that the volume fraction of the solute in the solution is negligible, a condition satisfied in the earlier discussion because in all the cases discussed earlier, $\Phi_2^m < 0.01$ and the basic solubility equation

$$\ln a_2^i = \ln x_2^m + \frac{V_2}{RT} \Phi_m{}^2 (\delta_2 - \delta_m)^2 \qquad (74)$$

reduces to

$$\ln a_2^i = \ln x_2^m + \frac{V_2}{RT} (\delta_2 - \delta_m)^2 \qquad (75)$$

as $\Phi_2^m \rightarrow 0$, $\Phi_m \rightarrow 1$.

But there are cases where the solubility of the solute is high enough to make $\Phi_2^m \neq 0$ such that $\Phi_1^s + \Phi_2^m + \Phi_3^s = 1$. In this section we shall discuss a few of these cases. Most of the experimental data available are for the solute naphthalene in different organic solvents, and hence our discussion will be limited to the case of naphathalene in different mixed solvents.

Notation

Before discussing the problems associated with concentrated solutions, we must first describe some of the notation we shall use in this section.

We shall use the superscript o , such as x_i^o and Φ_i^o , in the following discussion to denote these two quantities in solute-free (or pure) mixed solvents such that

$$x_1^o + x_3^o = 1 \tag{76}$$

$$\Phi_1^o + \Phi_3^o = 1 \tag{77}$$

We shall also use the superscript s , such as x_i^s and Φ_i^s , to denote these quantities in the saturated solutions such that

$$x_1^s + x_2^m + x_3^s = 1 \tag{78}$$

$$\Phi_1^s + \Phi_2^m + \Phi_3^s = 1 \tag{79}$$

(for solute we shall use superscript m to be consistent with earlier discussion). Comparing equations (76) and (77) with (78) and (79), one sees that there exist relationships such that

$$\frac{\Phi_1^s}{\Phi_1^o} = \frac{\Phi_3^s}{\Phi_3^o} = 1 - \Phi_2^m \tag{80}$$

$$\frac{x_1^s}{x_1^o} = \frac{x_3^s}{x_3^o} = 1 - x_2^m \tag{81}$$

which connect x_i^o's and Φ_i^o with x_i^s and Φ_i^s respectively.

Results: Naphthalene in CCl_4 - c-C_6H_{12} mixed solvent

The solubility of naphthalene in CCl_4 - c-C_6H_{12} mixed solvent was studied by Heric et al.[79] from 10° to 70°C. They used a "static method" to determine the saturation solubility. Unfortunately no data was reported at 25°C. For that reason, we plotted their results of the mole fraction saturation solubility of naphthalene, x_2, in a particular solvent against the absolute temperature (see Figure II.28) and the saturation solubility at 298°K. was read from the plot. The mole fraction saturation solubility of naphthalene calculated in this manner is given in Table II.9 along with the mole fractions and the volume fractions of CCl_4 (subscript 1) and c-C_6H_{12} (subscript 3) in a solute free pure mixed solvent denoted with subscript o.

Naphthalene in methylene iodide - c-C_6H_{12} mixed solvent

In Table II.10 we show the saturation solubility of naphthalene in methylene iodide - cyclohexane mixed solvents. These solubilities were determined by J. Lee[80] in this laboratory.

In Figure II.29a we plot the mole fraction of naphthalene in saturated solution against the x_1^o, i.e. the mole fraction of methylene iodide in pure mixed solvents. By pure mixed solvent we meant solute free mixed solvent such that $x_1^o + x_2^o = 1$

similarly

$$\Phi_1^o + \Phi_3^o = 1$$

In Figure II.29b we plot $-\ln x_2^m$ of naphthalene in the methylene iodide - $c\text{-}C_6H_{12}$ mixed solvent against Φ_1^o.

Discussion

As mentioned earlier and can be seen in Tables II.8 and II.9, in the cases of naphthalene Φ_2^m can no longer be assumed zero. For dilute solutions, we have assumed $\Phi_2 \rightarrow 0$ for all the expressions -- the excess terms and even the linear relationship between $(\ln a_2^i - \ln x_2^m)$ versus Φ_1^o. Clearly those expressions are no longer valid in these cases.

The obvious difficulty in calculating the thermodynamic properties for the concentrated solutions arises due to the fact that $\Phi_2^m \not\rightarrow 0$. There is another problem associated with naphthalene: there is no definite value for the ideal solubility of naphthalene to be found in the literature. The values reported by different authors range from 0.298 to 0.322 depending upon the source of data.[81,82]

We decided to calculate a_2^i for napthalene by other means. Recalling the original equation for the solubility in mixed solvent, i.e.

$$\ln a_2^i = \ln x_2^m - \frac{V_2 \Phi_m^{\ 2}}{RT} (\delta_2 - \delta_m)^2$$

it is seen that for the cases where $\delta_i > \delta_2 > \delta_j$, i.e. the solubility parameter of the solute lies between the solubility parameter of the two solvents, at certain mixed solvent composition, $\delta_m = \delta_2$ and the solubility of solute in that mixture becomes equal to the ideal solubility of the solute. We choose naphthalene as solute in methylene iodide - c-C_6H_{12} mixed solvent because the solubility parameter of naphthalene (δ_2) lies in between the solubility parameters of methylene iodide (δ_1(therm) = 11.8) and that of c-C_6H_{12} (δ_1(therm) = 8.2). Therefore this particular system satisfies the condition $\delta_1 > \delta_2 > \delta_3$. If the Regular Solution theory is applicable to this system, then we should be able to determine a_2^i for naphthalene by determining the solubility of naphthalene for the complete range of CH_2I_2 - c-C_6H_{12} mixed solvent composition. From Figure II.28 where the saturation mole fraction solubility of naphthalene in CH_2I_2 - c-C_6H_{12} x_2^m, is plotted against Φ_1^o , we see that the maximum value for x_2^m is 0.300 which is in excellent agreement with the range 0.298 to 0.322. (the reported values for a_2^i are found in the literature [81,82]) Considering that the uncertainty involved in calculating a_2^i from the thermal data because of the long extrapolation involved in these cases, we decided to use $x_2^m(\max) = 0.300$ as the a_2^i for naphthalene in further discussions. So far as we know, this is the only case where the $x_2^m(\max)$ for a simple solid solute in a mixed solvent system such that $\delta_1 > \delta_2 > \delta_3$ goes to ideal solubility. The only other studies reported in systems where $\delta_1 > \delta_2 > \delta_3$ are those for the solubility of phenanthrene in CH_2I_2 - c-C_6H_{12} mixed solvent. This work was done by Scott et al.[83] in 1952. Although they observed the expected enhancement of the solubility of phenanthrene, the solubility in the best solvent mixture fell short of the ideal. Phenanthrene and naphthalene have solubility parameters similar to one another, i.e. 9.8 for phenanthrene and 9.9 for naphthalene , but the nature of their interaction with cyclohexane is very different. Scott et al. found that the solubility parameter of c-C_6H_{12} has to be shifted from 8.2 (the thermodynamic value for c-C_6H_{12}) to 7.0 to satisfy the solubility equation for phenanthrene in cyclohexane, whereas for naphthalene in c-C_6H_{12} , although a re-evaluation of δ solubility parameter for cyclohexane is needed, the magnitude of shift from 8.2 to 7.66 is much smaller than that for phenanthrene in cyclohexane. At present, the reason for this lack of agreement between the predicted and experimental values for the solubility of phenanthrene in the best solvent mixture is not clear.

A close examination of the phase diagram for the binary system of methylene iodide - cyclohexane as given by Gordon and Scott reveals that at 298 °K there is a definite miscibility gap in the methylene iodide -

cyclohexane system when x_3^o lies between 0.28 and 0.58. Thus the stoichiometric composition of the best solvent mixture for phenanthrene lies close to the CH_2I_2 - $c\text{-}C_6H_{12}$ solvent-solvent critical temperature and composition. From this observation Scott et al.[83] suggested that there is an extensive "clustering" around the phenanthrene molecule in its best solvent mixture and this clustering is the reason for the apparent lack of agreement between the ideal solubility and the maximum solubility of phenanthrene in its best solvent mixture. It is true that there is a solvent-solvent miscibility gap when the mole fraction of cyclohexane in pure mixed solvent lies between 0.28 and 0.58. But we also observed that the solvent-solvent miscibility gap disappears in the presence of naphthalene in the ternary systems of CH_2I_2 - naphthalene - $c\text{-}C_6H_{12}$. Besides, for naphthalene, the stoichiometric composition of the best solvent mixture is also near to the solvent-solvent critical composition and temperature. But our observation that the maximum solubility of naphthalene in the best solvent mixture is equal to the ideal solubility of napthalene, suggests that the "clustering" as mentioned by Scott cannot be a main factor for the discrepancies observed in the case of phenanthrene in CH_2I_2 - $c\text{-}C_6H_{12}$ mixed solvents.

Subsequently we established that in the case of naphthalene, $x_2^m(\max)$ in the best solvent can be used safely to replace a_2^1 for naphthalene in further calculations. Using $a_2^1 = 0.300$, we calculated δ_m, δ_1, and δ_3 for systems with naphthalene as solute. In Table II.11 we give the experimental δ_m's for CCl_4 - naphthalene - $c\text{-}C_6H_{12}$ and in Table II.12 we show the experimental δ_m values for CH_2I_2- naphthalene - $c\text{-}C_6H_{12}$. In these calculations the δ_2 value for naphthalene was taken as 9.9 -- the thermodynamic solubility parameter for naphthalene.

Next we chose to calculate δ_m for the mixed solvent. We showed earlier that δ_m can be calculated

$$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$$

such that

$$\Phi_1^o + \Phi_3^o = 1$$

or

$$\delta_m^* = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$$

such that

$$\Phi_1^* + \Phi_3^* = 1$$

and Φ_1^* and Φ_3^* are defined as

$$\frac{\Phi_1^*}{\Phi_3^*} = \frac{\Phi_1^o}{\Phi_3^o}\,\frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2}$$

In Table II.13 we compare the δ_m calculated from the experimental saturation solubility of naphthalene with the δ_m written in terms of Φ_1^o and in terms of Φ_1^* for CCl_4 - $c\text{-}C_6H_{12}$ system. Clearly δ_m^* (written in terms of Φ_1^*'s) is in better agreement with the δ_m(experimental) -- a situation we also faced in dilute solutions. But we also see in the Table II.13 that the agreement between the experimental δ_m and the δ_m^* (calculated from Φ^*'s) are not so good for the mixed solvent in which the concentration of carbon tetrachloride is very small. From the definition of "effective" volume fraction, we clearly see that in the case of carbon tetrachloride - naphthalene - cyclohexane system, carbon tetrachloride is a preferred solvent for naphthalene than cyclohexane. We also see that in the case of the mixed solvent where $\Phi_1^o = 0.1575$, the volume fraction of naphthalene, Φ_2^m , in solution is greater than the volume fraction, Φ_2^s , of carbon tetrachloride in the solution -- a situation we did not come across in the case of dilute solution. This phenomenon becomes more prominent for naphthalene in CH_2I_2 - c-C_6H_{12} mixed solvents. In Table II.14 we compare δ_m(expt) with δ_m(calc'd) and δ_m^*'s. We see in Table II.14 that δ_m calculated from the experimental solubility of naphthalene agrees with δ_m^* (calculated from Φ^*'s) when the volume fraction of methylene iodide in pure mixed solvent is greater than 0.403. We also see in Table II.14 that at very low concentration of methylene iodide δ_m's (calculated from Φ_1^o) rather than δ_m^*'s (calculated from Φ^*'s) is in much better agreement with δ_m(expt). But in most of the cases where $\Phi_1^o \leq 0.403$ we see that

δ_m(expt) lies between δ_m's (calculated from Φ^0) and δ_m^*'s (calculated from Φ^*). Or in other words we could say there is a minimum value for the volume fraction of CH_2I_2 up to which the "effective" volume fractions concept is acceptable. But if the volume fraction of methylene iodide is less than that minimum value, the nearest neighbour of the solute is neither defined by the "effective" volume fractions Φ^* nor by Φ 's. The reason why Φ's do not adequately describe the nearest environment of the solute has been discussed earlier.

For concentrated solutions, it seems that there exists a minimum value for the number of moles of the preferred solvents which must exist in the solution so that the nearest neighbours of the solute in a mixed solvent may be adequately described by the effective volume fractions. At present we were not able to predict this minimum value for the preferred solvent but from the experimental results it is clear that Φ_1^s (the volume fraction of the preferred solvent in the solution) must be greater than the Φ_2^s (the volume fraction of the solute in solution). In Table II.13 we compare the δ_m(experimental) with both δ_m and δ_m^* for CCl_4 - naphthalene - c-C_6H_{12} system. The situation is analysed in more detail in the case of methylene iodide -naphthalene - cyclohexane because more experimental data are available for this system. In Table II.14 δ_m(expt) is compared with δ_m(calc'd) and δ_m^*. In Table II.14 we also give the values of Φ_1^s and Φ_2^s for this system. It can be seen that when Φ_1^s is less than Φ_2^s, δ_m (expt) is less than δ_m^* but greater than δ_m(calc'd). However δ_m(expt) is adequately described by δ_m^* when $\Phi_1^s \geq \Phi_2^s$. For the methylene iodide- naphthalene - cyclohexane system, the experimental results suggest that the minimum value for $\frac{\Phi_1^s}{\Phi_2^s}$ in the solution must be equal to one if the nearest neighbour environment of the solute may be adequately described by the "effective" volume fraction term. When $\Phi_1^s < \Phi_2^s$, neither Φ_1^s nor Φ_1^* describes the immediate environment of solute correctly.

Next we looked into the problem of the square root plot, i.e. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_1^o (or Φ_1^*) as described in Sections 1 and 2 of this chapter. As mentioned in those sections $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^* have a linear relationship if and only if $\Phi_2 \to 0$, i.e. very dilute solution. For concentrated solution such relationships may be found between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_1^*. A very similar relationship is derived by following the same procedure as before. Writing the solubility equation for component 2 in a mixed solvent in terms of Regular Solution theory we find

$$\ln a_2^i = \ln x_2^m + \frac{V_2}{RT} \Phi_m{}^2(\delta_2 - \delta_m)^2$$

or

$$(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} = (\frac{V_2}{RT})^{\frac{1}{2}} \Phi_m(\delta_2 - \delta_m)$$

$$= (\frac{V_2}{RT})^{\frac{1}{2}} \Phi_m[(\delta_2 - \delta_1) + \Phi_1^o(\delta_2 - \delta_3)] \quad (82)$$

Equation (82) was derived by writing

$$\delta_m = \Phi_1^o \delta_1 + (1 - \Phi_1^o)\delta_3$$

Similarly the solubility equation for component 2 in a pure solvent 1 is

$$\ln a_2^i = \ln x_2^1 + \frac{V_2}{RT} \Phi_1{}^2(\delta_1 - \delta_2)^2$$

or $$(\ln a_2^i - \ln x_2^1)^{\frac{1}{2}} = (\frac{V_2}{RT})^{\frac{1}{2}} \Phi_1(\delta_1 - \delta_2)^2 \quad (83)$$

Dividing equation (82) by equation (83) we obtain

$$\frac{(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}}{(\ln a_2^i - \ln x_2^1)^{\frac{1}{2}}} = \frac{\Phi_m}{\Phi_1} \left\{ 1 + \Phi_3^o \frac{\delta_1 - \delta_3}{\delta_2 - \delta_1} \right\} \quad (84)$$

where Φ_1 in equations (83) and (84) is the same and denotes the volume fraction of component 1 in the saturated solution of solute 2 in pure solvent 1; Φ_1 is a constant in equation (84) because it is the property of the binary system containing components 1 and 2 only. Equation (84) can be plotted two ways:

(i) If we assume $\frac{\Phi_m}{\Phi_1}$ is constant and $\Phi_m \approx \Phi_1$, then $\frac{\Phi_m}{\Phi_1} \approx 1$ or equation (84) reduces to

$$(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} = (\ln a_2^i - \ln x_2^1)^{\frac{1}{2}}$$

$$+ (\ln a_2^i - \ln x_2^1)^{\frac{1}{2}} \Phi_3^o \frac{\delta_1 - \delta_3}{\delta_2 - \delta_1} \qquad (85)$$

Equation (85) is the same as equation (26) in section 1 of this chapter except that in the derivation of equation (26) we assumed $\Phi_2 \to 0$ and in the case of equation (85) we assumed that $\frac{\Phi_m}{\Phi_1} \approx 1$.

In Table II.15 we show the ratio $\frac{\Phi_m}{\Phi_1}$ for carbon tetrachloride- naphthalene - cyclohexane and CH_2I_2 - naphthalene - cyclohexane systems. For the CCl_4- naphthalene - cyclohexane system, $\frac{\Phi_m}{\Phi_1}$ is very close to unity and we should expect a straight line for this system when $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ is plotted against either Φ_3^o or Φ_3^* because equations (84) and (85) can be derived in terms of Φ_3^* by writing $\delta_m = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$. In Figure II.30 we plotted $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ for the CCl_4 - naphthalene - c-C_6H_{12} system against both Φ_3^o and Φ_3^* . As is found in the case of dilute solutions, we see that for concentrated solutions, $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_3^o plot is far from a straight line, i.e. no linear relationship exists between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_3^o . But in Figure II.30 there exists a linear relationship of $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_3^* -- with a slope equal to 0.41, compared to 0.39, the expected value for the slope. The intercept of $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_3^* plots was made equal to the expected value. In Figure II.30 we show a similar plot for CH_2I_2- naphthalene - c-C_6H_{12} system. For this system, with $\delta_1 > \delta_2 > \delta_3$, we observe that when $\delta_m = \delta_2$, $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ is zero and we obtain two straight lines -- one with the saturation solubility of component 2 in pure solvent 1 as reference state, and the other with the saturation solubility of component 2 in pure solvent 3 as the reference state. These types of systems, where $\delta_1 > \delta_2 > \delta_3$, have been discussed earlier in terms of dilute solutions and we find that the same thing can be said about the concentrated solutions. In Figure II.30 we plotted $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ against Φ_3^* and found that the slopes of the best line drawn through the experimental points are -1.19 and 1.40 which compare fairly well with the calculated values -1.18 and 1.45 respectively.

The first set of the calculated and experimental values for the slopes are with x_2^1 as the reference state and the second set of values for slopes are with x_2^3 as the reference state. In that part of the plot we assume $\frac{\Phi_m}{\Phi_3}$ is equal to one instead of $\frac{\Phi_m}{\Phi_1}$ equal to one. In Table II.15, we show the ratio of $\frac{\Phi_m}{\Phi_1}$ and $\frac{\Phi_m}{\Phi_3}$ for this system. It is seen that $\frac{\Phi_m}{\Phi_1}$ is very close to unity and so we obtain a straight line up to $\Phi_3^* = 0.4$ when $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ is plotted against Φ_3^* as in Figure II.31. It can also bee seen from Table II.15 that $\frac{\Phi_m}{\Phi_3}$

is not equal to unity for cases where $\Phi_3^* < 0.4$ and in Figure II.31 the agreement between the experimental points and the calculated line is not good in the region $\Phi_3 < .4$. But in general we see that in a fair approximation, $\frac{\Phi_m}{\Phi_1}$ is equal to unity, and there exists a linear relationship between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ^* even for the concentrated solution.

(ii) Equation (84) can also be rewritten as

$$\frac{(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}}{\Phi_m} = \frac{1}{\Phi_1}(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} + \frac{1}{\Phi_1}(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}\Phi_3^o\,\frac{\delta_1 - \delta_3}{\delta_2 - \delta_1} \qquad (86)$$

Equation (86), which is written in terms of the same notation as in equation (84), implies a linear relationship exists for a concentrated solution between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}/\Phi_m$ and Φ_3^o for which the slope should be equal to

$$\frac{1}{\Phi_1}(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}\,\frac{\delta_1 - \delta_3}{\delta_2 - \delta_1}$$

and the intercept at $\Phi_3^o = 0$ would be equal to

$$\frac{1}{\Phi_1}(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}\,\frac{\delta_1 - \delta_3}{\delta_2 - \delta_1}$$

Both slopes and intercept can be compared with the experimental values.

Equation (86) is a direct consequence of the Regular Solution theory for a ternary system and so far no additional assumption has been made, even though it is more rigorous than the equation (85). From our earlier experience, we know that δ_m(expt) is better described by δ_m^* instead of δ_m. If the solubility equation for component 2 in a mixed solvent is written in terms of δ_m^* instead of δ_m, equation (86) becomes

$$\frac{(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}}{\Phi_m} = \frac{1}{\Phi_1}(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}} + \frac{1}{\Phi_1}(\ln a_2^i - \ln x_2^1)^{\frac{1}{2}} \Phi_3^* \frac{\delta_1 - \delta_3}{\delta_2 - \delta_1} \qquad (87)$$

The only difference between equations (86) and (87) is that equation (87) implied a linear relationship between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}/\Phi_m$ and Φ_3^* (not Φ_3^o as in the case of equation (91)) for which slope and intercepts are the same as for equation (86).

In Figure II.32 we plot $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}/\Phi_m$ against Φ_3^o and Φ_3^* for the CCl_4 -naphthalene - c-C_6H_{12} system. In Figure II.33 we show the same plot for the Cl_2I_2 - naphthalene - c-C_6H_{12} system.

For the naphthalene in CCl_4 - c-C_6H_{12} system, we compare the theoretical line against the experimental points and the agreement between the experimental points and the theoretical values is good when plotted against Φ_3^* and not Φ_3^o. But the agreement is not so good for naphthalene in methylene iodide - c-C_6H_{12} . This is not surprising because as we said earlier, neither Φ_3^o nor Φ_3^* describes the nearest solute environment correctly when Φ_1^s is less than Φ_2^s . In Figure II.33 we see that agreement between the expected line and the experimental point is good for the mixed solvents concentrated in methylene iodide and is bad for mixed solvents dilute in methylene iodide -- a situation which concurs with our earlier discussion on δ_m's for concentrated solutions.

As in the solubility equations, Φ_1 , Φ_3 and Φ_m's are retained and no attempt to calculate excess properties for concentrated solution is made because the equations cannot be derived in terms of the properties of the pure solvent as was done in the case of dilute solutions. So we did not try to plot any excess properties for the concentrated solutions.

Conclusion

In general it is seen that the presently available experimental data is well interpreted by this extension of the Regular Solution theory to two component solvent systems. The postulated "preferential solvation" of the solute by one component of the solvent mixture is well borne out for dilute solutions. For the concentrated solutions of a solute in a two component solvent mixture we showed that there exists a minimum value for the number of molecules of the preferred solvent which must exist in the solution in order to observe the full effect of the "preferential solvation" in the studies of the solubility of solute 2 in the two component solvent systems.

The relationship between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1 or Φ_1^* for dilute three component systems, depends only upon the definition of δ_m. All systems considered as dilute solutions show that the expected linearity is found only if Φ_1^*, the effective volume fraction term, is used. For the concentrated three component systems, the linear relationship exists between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}/\Phi_m$, instead of $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$, and Φ_1^o or Φ_1^*. For concentrated solutions we also show that, in certain cases, a linear relationship can be observed between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^o or Φ_1^*. However, this linear relationship between $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ and Φ_1^o or Φ_1^* depends upon the validity of the assumption that the volume fraction of the mixed solvent in the saturated solution of the solute 2 in the mixed solvent is equal or approximately equal to the volume fraction of the reference solvent in the saturated solution. We also see that, for a concentrated solution, the above-mentioned linear relationship exists between Φ^*'s instead of Φ^o.

The necessity of using the effective volume fraction, which reflects the interaction of the solute molecule with its immediate solvent environment, is again shown by the three excess saturation solubility terms for the dilute solution of 2 in two component mixed solvents. (We have not derived any expression for excess saturation solubility terms for concentrated solution of 2 in two component mixed solvent.) If we contrast the $\Delta(\ln x_2^m)$ and the $\Delta(\ln x_{2*}^m)$ terms (i.e. in each the thermodynamic reference state is Φ_1 , the bulk solvent volume fraction), we note that the magnitude of the excess term arises mainly from the need to define δ_m using Φ_1^* .

Table II.1

Saturation solubility and partial molal volume of iodine in a mixed benzene-cyclohexane solvent: All data at 25 ° C.

Volume fraction of benzene, Φ_1	Saturation Solubility $-R \ln x_2$	Entropy of Solution $R\left\{\frac{\partial \ln x_2}{\partial \ln T}\right\}_P$	Partial Molal Volume, cc mole^{-1}
0	9.3845	22.201	68.2
0.2551	7.9884	20.835	65.5
0.5093	7.1384	18.245	64.4
0.6927	6.5758	18.000	63.3
0.7604	6.449	17.710	
0.8657	6.250	16.623	62.9
1.00	6.0318	16.30	62.4

Table II.2

Iodine in benzene-cyclohexane solvent:

All data at 25 ° C.

Volume fraction of benzene, Φ_1	δ_m (expt)	δ_m using Φ_1	δ_m using Φ_1^*
0.2551	8.92	8.46	8.92
0.5093	9.36	9.12	9.41
0.6211	9.56	9.32	9.57
0.6804	9.62	9.42	9.66
0.7604	9.74	9.56	9.75
0.8451	9.85	9.71	9.84
0.8657	9.86	9.75	9.86

(δ values used in this calculation are:

$\delta_1 = \delta_{\text{benzene}} = 9.99$

$\delta_2 = \delta_{\text{iodine}} = 14.1$

$\delta_3 = \delta_{c\text{-}C_6H_{12}} = 8.2$)

Table II.3

Iodine in benzene - carbon tetrachloride solvent:

All data at 25 ° C.

Volume fraction of benzene, Φ_1	δ_m (exp)	δ_m using Φ_1	δ_m using Φ_1^*
0.1219	8.75	8.65	8.78
0.2068	8.96	8.78	8.96
0.4456	9.39	9.22	9.45
0.5210	9.42	9.26	9.49
0.8157	9.82	9.70	9.81
0.8858	9.89	9.82	9.88

(δ values used in this calculation are:

$\delta_1 = \delta_{benzene} = 9.99$

$\delta_2 = \delta_{iodine} = 14.1$

$\delta_3 = \delta_{CCl_4} = 8.45$)

Table II.4

Iodine in benzene-cyclohexane and benzene - carbon tetrachloride solvents:

All data at 25 ° C.

$$(\ln x_2^m) = \Phi_1 \ln x_2^1 + \Phi_3 \ln x_2^3$$

$$(\ln x_2^m)^* = \Phi_1^* \ln x_2^1 + \Phi_3^* \ln x_2^3$$

Benzene-Cyclohexane Solvent				Benzene - Carbon Tetrachloride Solvent			
Φ_1	$\ln x_2^m$ (expt)	$\ln x_2^m$	$(\ln x_2^m)^*$	Φ_1	$\ln x_2^m$ (expt)	$\ln x_2^m$	$(\ln x_2^m)^*$
0.2551	4.0224	4.2925	4.0125	0.1219	4.2037	4.3310	4.2063
0.5093	3.5944	3.8635	3.5733	0.2068	4.0521	4.2060	4.0306
0.6211	3.4119	3.6749	3.4224	0.4456	3.5691	3.7804	3.5532
0.6804	3.3359	3.5748	3.3502	0.5210	3.5469	3.7431	3.5217
0.7604	3.2475	3.4399	3.2609	0.8157	3.1970	3.3087	3.1956
0.8451	3.1577	3.2970	3.1731	0.8858	3.1353	3.1955	3.1319
0.8657	3.1471	3.2622	3.1555	-	-	-	-

Table II.5

SnI_4 in benzene - c-C_6H_{12} mixture:

(a_2^i for SnI_4 = 0.113[24]; δ_2 for SnI_4 = 11.8[24])

Volume fraction of benzene, Φ_1	Saturation solubility $x_2^m \times 10^{-2}$	$-\ln x_2^m$	$(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$
0	0.7279	4.9236	1.6653
0.165	0.9896	4.6166	1.5704
0.26	1.01131	4.4991	1.5325
0.378	1.3475	4.3078	1.4688
0.585	1.608	4.1311	1.4074
0.76	1.8546	3.9878	1.3555
1	2.181[24]		

Table II.6

Solubility parameters of C_6H_6 - c-C_6H_{12} mixed solvents for C_6H_6 - SnI_4 - c-C_6H_{12} systems:

Volume fraction of benzene		δ_m (expt)	$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$	$\delta_m^* = \Phi_1^{o*}\delta_1 + \Phi_3^{o*}\delta_3$
Φ_1	Φ_1^*			
0	-	9.24	-	-
0.165	0.25	8.678	8.620	8.686
0.26	0.3677	8.765	8.70	8.772
0.378	0.5012	8.89		8.87
0.5850	0.70	9.013	8.93	9.016
0.76	0.84	9.116	9.05	9.119
1	-	8.5		

Table II.7

ΔV^E in mixed solvents:

I_2 in C_6H_6 - c-C_6H_{12}:

Volume fract. benzene	ΔV^E cc $mole^{-1}$ (calc'd)	ΔV^E cc $mole^{-1}$ (expt)
0.2551	-1.08	-1.19
0.5093	-1.34	-1.16
0.6211	-1.13	-1.18
0.6804	-1.05	-0.98
0.6924	-1.00	-0.88
0.8451	-0.55	-0.38
0.8654	-0.48	-0.53

Br_2 in CCl_4 - $cC_4Cl_2F_6$:

Volume fract. CCl_4	ΔV^E cc $mole^{-1}$ (calc'd)	ΔV^E cc $mole^{-1}$ (expt)
0.0525	-0.98	-1.52
0.108	-1.18	-1.30
0.1615	-1.33	-4.06
0.28	-1.49	-2.18
0.72	-1.154	-1.46
0.94	-0.18	-0.46

Br_2 in CCl_4 - n-C_7F_{16}:

Volume fract. CCl_4	ΔV^E cc $mole^{-1}$ (calc'd)	ΔV^E cc $mole^{-1}$ (expt)
0.031	-5.04	-0.45
0.063	-5.29	-0.69
0.122	-6.38	-3.84
0.175	-9.58	-6.20

Table II.8

Partial molal volume of solute in pure solvents:

Solute	Solvent	$\overline{V}_2$(expt) cc/mole	$\overline{V}_2$(calc'd) cc/mole
I_2	c-C_6H_{12}	68.2	69.8
I_2	C_6H_6	62.4	63.3
Br_2	CCl_4	54.1[64]	53.68
Br_2	c-$C_4Cl_2F_6$	64.3[64]	60.69
Br_2	n-C_7F_2	71.8[64]	77.08

(δ for benzene was assumed to be equal to 9.99)

Table II.9

Saturation solubility of naphthalene in CCl_4 - $c\text{-}C_6H_{12}$ mixed solvent at 298 °K:[79]

Volume fract. of CCl_4 in solute-free solvent, Φ_1^o	Volume fract. of CCl_4 in solution, Φ_1^s	Volume fract. of naphthalene in solution, Φ_2^m	δ_m (expt)
1	0.7085	0.2915	8.45
0.5518	0.4117	0.2538	8.22
0.3637	0.2379	0.2413	8.05
0.1575	0.1271	0.193	7.85
0	0	0.1587[80]	7.66

Table II.10

Saturation solubility of naphthalene in CH_2I_2 - c-C_6H_{12} mixed solvent at 25 ° C:

Mole fraction of methylene iodide in pure mixed solvent, x_1^o	volume fraction of I_2 in pure mixed solvent, Φ_1^o	saturation solubility of naphthalene, $-\ln x_2^m$
0	0	1.9440
0.12	0.097	1.5997
0.185	0.1443	1.4872
0.25	0.196	1.3509
0.37	0.301	1.2765
0.48	0.408	1.2174
0.541	0.47	1.2063
0.67	0.604	1.2344
0.75	0.695	1.2694
0.85	0.805	1.3168
1.0	1.0	1.4569

Table II.11

Solubility parameters of mixed solvents in the CCl_4- naphthalene - c-C_6H_{12} system.[79]

Volume fraction of CCl_4 , Φ_1^o	effective vol. fraction of CCl_4 , Φ_1^*	δ_m (expt)	$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$	$\delta_m = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$
0.1575	0.3138	7.85	7.76	7.89
0.3637	0.5831	8.05	7.93	8.11
0.5518	0.7508	8.22	8.08	8.24

(δ values used in this calculation are:

$\delta_1 = \delta_{CCl_4} = 8.45$

$\delta_2 = \delta_{naphthalene} = 9.9$

$\delta_3 = \delta_{c\text{-}C_6H_{12}} = 7.66$)

Table II.12

δ values for CH_2I_2 - c-C_6H_{12} mixed solvent for CH_2I_2- naphthalene - c-C_6H_{12} system:

Volume fraction of c-C_6H_{12} (i.e. Φ_3^o)	Φ_3^*	δ_m (expt)	$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3$	$\delta_m = \Phi_1^*\delta_1 + \Phi_3^*\delta_3$
1	-	7.66	-	-
0.903	0.8224	8.11	8.03	8.34
0.8557	0.7469	8.33	8.21	8.63
0.8067	0.6749	8.47	8.39	8.90
0.699	0.5361	9.03	8.80	9.43
0.597	0.4243	9.51	9.20	9.85
0.53	0.3594	10.06	9.46	10.11
0.396	0.2460	10.50	9.97	10.54
0.305	0.1792	10.77	10.31	10.80
0.197	0.1088	11.03	10.73	11.06
0.0994	0.052	11.20	11.10	11.28
0	-	11.48	-	-

Table II.13

$\delta_m^{(expt)}$ for CCl_4 - c-C_6H_{12} in CCl_4 - naphthalene c-C_6H_{12} system, along with $\frac{N_1^s}{N_2^s}$ values:

Φ_1^o (i.e. Φ_{CCl_4})	Φ_2^m	Φ_2^s	δ_m (expt)	δ_m^*	$\frac{N_1^s}{N_2^s}$	$\frac{(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}}{\Phi_m}$
1	0.2915	0.7085	8.45	-	2.4305	0.6610
0.1575	0.193	0.1271	7.85	7.89	0.8350	0.9382
0.3637	0.2413	0.2379	8.05	8.11	1.2501	0.8463
0.5518	0.2538	0.4117	8.22	8.245	2.0578	0.7664

Table II.14

$\delta_m^{(expt)}$ for CH_2I_2 - c-C_6H_{12} in CH_2I_2 - naphthalene - c-C_6H_{12} system along with $\frac{N_1}{N_2}$:

Φ_1^o ($\Phi_{CH_2I_2}$)	Φ_2^m	Φ_1^s	δ_m (expt)	δ_m^*	$\frac{N_1^s}{N_2^s}$	$\left(\frac{\ln a_2^i - \ln x_2^m}{\Phi_m}\right)^{\frac{1}{2}}$
1	0.3198	0.6802	11.45	-	3.23	0.7201
0.924	0.3387	0.6116	11.20	11.28	2.7394	0.8144
0.803	0.3456	0.5255	11.03	11.06	2.3089	0.7174
0.695	0.3542	0.4488	10.77	10.80	1.9241	0.6561
0.604	0.3579	0.3878	10.50	10.54	1.6453	0.3988
0.47	0.3592	0.3012	10.06	10.11	1.2733	0.1784
0.403	0.3505	0.2617	9.51	9.85	1.1337	0.0752
0.301	0.3247	0.2033	9.03	9.43	0.9507	0.2718
0.1933	0.2750	0.1401	8.47	8.90	0.7737	0.3961
0.1433	0.2571	0.1065	8.33	8.63	0.6290	0.5133
0.097	0.2275	0.0749	8.11	8.34	0.4999	0.5947
-	0.1587	-	7.66	-	-	1.0225

Table II.15

Values for $\frac{\Phi_m}{\Phi_1}$ for CCl_4- naphthalene - c-C_6H_{12} and CH_2I_2- naphthalene - c-C_6H_{12} systems:

CCl_4 - naphthalene - c-C_6H_{12}:

Φ_1^o	$\frac{\Phi_m}{\Phi_1}$ (1,2)
0.1575	1.1397
0.3637	1.0709
0.5598	1.0532

CH_2I_2 - naphthalene- c-C_6H_{12}:

Φ_1^o	$\frac{\Phi_m}{\Phi_1}$ (1,2)	$\frac{\Phi_m}{\Phi_3}$ (2,3)
0	-	-
0.097	1.1342	0.9182
0.1443	1.0907	0.8830
0.1933	1.0659	0.8618
0.301	0.9928	0.8027
0.403	0.9549	0.7720
0.47	0.9422	0.7617
0.604	0.9440	0.7632
0.695	0.9494	0.7676
0.803	0.9621	0.7778
0.9006	0.9722	0.7860
1	-	-

$\Phi_1(1,2)$ is the volume fraction of 1 in the saturated solution of 2 in solvent 1.

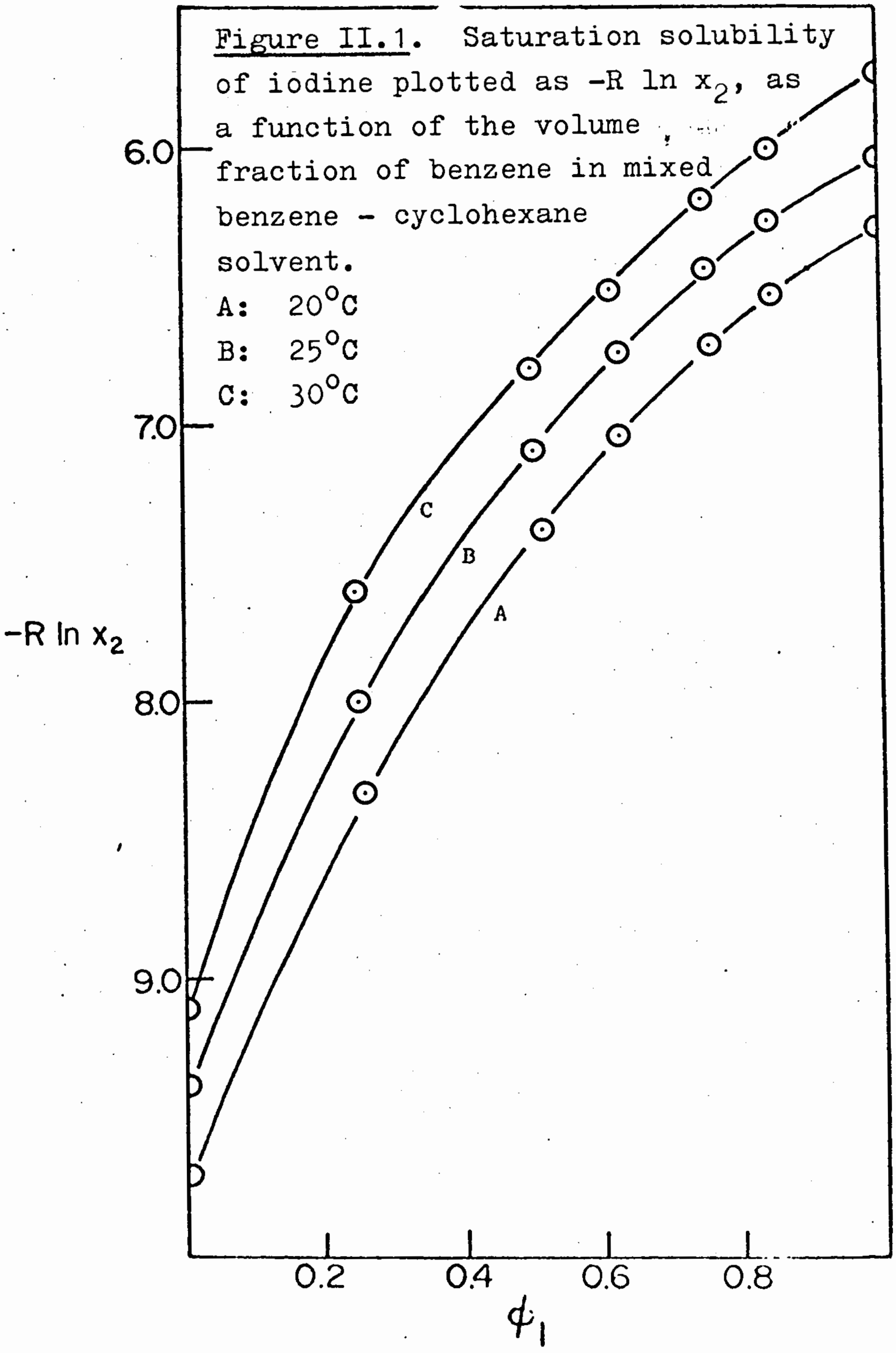


Figure II.1. Saturation solubility of iodine plotted as $-R \ln x_2$, as a function of the volume fraction of benzene in mixed benzene - cyclohexane solvent.

A: 20°C
B: 25°C
C: 30°C

Figure II.2. Excess saturation solubility term ($\Delta \ln x_2^m$) and excess partial molal volume term ($\Delta \overline{V}_2^M$) plotted as a function of benzene volume fraction in the mixed benzene-cyclohexane solvent. Data at 25°C.

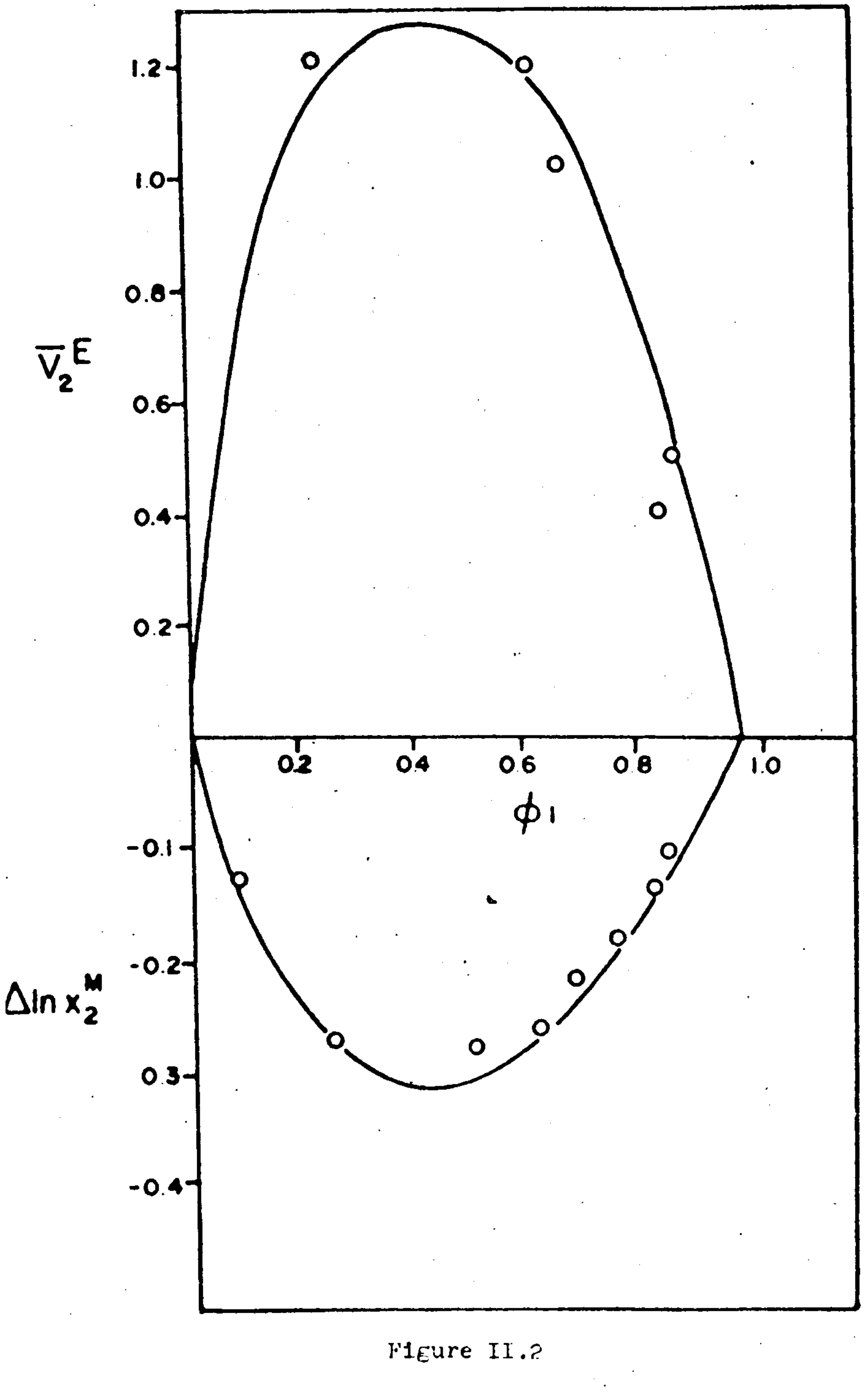

1.2
1.0
0.8
0.6
0.4
0.2
$\overline{V}_2^E$
0.2
0.4
0.6
0.8
1.0
ϕ_1
-0.1
-0.2
0.3
-0.4
$\Delta \ln x_2^M$

Figure II.2

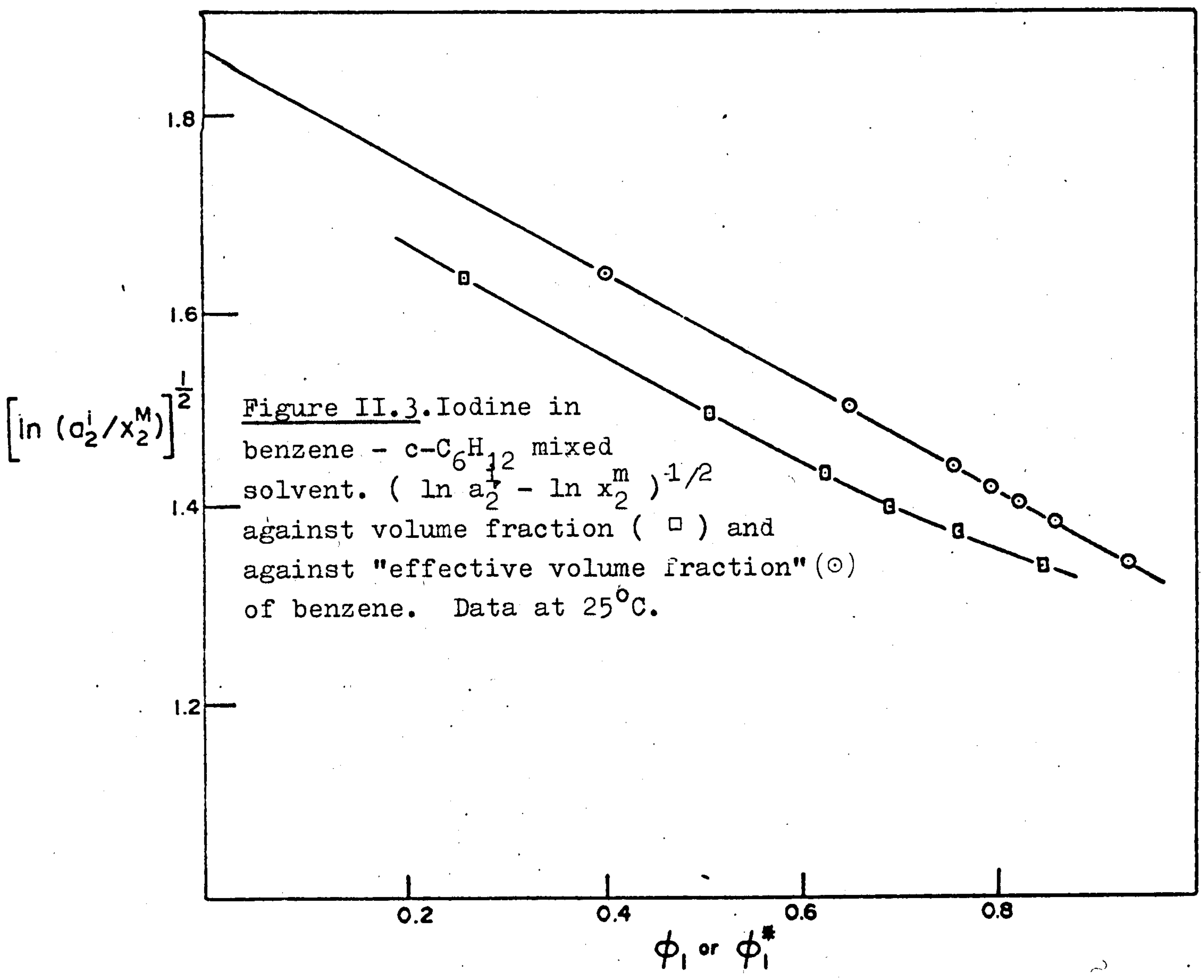


Figure II.3. Iodine in benzene - c-C_6H_{12} mixed solvent. (ln a_2^i - ln x_2^m)$^{-1/2}$ against volume fraction (□) and against "effective volume fraction" (⊙) of benzene. Data at 25°C.

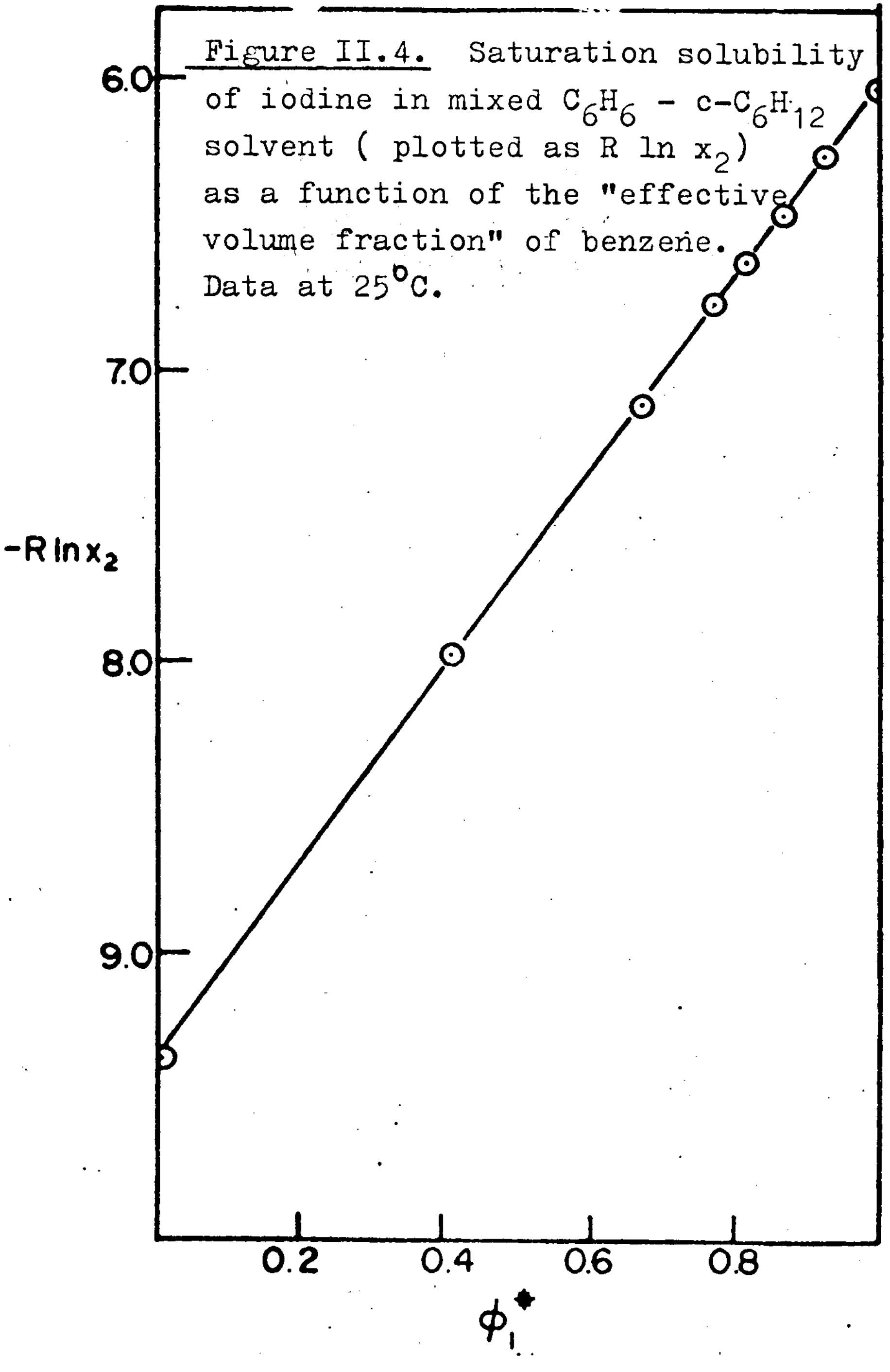


Figure II.4. Saturation solubility of iodine in mixed C_6H_6 - c-C_6H_{12} solvent (plotted as R ln x_2) as a function of the "effective volume fraction" of benzene. Data at 25°C.

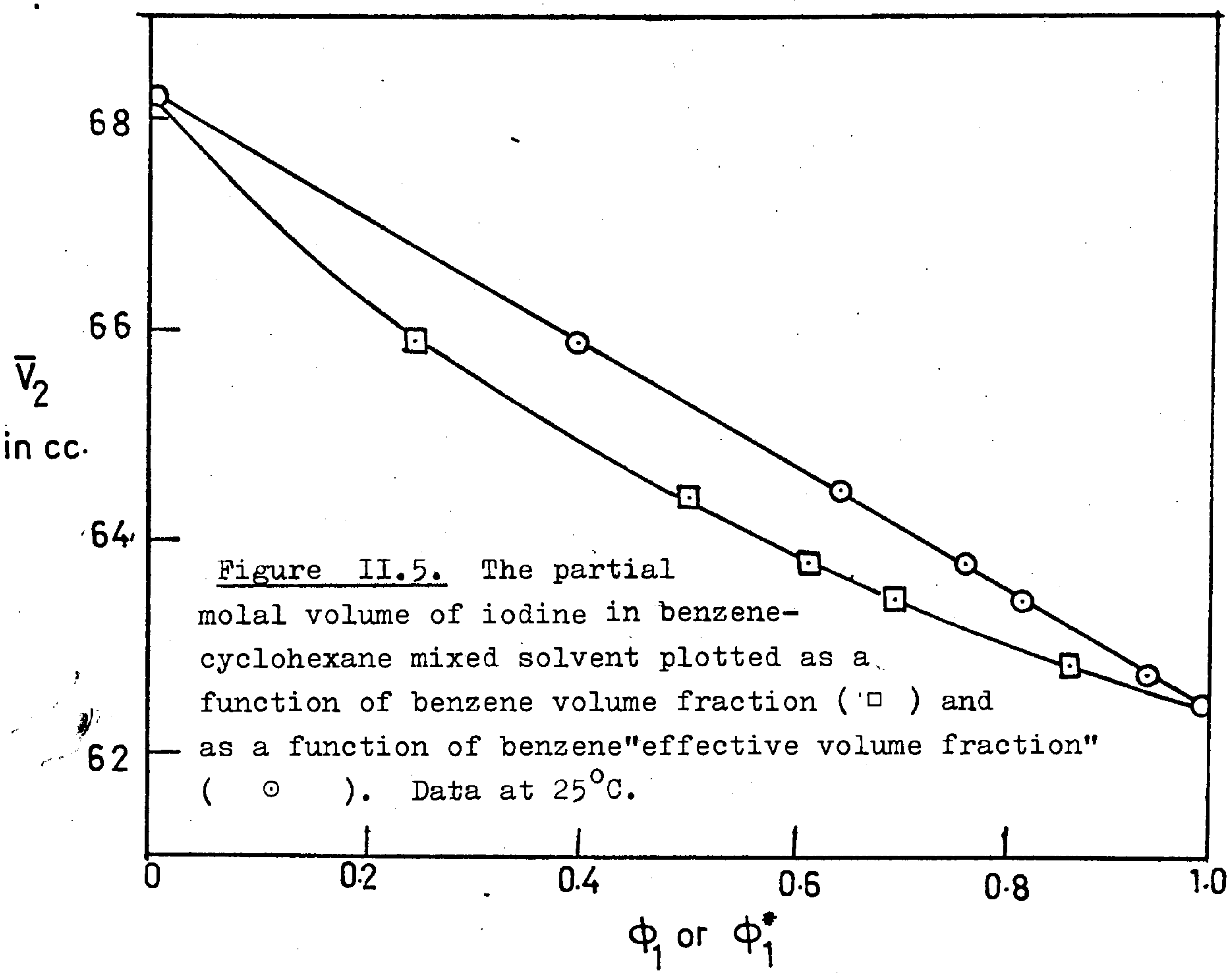


Figure II.5. The partial molal volume of iodine in benzene-cyclohexane mixed solvent plotted as a function of benzene volume fraction (□) and as a function of benzene "effective volume fraction" (⊙). Data at 25°C.

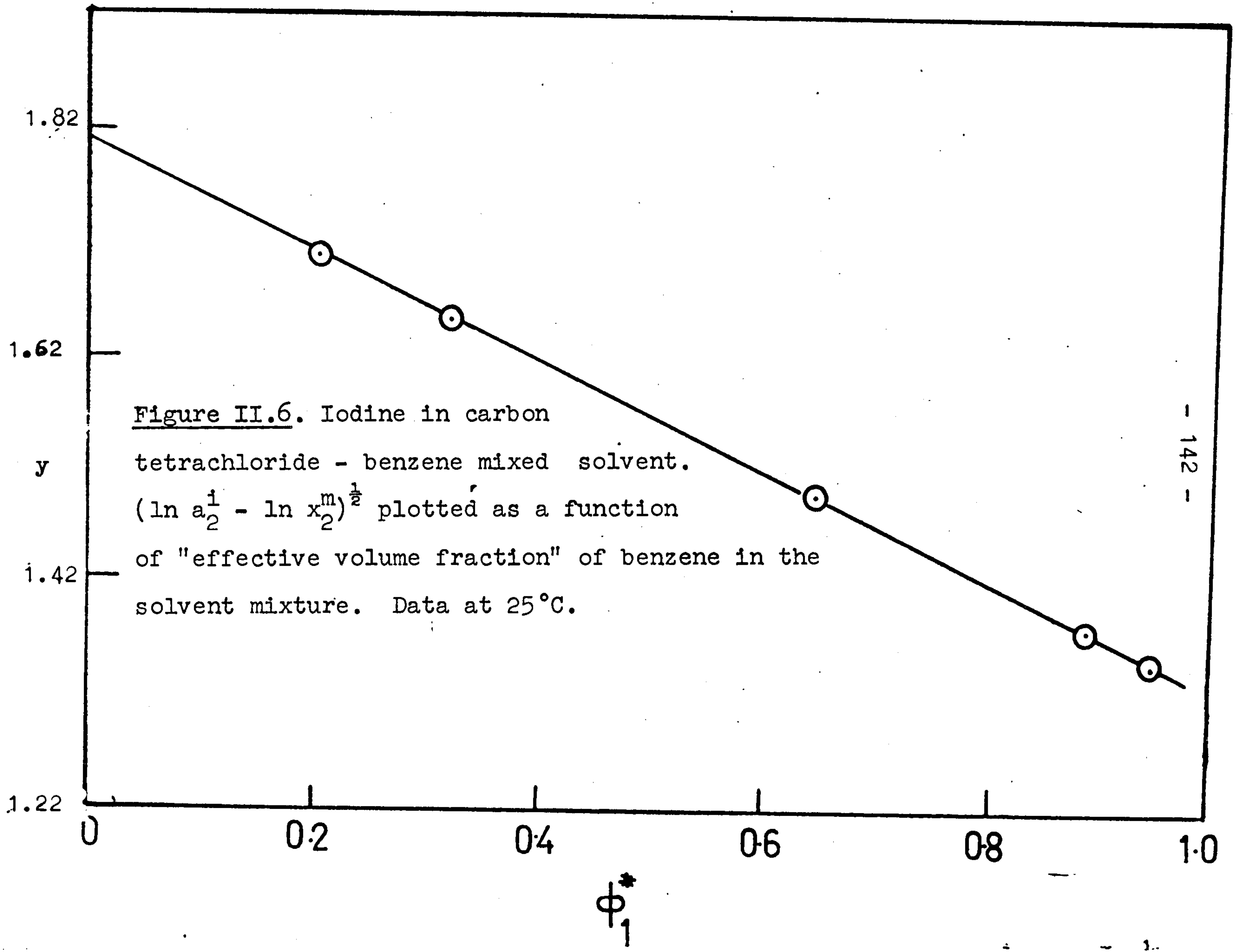


Figure II.6. Iodine in carbon tetrachloride - benzene mixed solvent. $(\ln a_2^1 - \ln x_2^m)^{\frac{1}{2}}$ plotted as a function of "effective volume fraction" of benzene in the solvent mixture. Data at 25°C.

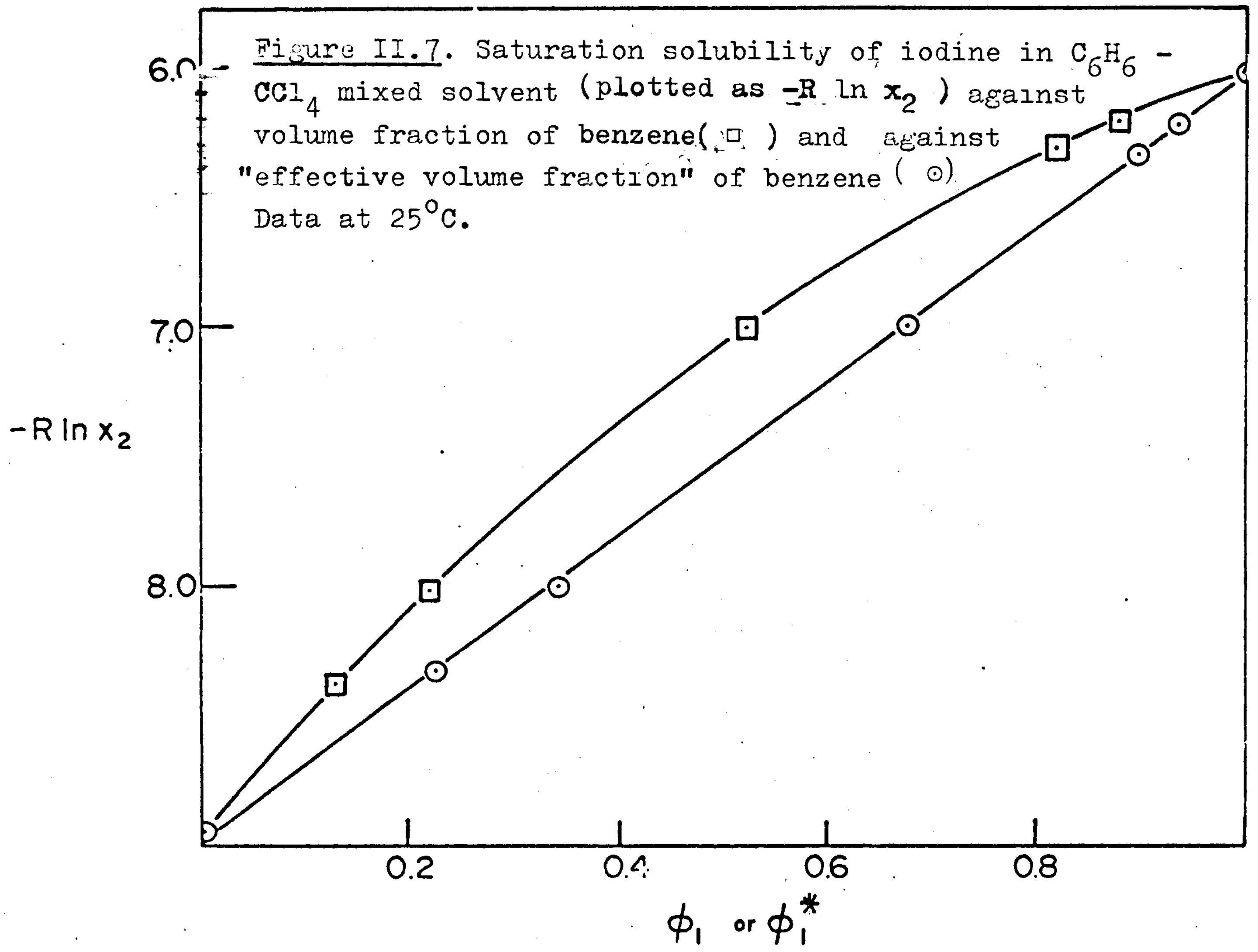


Figure II.7. Saturation solubility of iodine in C_6H_6 - CCl_4 mixed solvent (plotted as $-R \ln x_2$) against volume fraction of benzene(□) and against "effective volume fraction" of benzene (⊙) Data at 25°C.

Figure II.8. Iodine in mixed carbon tetrachloride perfluoroheptane solvent. Data points plotted against simple volume fraction of carbon tetrachloride in mixed solvent (⊡) and against "effective volume fraction" of carbon tetrachloride (⊙). Solid line represents the theoretical $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ versus Φ_1 or Φ_1^* relationship. Data at 25.0°C.

Figure II.8

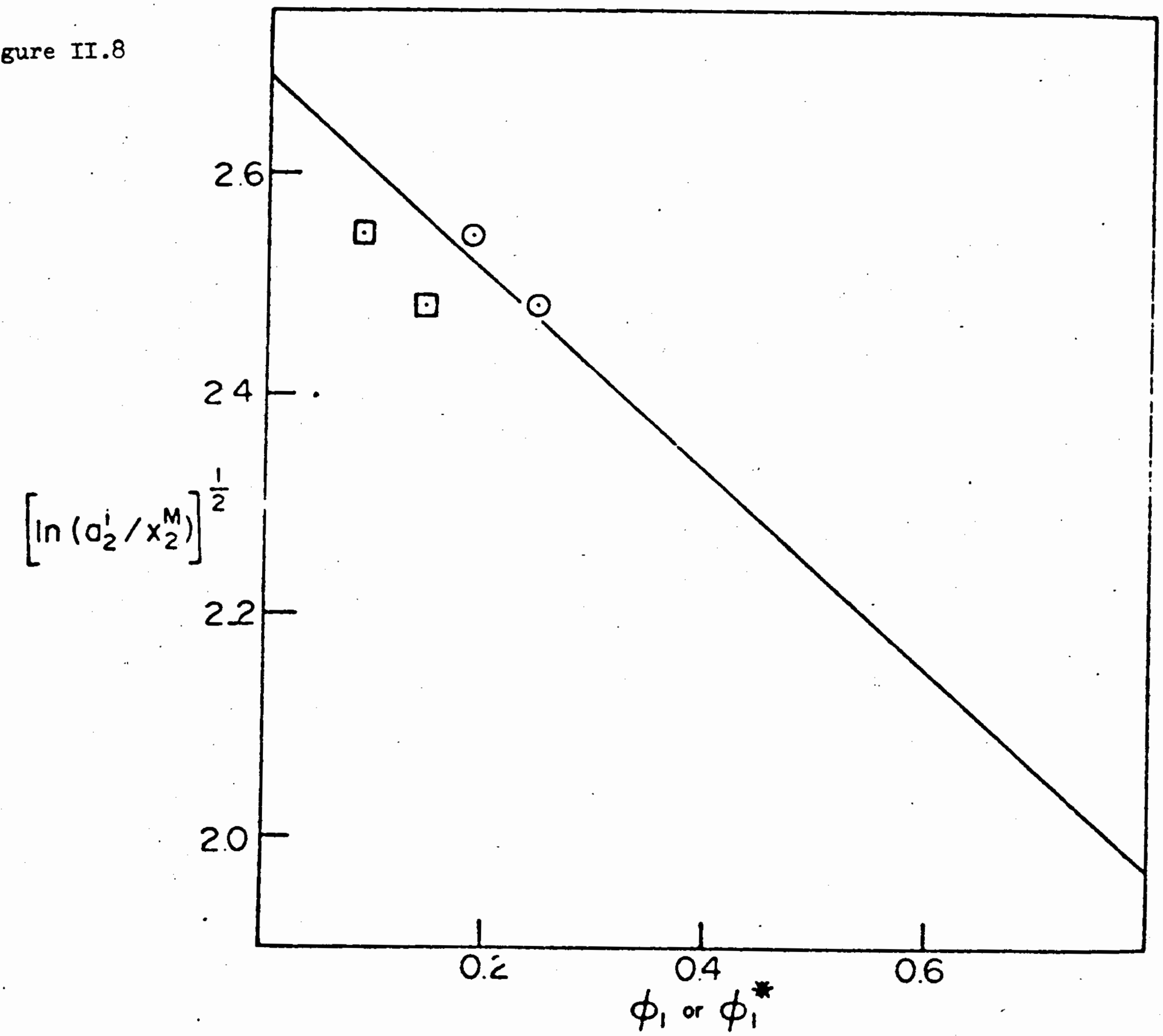


Figure II.9. Saturation solubility of SnI_4 in mixed benzene-cyclohexane solvent plotted (as $\ln x_2^m$) as a function of volume fraction of benzene. Data at 25°C.

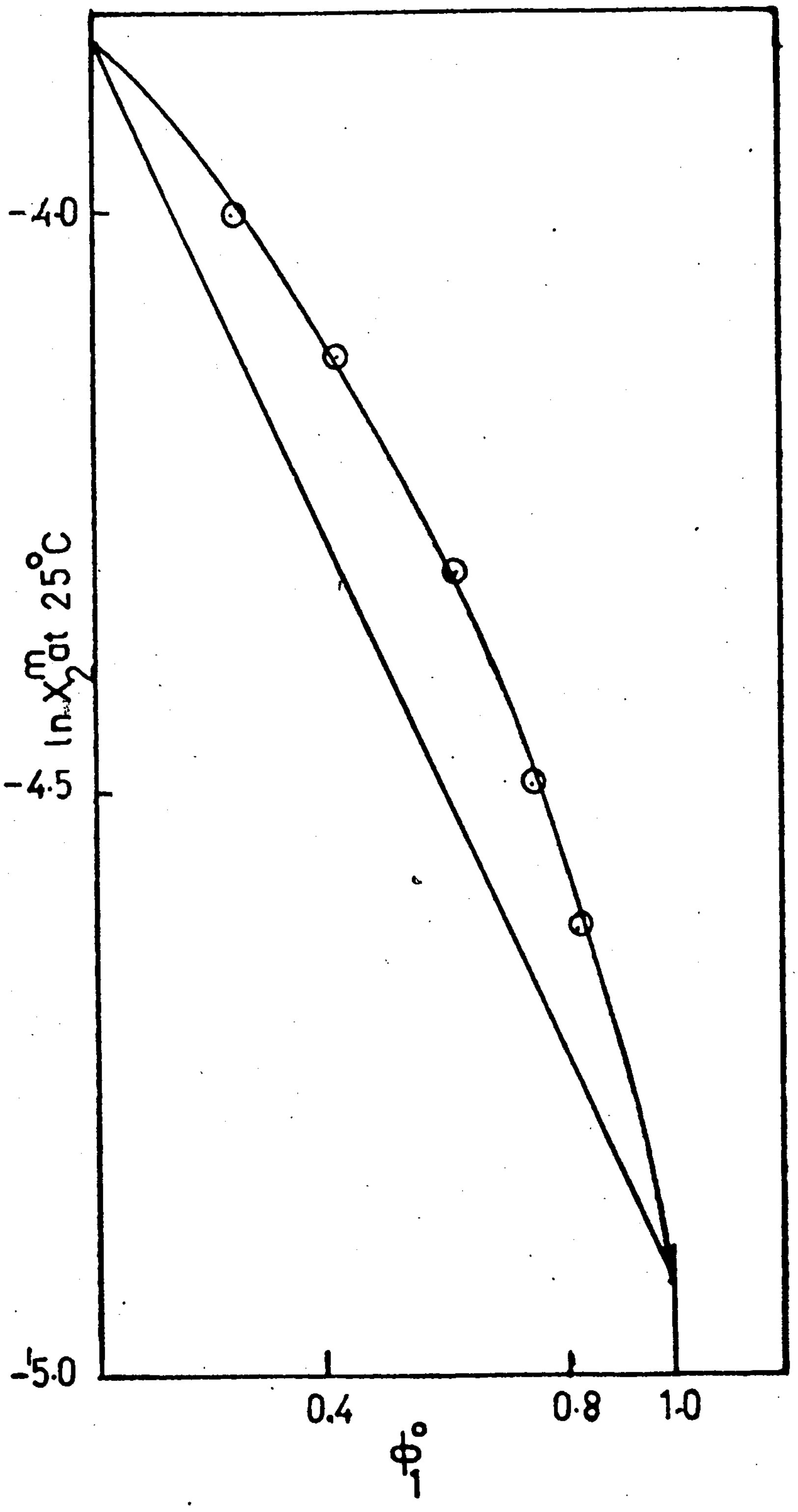


Figure II.9

Figure II.10. SnI_4 in benzene-cyclohexane mixed solvent. Y (i.e. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$) plotted as a function of volume fraction of benzene (⊙) and as a function of effective volume fraction of benzene (⊡). Data at 25 ° C.

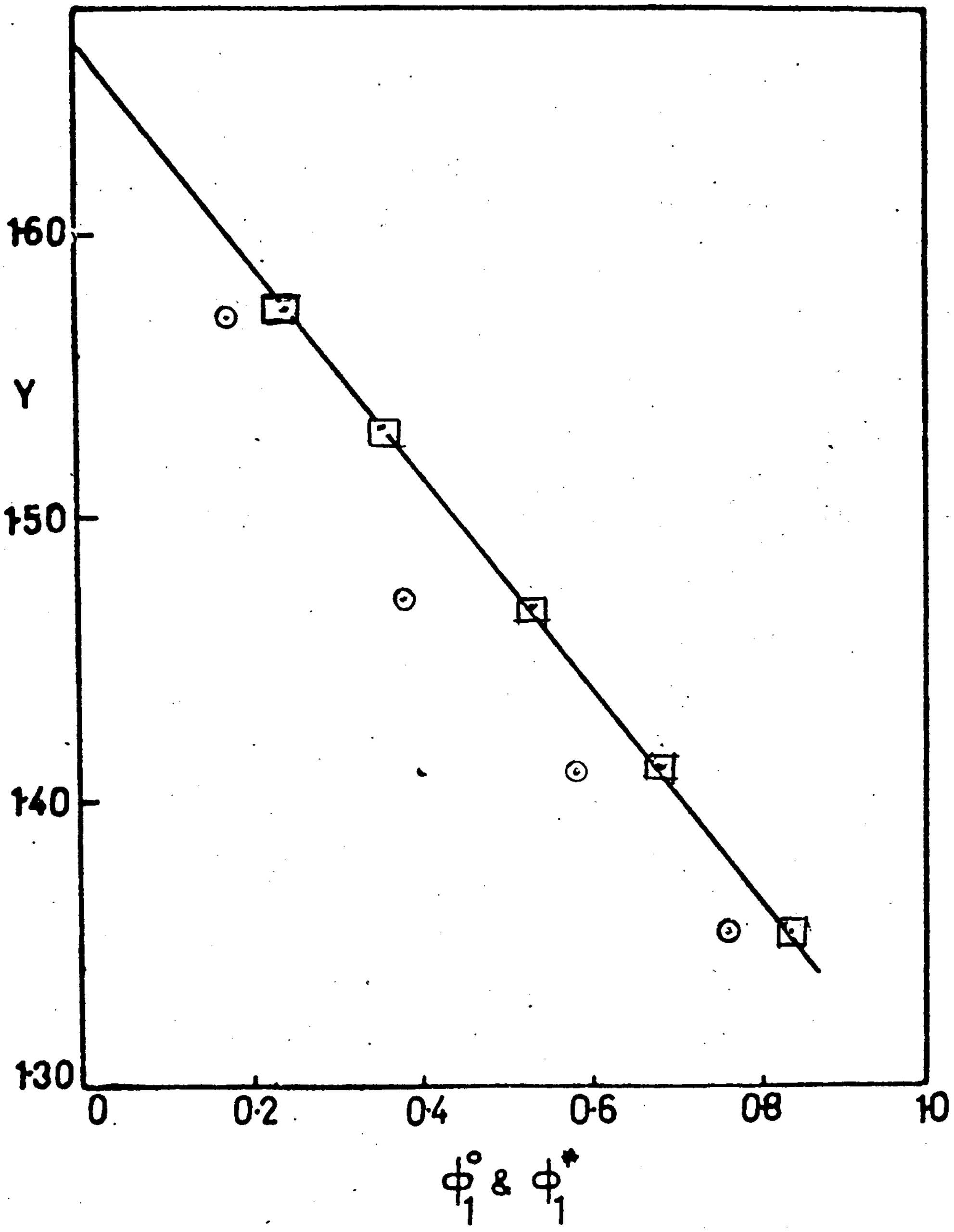


Figure II.10

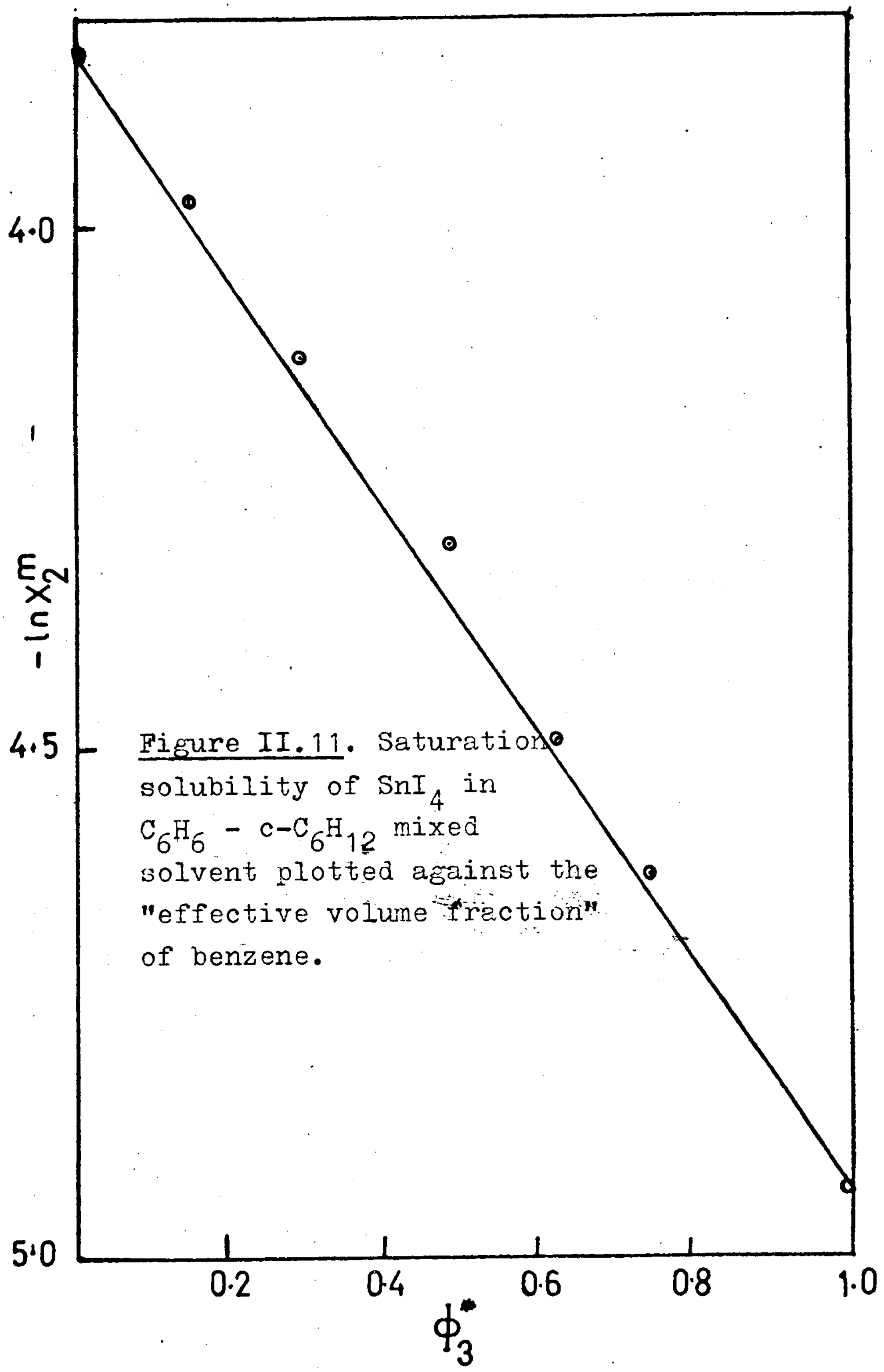


Figure II.11. Saturation solubility of SnI_4 in C_6H_6 - c-C_6H_{12} mixed solvent plotted against the "effective volume fraction" of benzene.

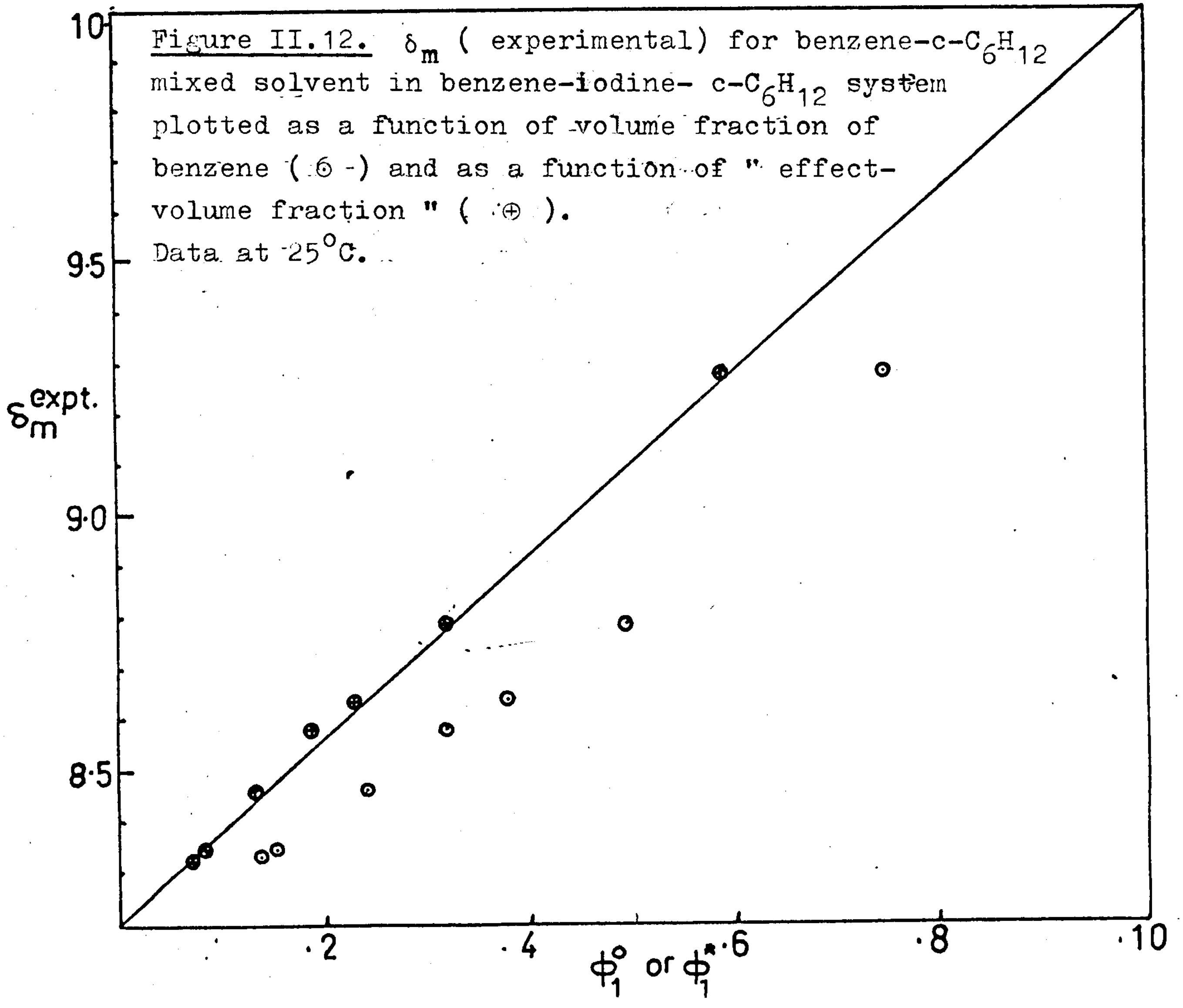


Figure II.12. δ_m (experimental) for benzene-c-C_6H_{12} mixed solvent in benzene-iodine- c-C_6H_{12} system plotted as a function of volume fraction of benzene (⊙ -) and as a function of " effect-volume fraction " (⊕).

Data at 25°C.

Figure II.13. δ_m(experimental) for benzene-cyclohexane in benzene - SnI_4 - cyclohexane system. Plotted as a function of volume fraction of benzene (⊙) and "effective volume fraction" of benzene (⊕). Solid line represents theoretical δ_m versus Φ_1^o or Φ_1^*. Data at 25° C.

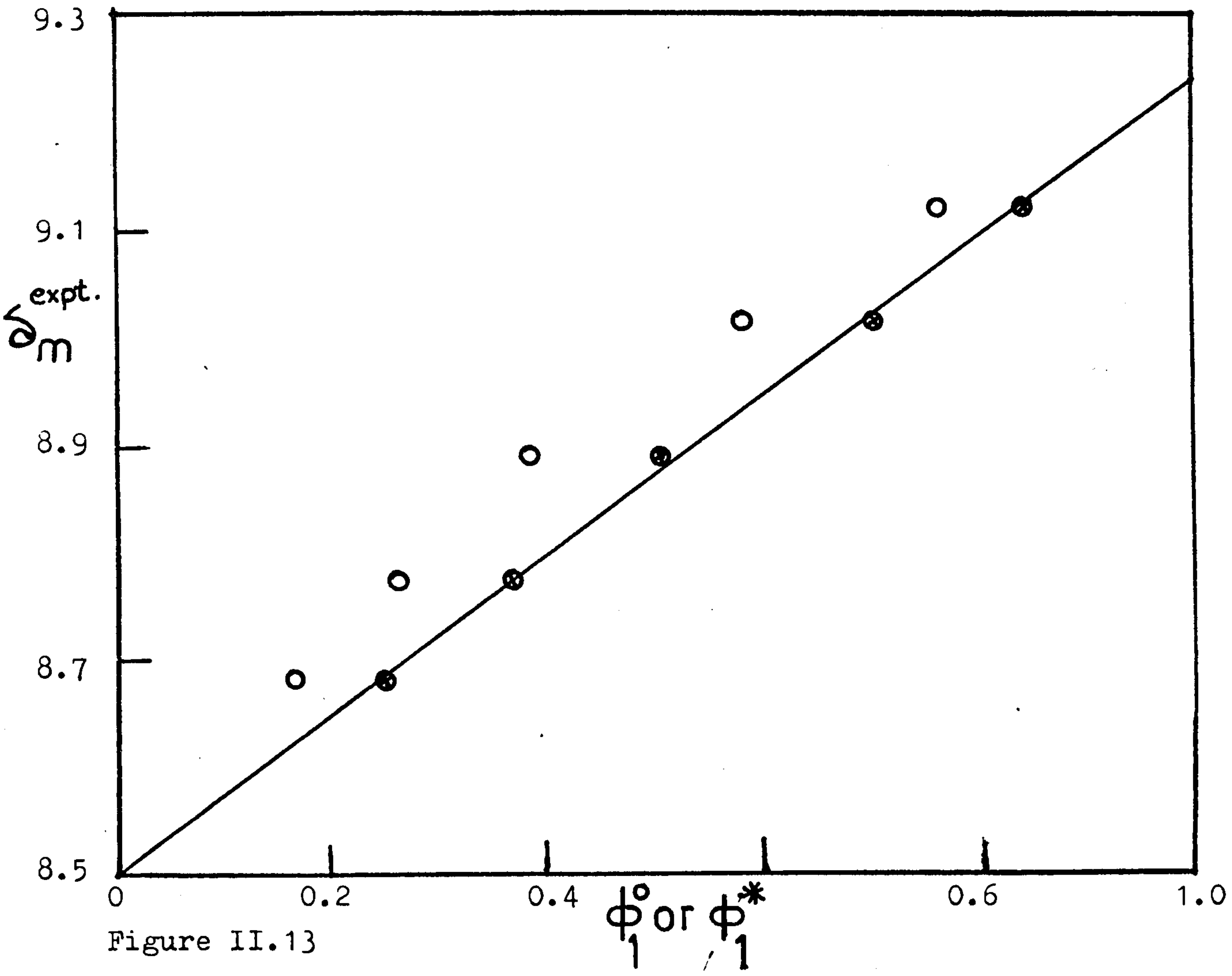


Figure II.13

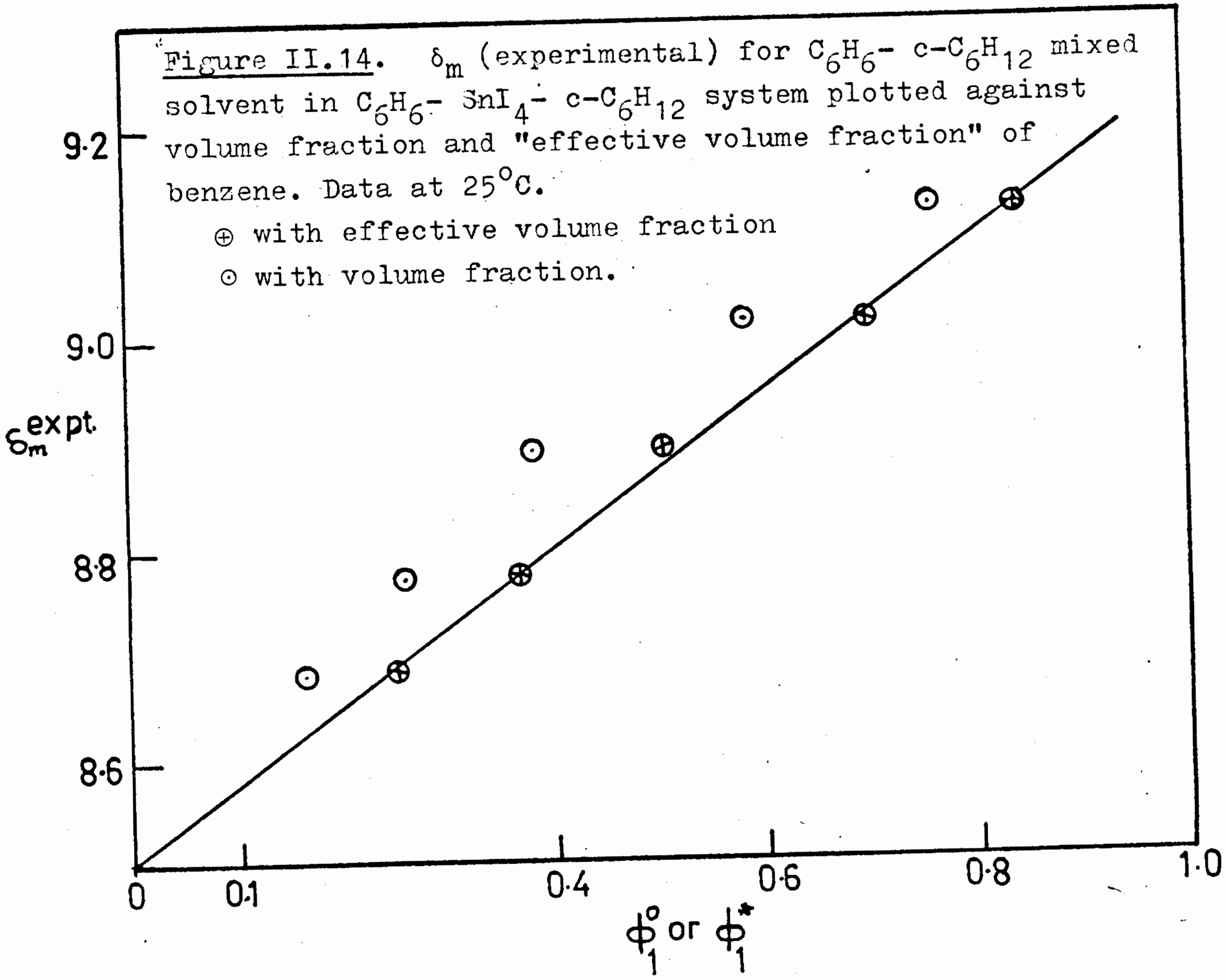


Figure II.14. δ_m (experimental) for C_6H_6- c-C_6H_{12} mixed solvent in C_6H_6- SnI_4- c-C_6H_{12} system plotted against volume fraction and "effective volume fraction" of benzene. Data at 25°C.

⊕ with effective volume fraction

⊙ with volume fraction.

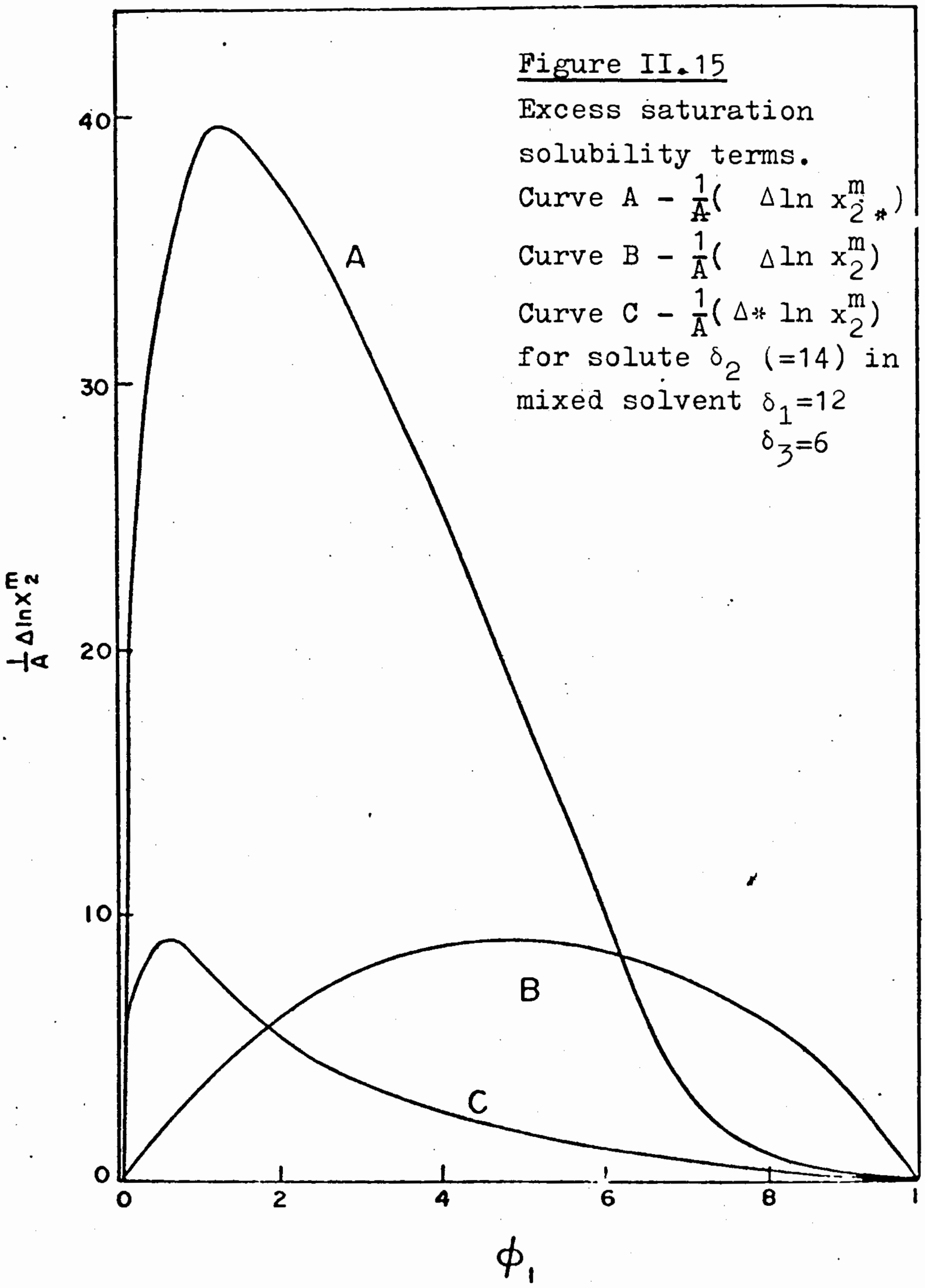


Figure II.15

Excess saturation solubility terms.

Curve A - $\frac{1}{A}(\Delta \ln x^m_{2*})$

Curve B - $\frac{1}{A}(\Delta \ln x^m_2)$

Curve C - $\frac{1}{A}(\Delta{*} \ln x^m_2)$

for solute δ_2 (=14) in mixed solvent $\delta_1=12$ $\delta_3=6$

Figure II.16. Excess saturation solubility term for iodine in a mixed benzene-cyclohexane solvent. 25 ° C.

Curve A: $\Delta(\ln x_{2*}^{m})$

Curve B: $\Delta(\ln x_{2}^{m})$

Curve C: $\Delta^{*}(\ln x_{2}^{m})$

Experimental data ⊙

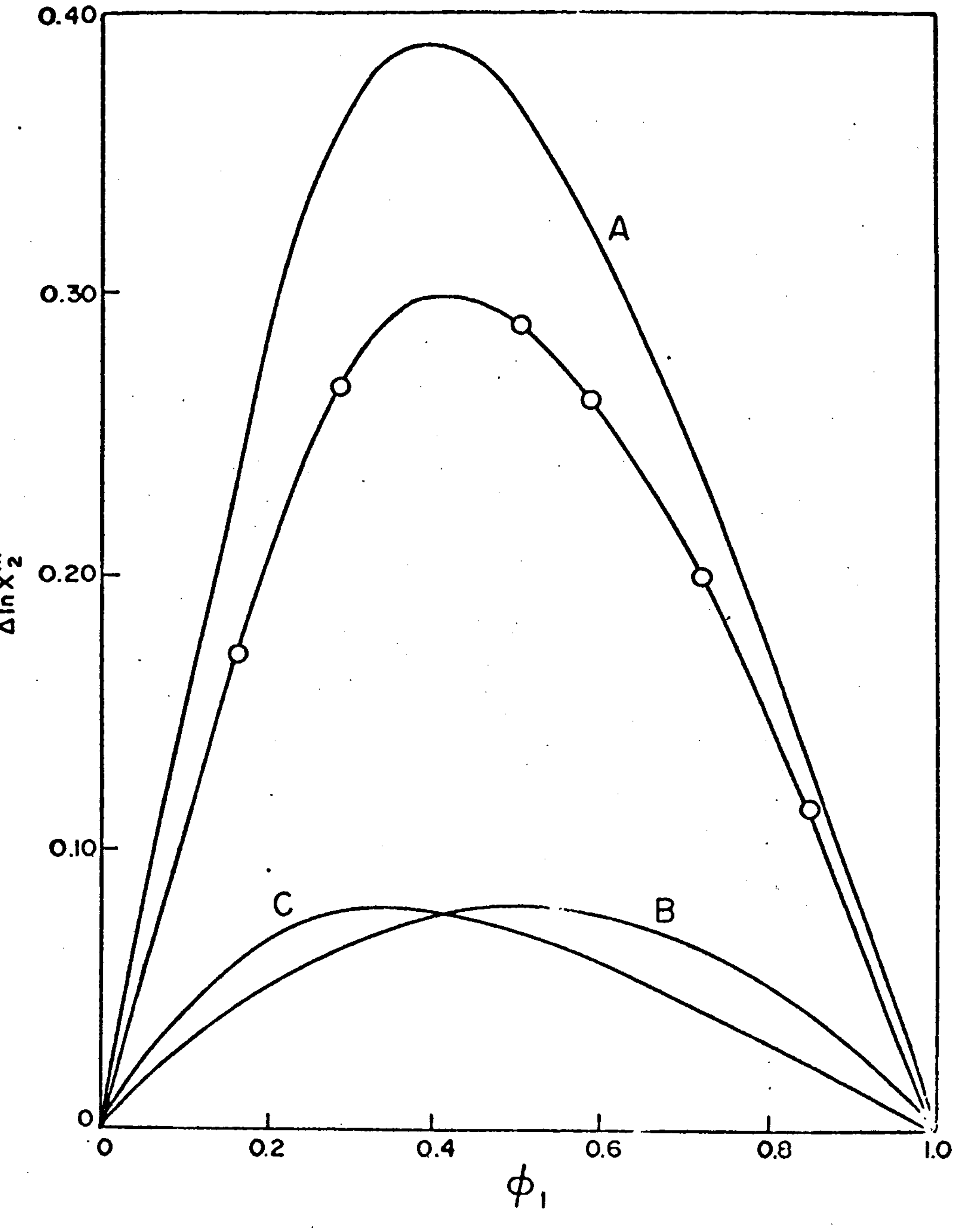


Figure II.16

Figure II.17. Excess saturation solubility curve for iodine in mixed benzene - carbon tetrachloride solvent. 25°C.

Curve A: $\Delta(\ln x_{2*}^{m})$

Curve B: $\Delta(\ln x_{2}^{m})$

Experimental data points ○

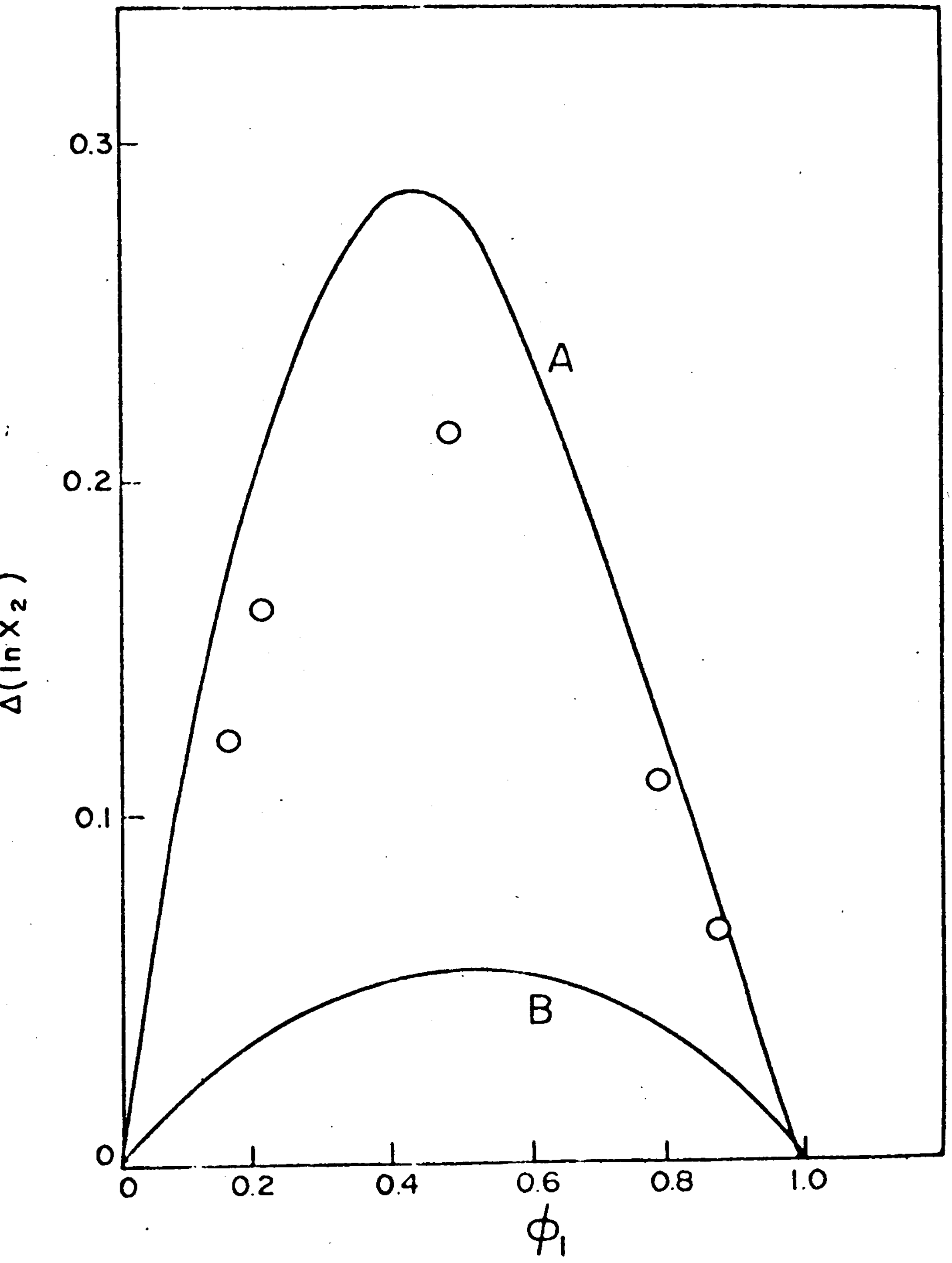


Figure II.17

Figure II.18. Excess saturation solubility curve for SnI_4 in benzene-cyclohexane mixed solvent.

Curve A: $\Delta \ln x_{2*}^{m}$

Curve B: $\Delta^{*} \ln x_{2}^{m}$

Curve C: $\Delta \ln x_{2}^{m}$

⊙ experimental points.

All data at 25° C.

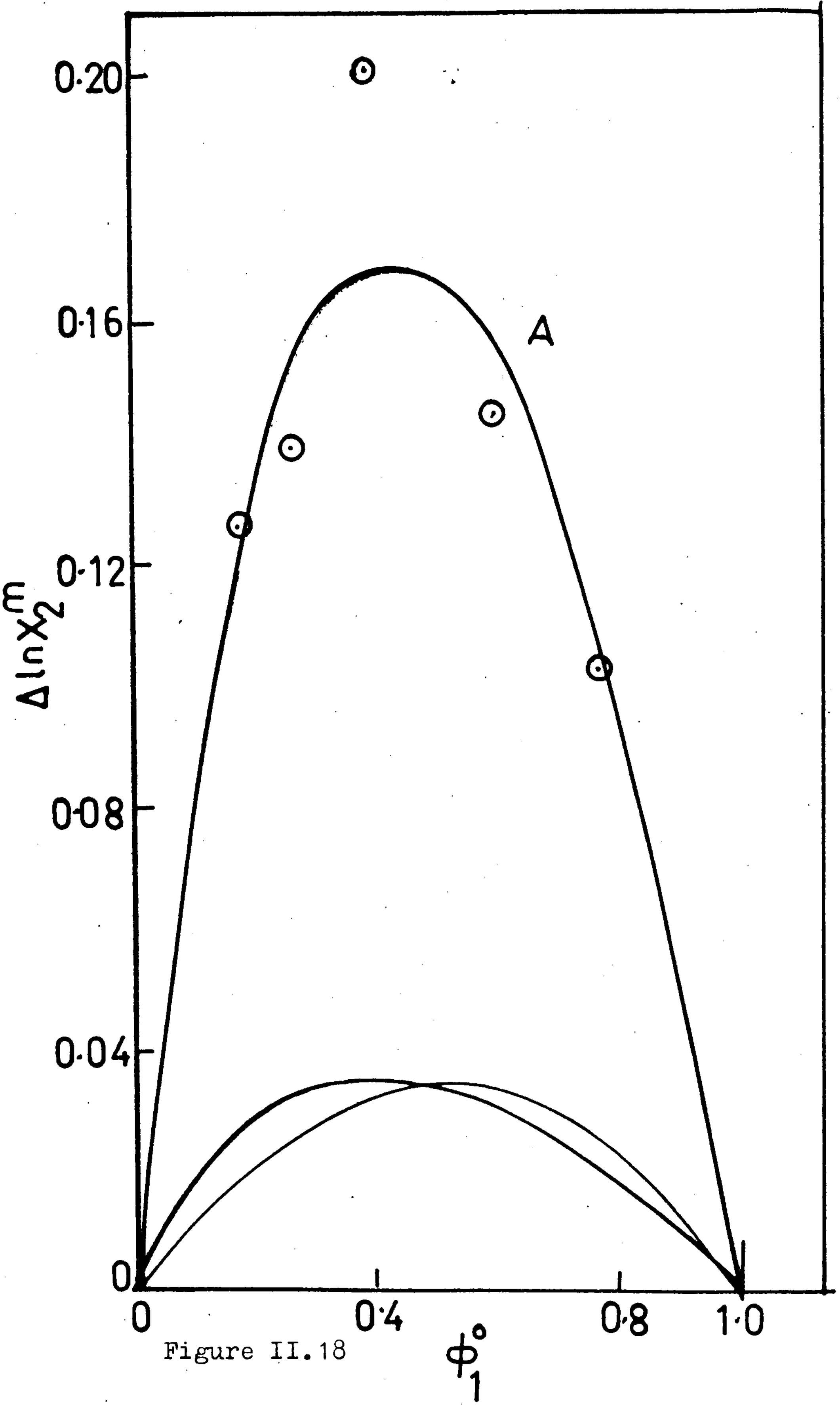


Figure II.18

Figure II.19. Excess saturation solubility term for iodine in a mixed carbon tetrachloride - perfluoroheptane solvent. 25 °C.

Curve A: $\Delta(\ln x_{2*}^{m})$

Curve B: $\Delta(\ln x_{2}^{m})$

Experimental data points

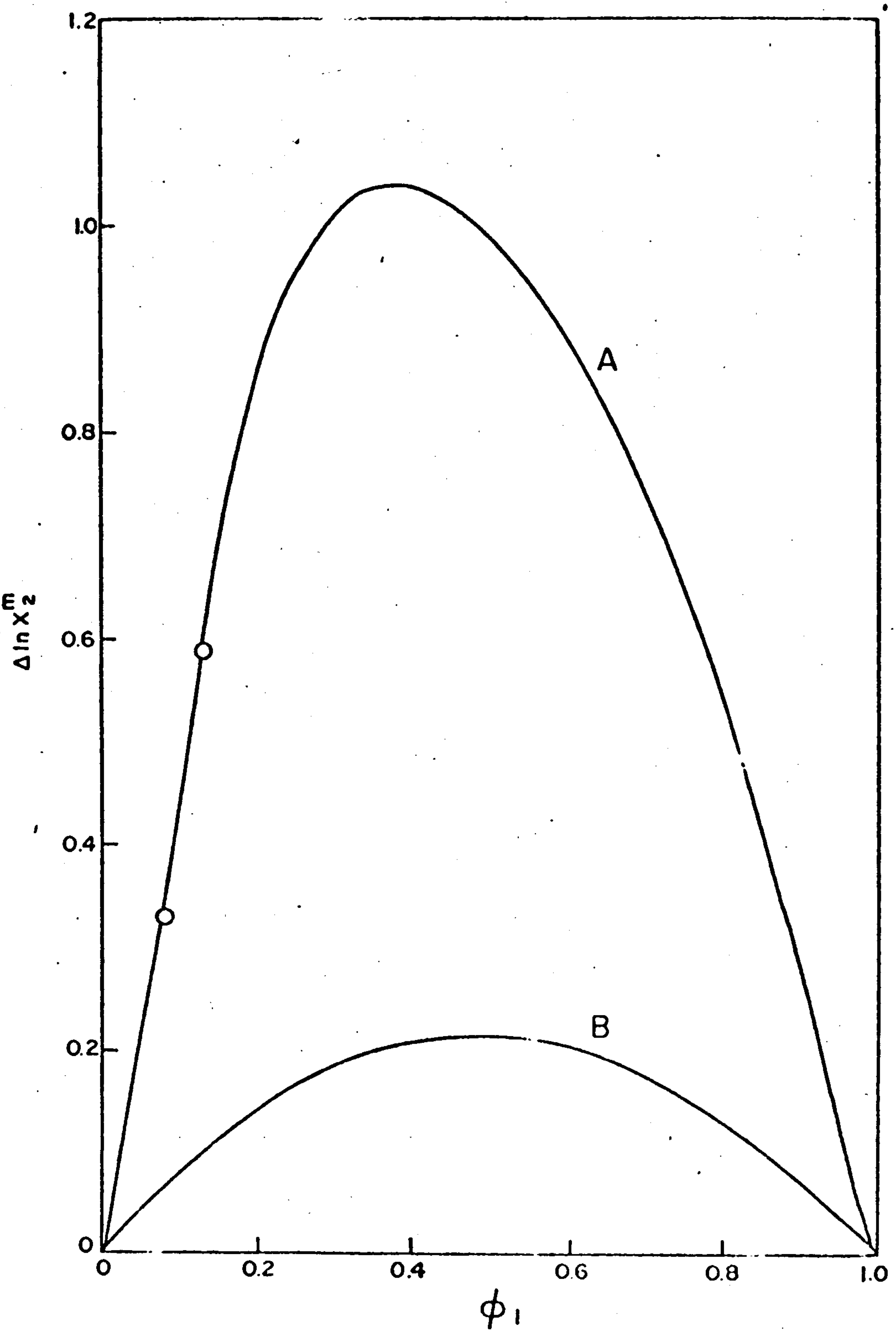


Figure II.19

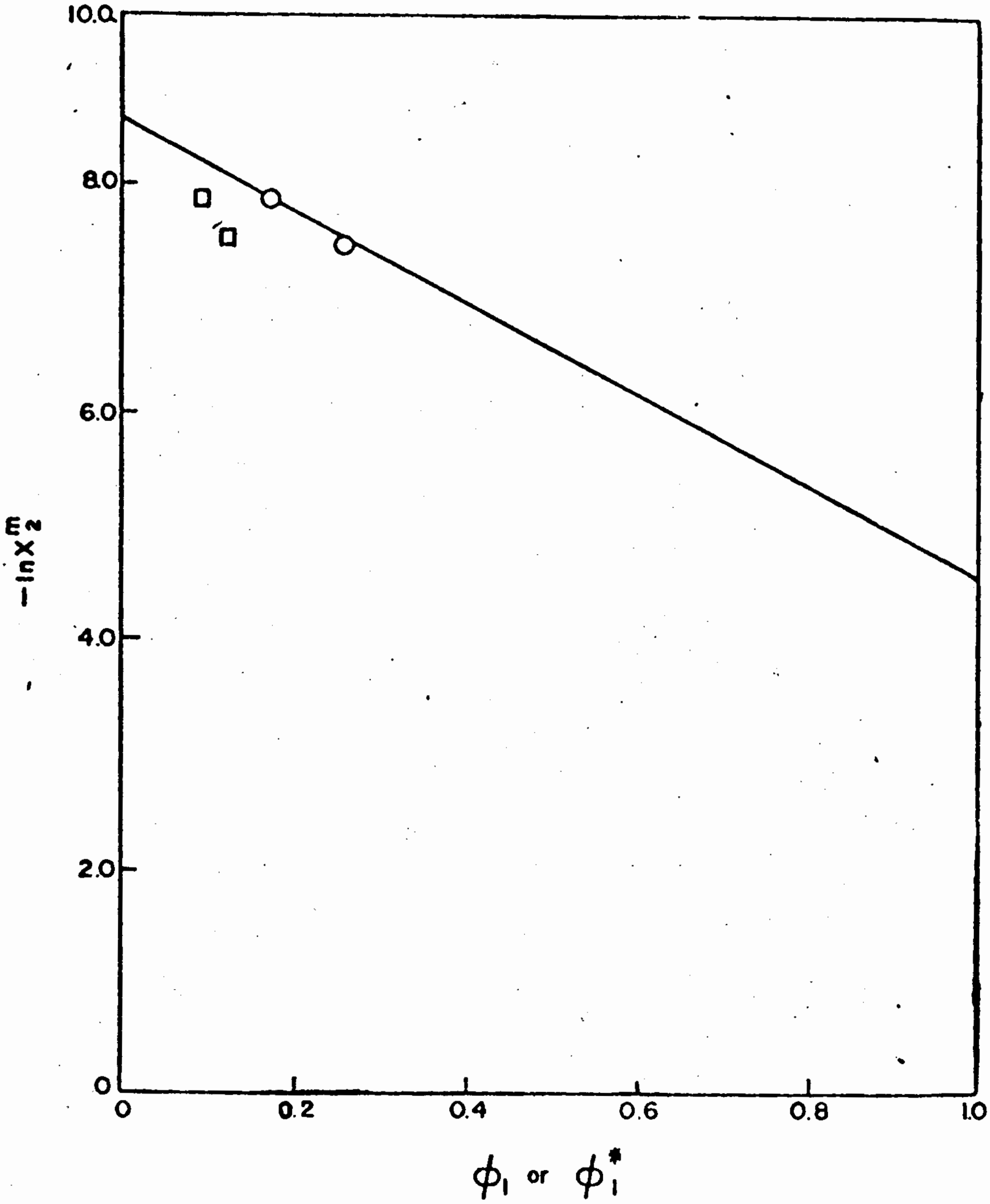


Figure II.20. Saturation solubility of iodine in CCl_4 - n-C_7F_{16} mixed solvent plotted (as ln x_2^m) as a function of the "effective volume fraction" and the volume fraction of CCl_4. Data at 25° C.

Figure II.21. Excess saturation solubility curves, $\Delta(\ln x^m_{2*})$ for naphthalene (δ_2 = 10) in hypothetical mixed solvents.

Curve A: $\delta_1 = 6$; $\delta_3 = 14$

Curve B: $\delta_1 = 8$; $\delta_3 = 12$.

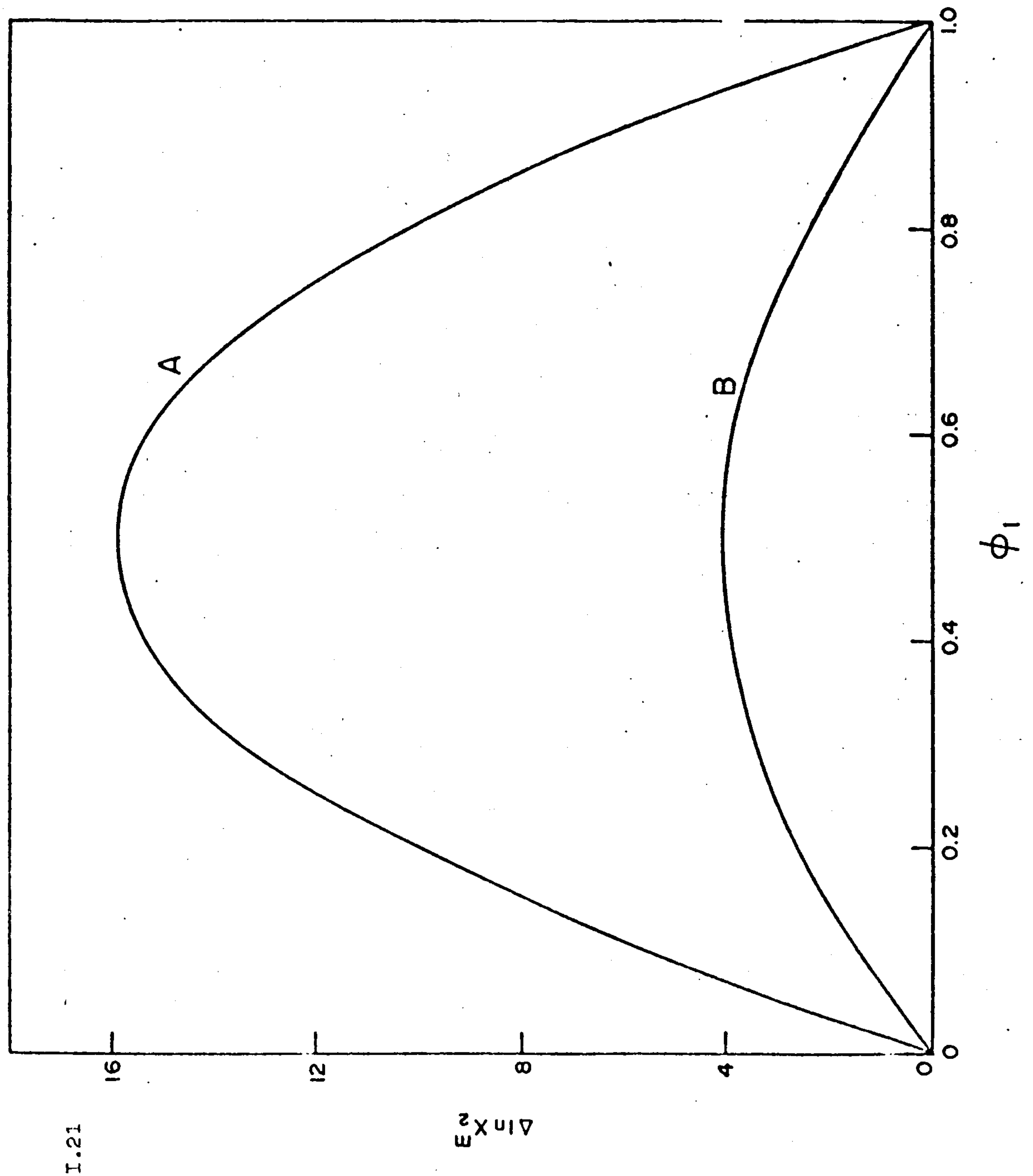


Figure II.21

Figure II.22. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ plotted against effective volume fraction Φ_1^* for naphthalene in hypothetical mixed solvents.

Curve A: $\delta_1 = 6$; $\delta_3 = 14$.

Curve B: $\delta_1 = 8$; $\delta_3 = 12$.

(for this system $\Phi_1^* \equiv \Phi_1$)

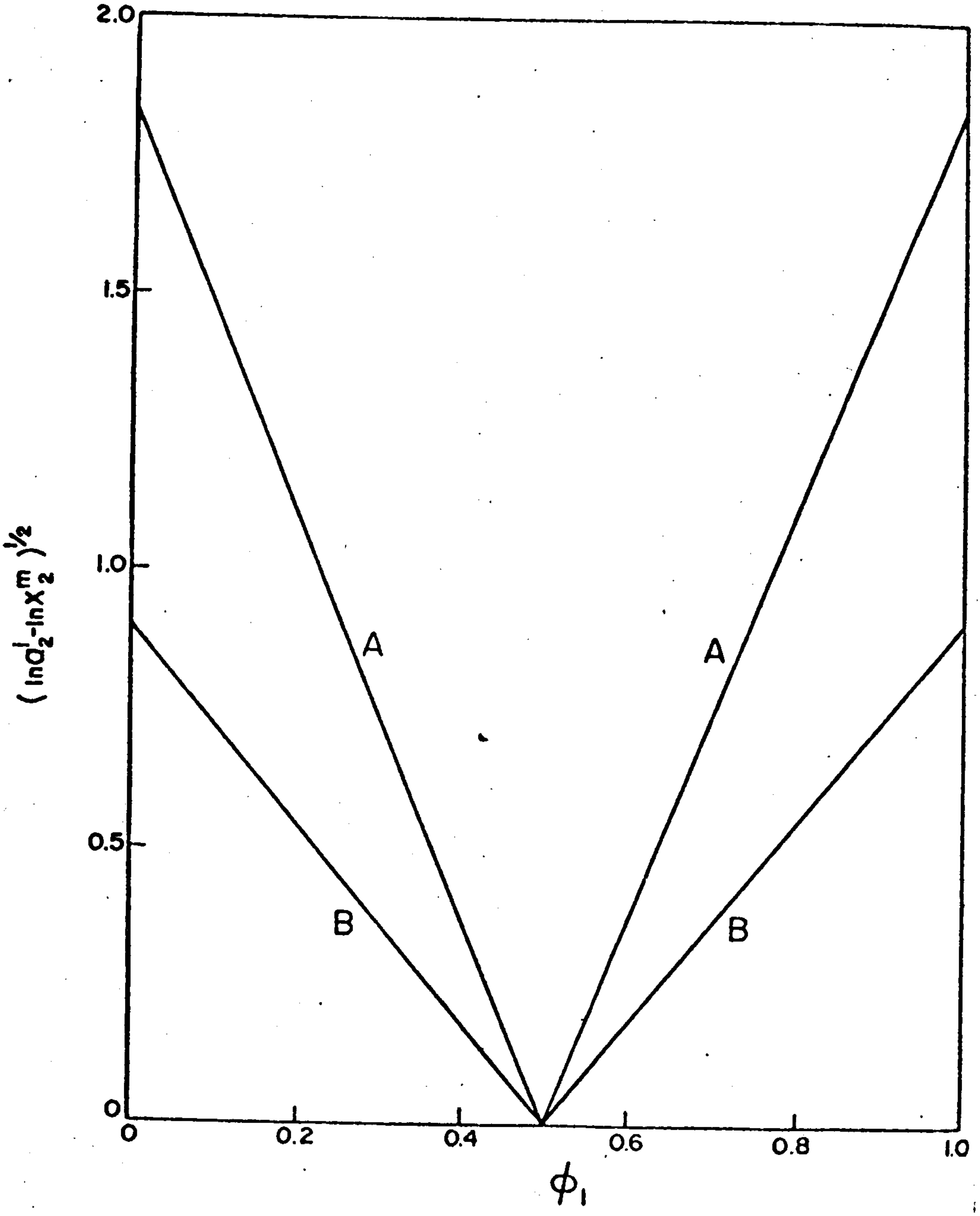


Figure II.22

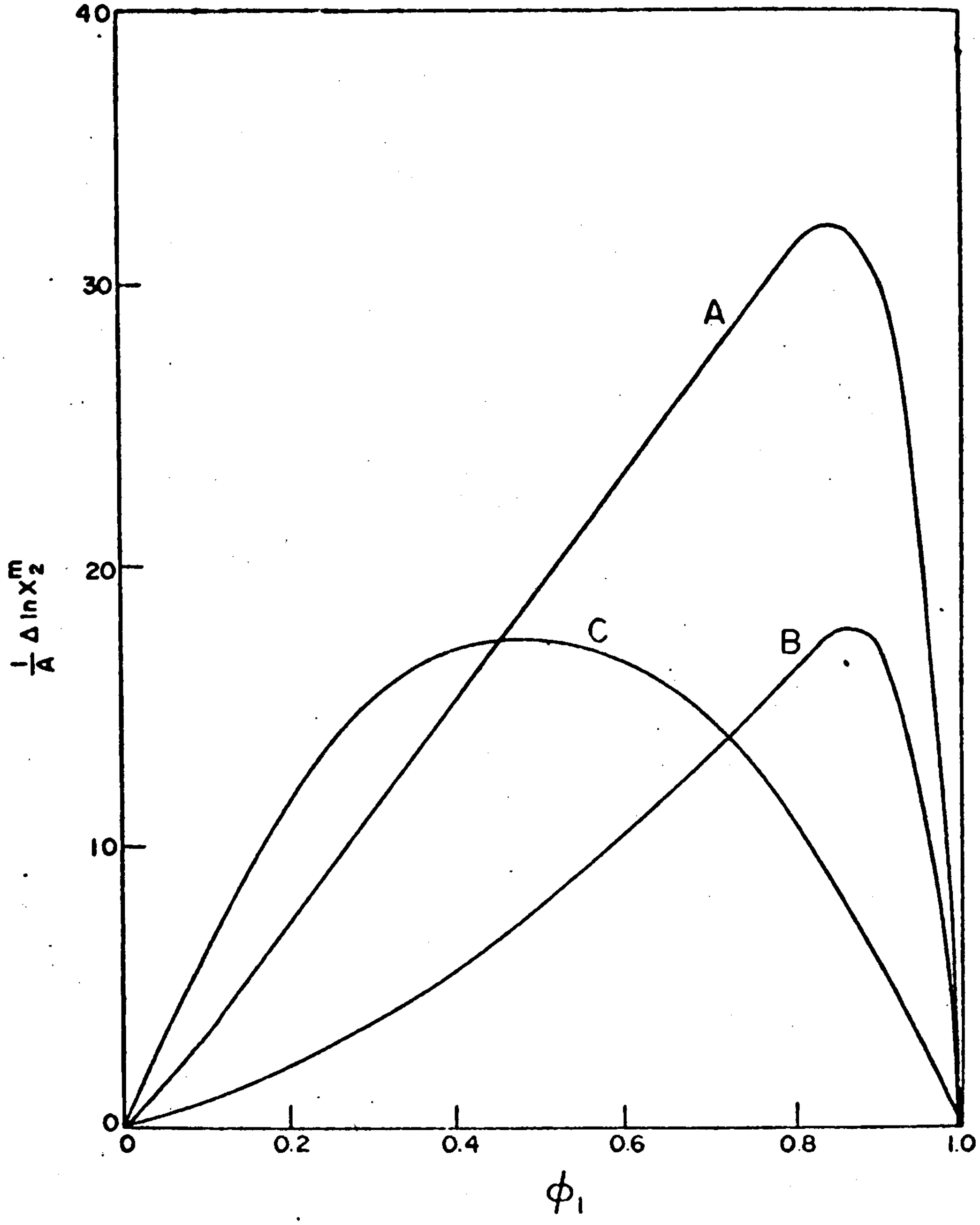


Figure II.23. Excess saturation solubility for SnI_4 (δ = 11.7) in hypothetical mixed solvent (δ_1 = 5.6; δ_3 = 14.0).

Curve A: $\Delta(\ln x_{2*}^m)$; Curve B: $\Delta*(\ln x_3^m)$; Curve C: $\Delta(\ln x_2^m)$

Figure II.24. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$ plotted as a function of Φ_1^* (linear plot A) and as a function of Φ_1 (curve B) for stannic iodide ($\delta_2 = 11.7$) in hypothetical mixed solvent $\delta_1 = 5.6$; $\delta_3 = 14.0$.

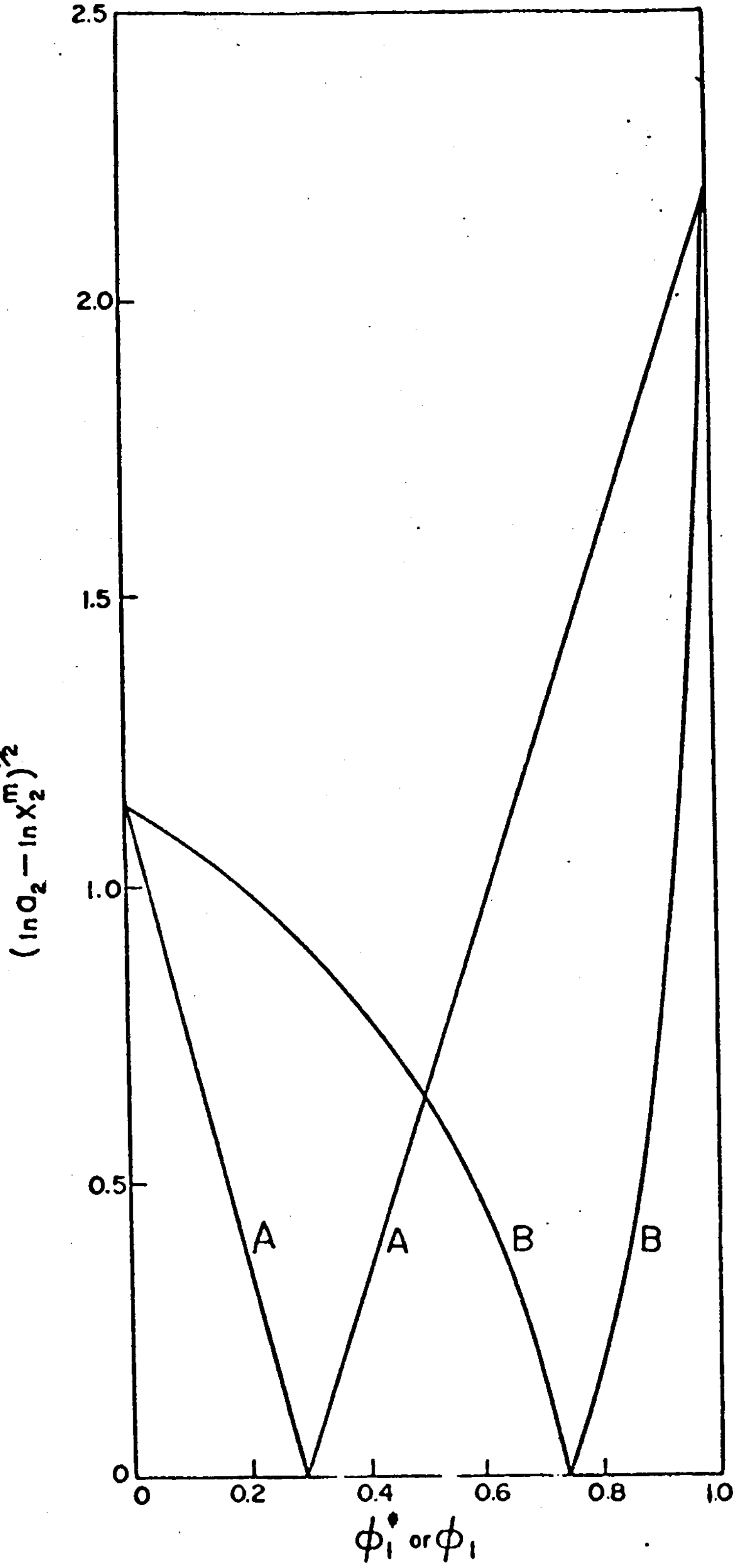

2.5
2.0
1.5
1.0
0.5
0
$(\ln a_2 - \ln X_2^m)^{1/2}$
A
A
B
B
0
0.2
0.4
0.6
0.8
1.0
$\phi_1^{\bullet}$ or ϕ_1

Figure II.24

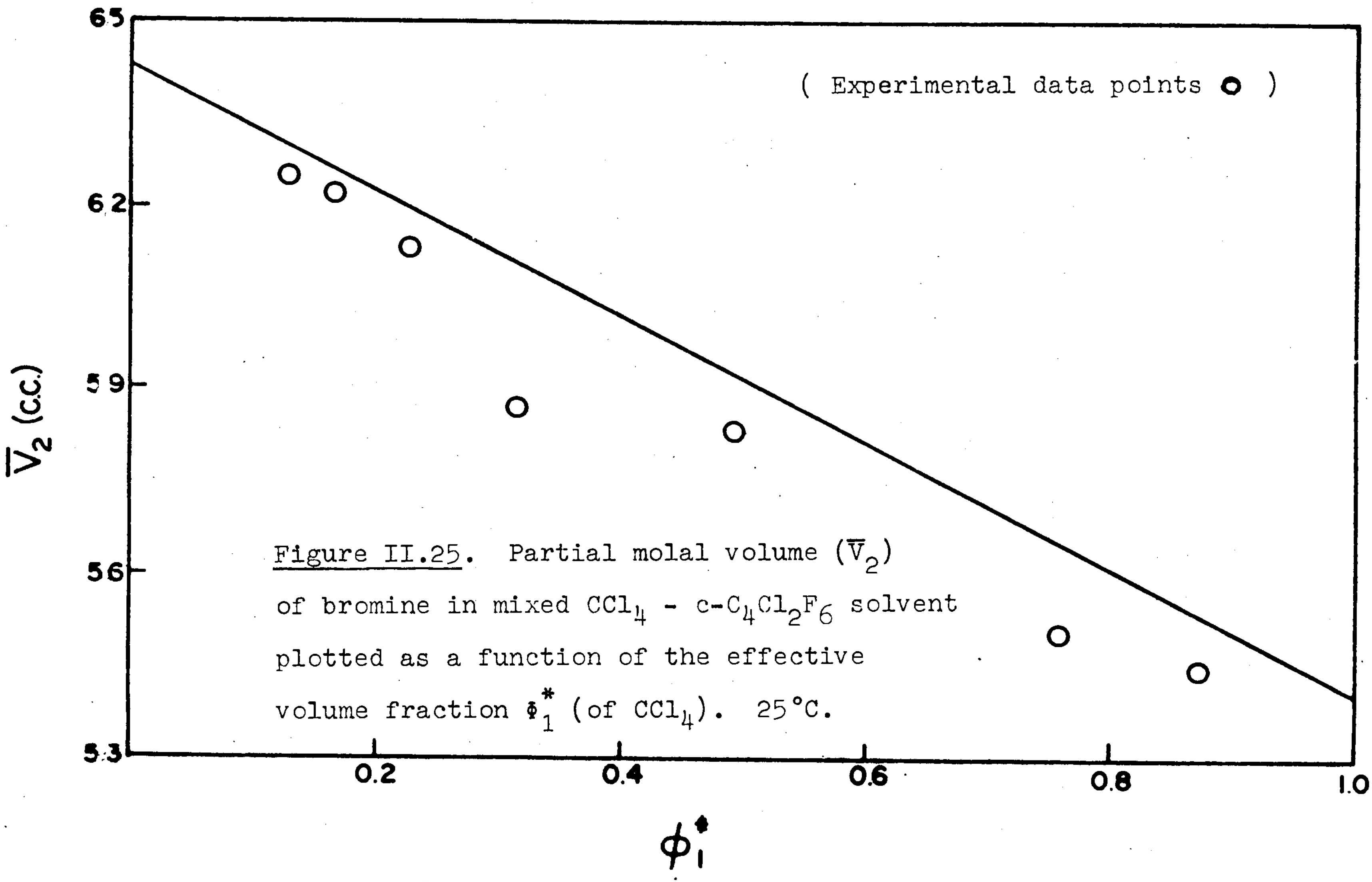


Figure II.25. Partial molal volume ($\overline{V}_2$) of bromine in mixed CCl_4 - c-$C_4Cl_2F_6$ solvent plotted as a function of the effective volume fraction Φ_1^* (of CCl_4). 25°C.

Figure II.26. Excess volume of mixing function $-\Delta V^E$ for iodine in a mixed C_6H_6 - c-C_6H_{12} solvent, as a function of volume fraction Φ_1 (assuming effective volume fraction definition for δ_m). Data at 25°C.

Full curve - calculated from equation (65).

Experimental data points (according to equation (66))

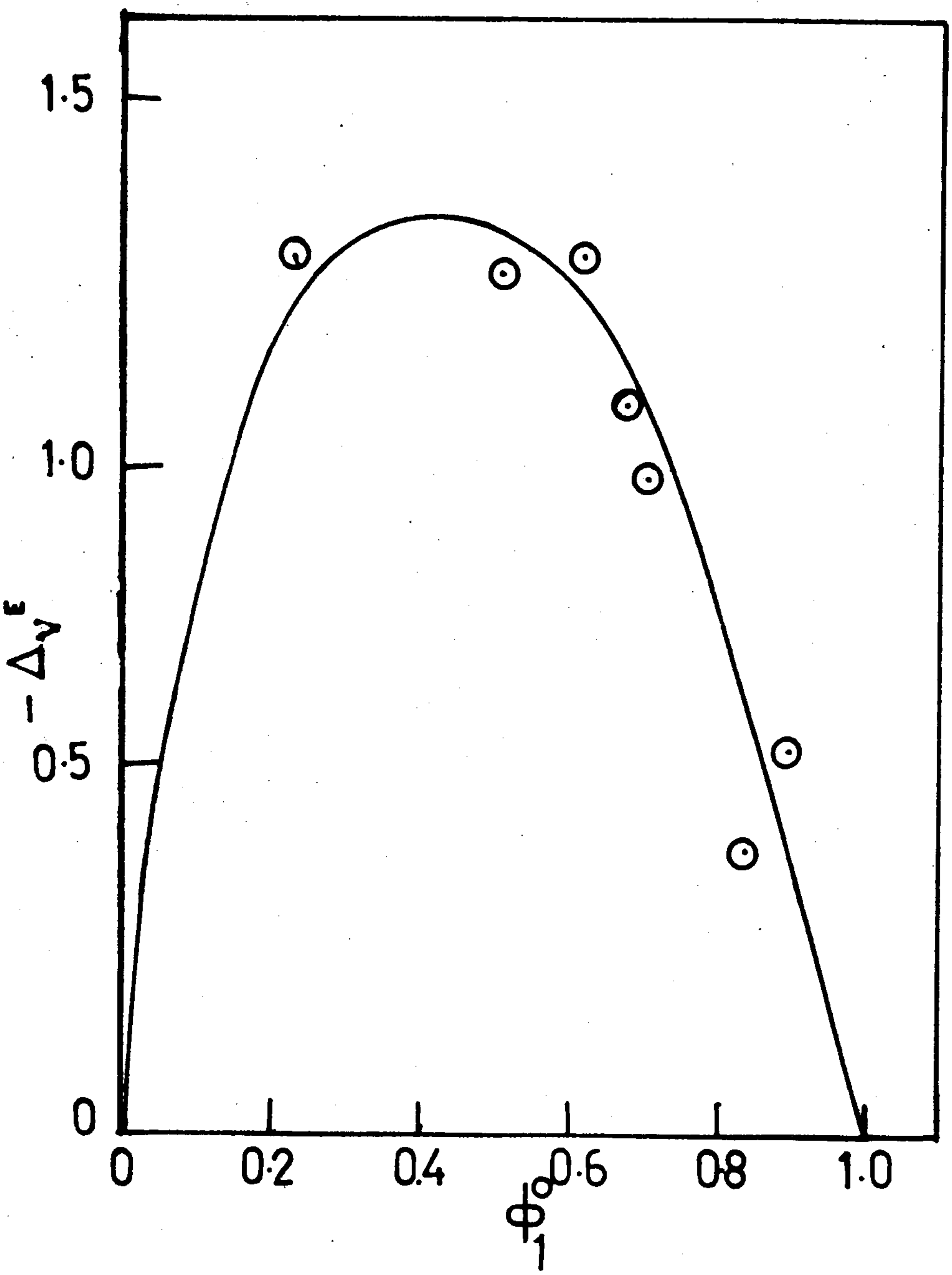


Figure II.26

Figure II.27. Excess volume of mixing term $-\Delta V^E$ for bromine in a mixed CCl_4 - c-$C_4Cl_2F_6$ solvent, 25 ° C, plotted against volume fraction of CCl_4 .

Theoretical curve - full line - assuming effective volume fraction definition of δ_m .

Experimental data points ⊙

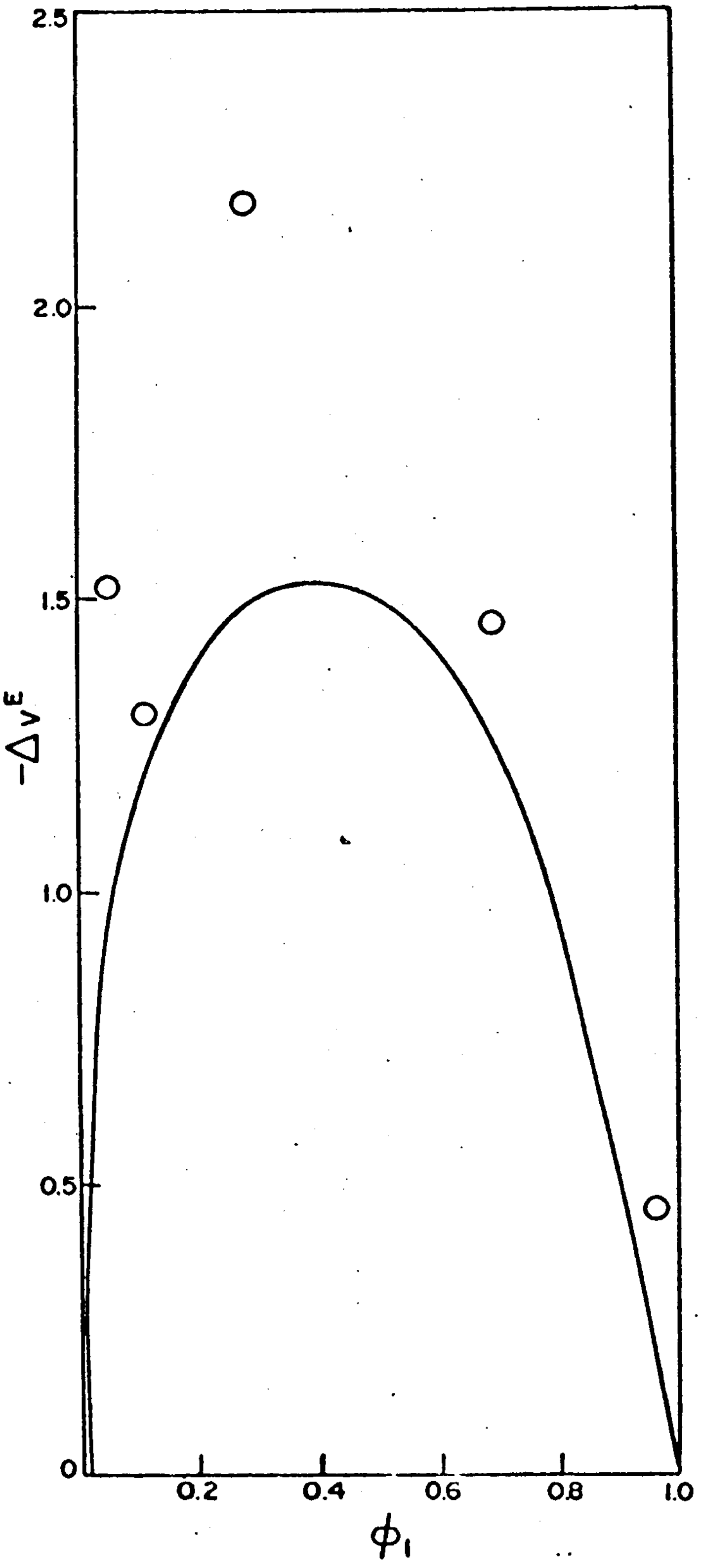


Figure II.27

Figure II.28 Saturation solubility of naphthalene in CCl_4 - c-C_6H_{12} mixed solvent of different composition, plotted (as x_2^m) as a function of temperature.

Curve A: pure CCl_4

Curve B: $\Phi_1^o = \Phi_{CCl_4} = 0.5518$

Curve C: $\Phi_1^o = \Phi_{CCl_4} = 0.3637$

Curve D: $\Phi_1^o = \Phi_{CCl_4} = 0.1575$

Curve E: pure c-C_6H_{12}

(All data taken from the reference- 79)

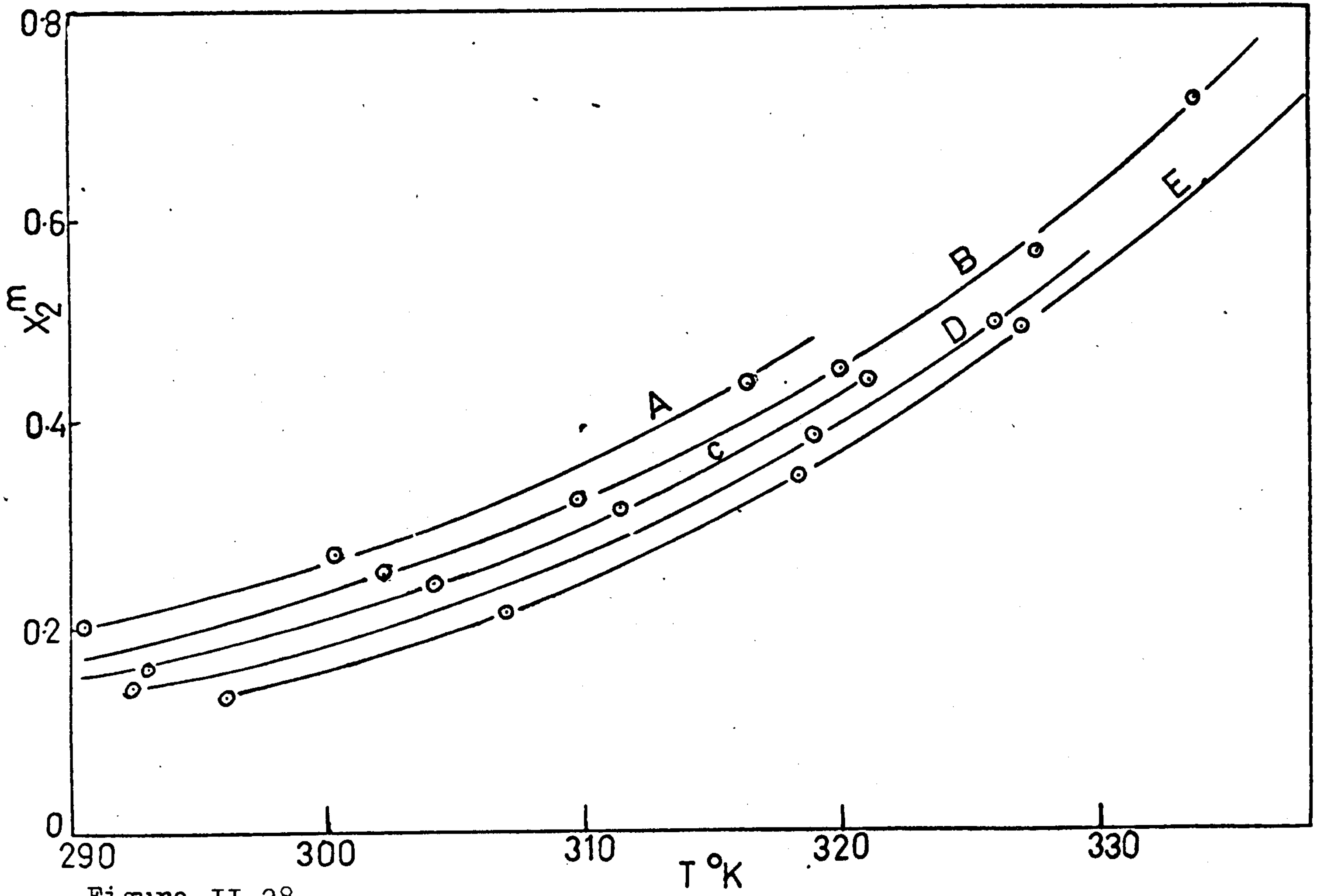


Figure II.28

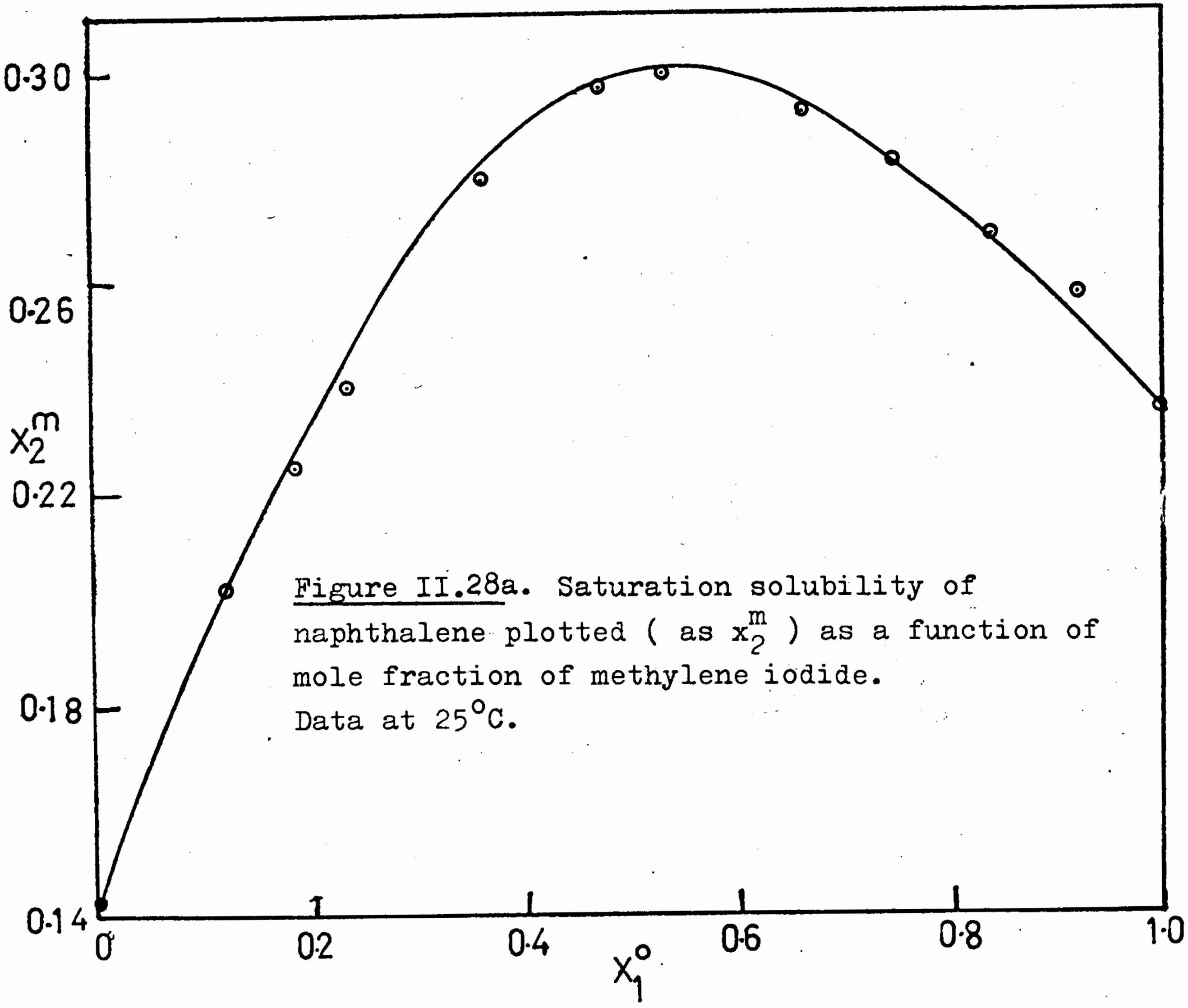


Figure II.28a. Saturation solubility of naphthalene plotted (as x_2^m) as a function of mole fraction of methylene iodide.
Data at 25°C.

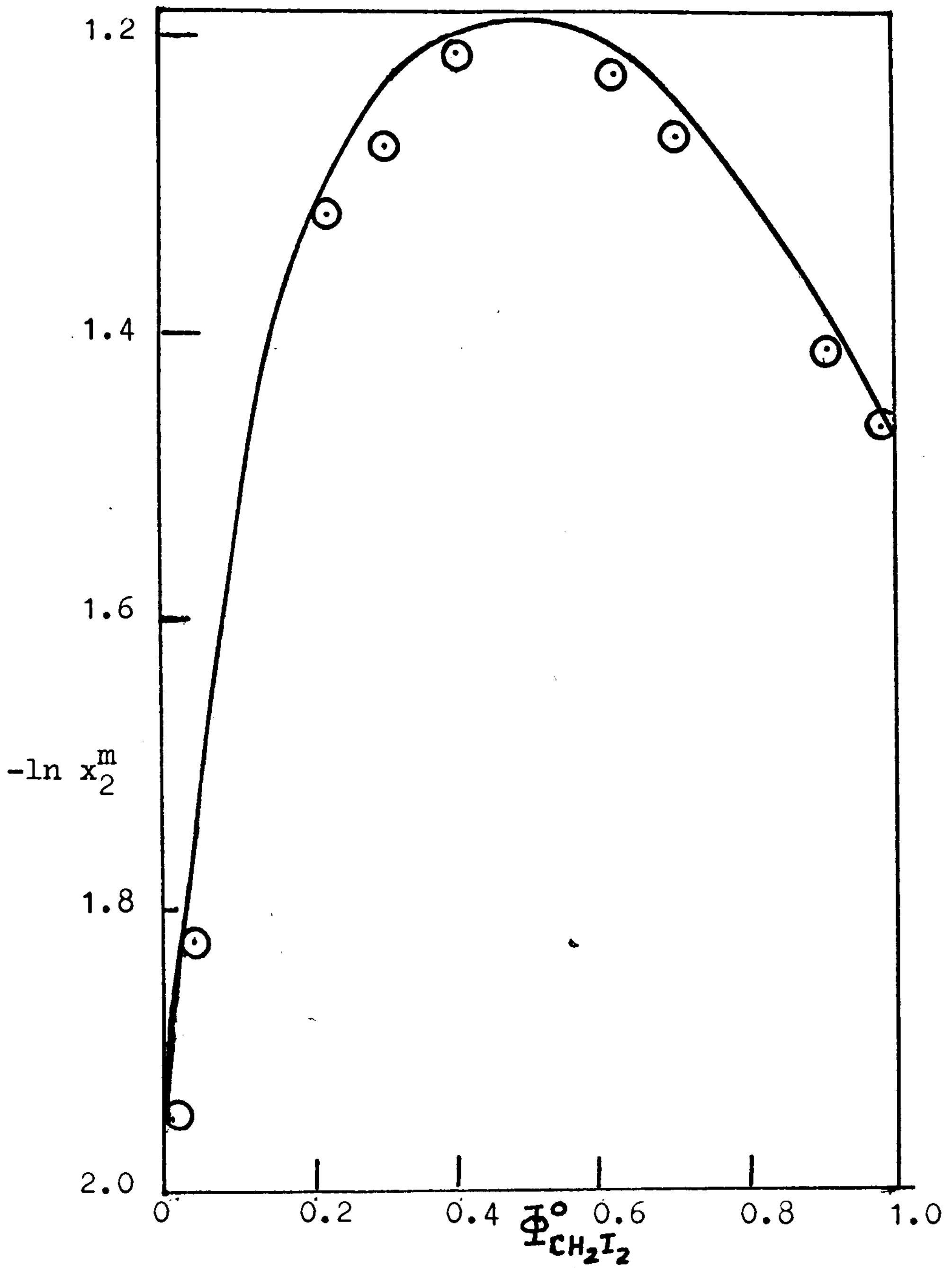


Figure II.29b. Saturation solubility of naphthalene plotted (as $-\ln x_2^m$) as a function of volume fraction of methylene iodide in solute-free methylene iodide - cyclohexane mixed solvent. Data at 25°C.

Figure II.30. Naphthalene in carbon tetrachloride - cyclohexane mixed solvent. Y (i.e. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$) plotted as a function of volume fraction of cyclohexane (○) and the effective volume fraction of cyclohexane (⊗). In this plotting it has been assumed that $\frac{\Phi_m}{\Phi_1(1,2)} \approx 1$. (see Table II.15 and Table II.9) Data at 25° C.

Figure II.30

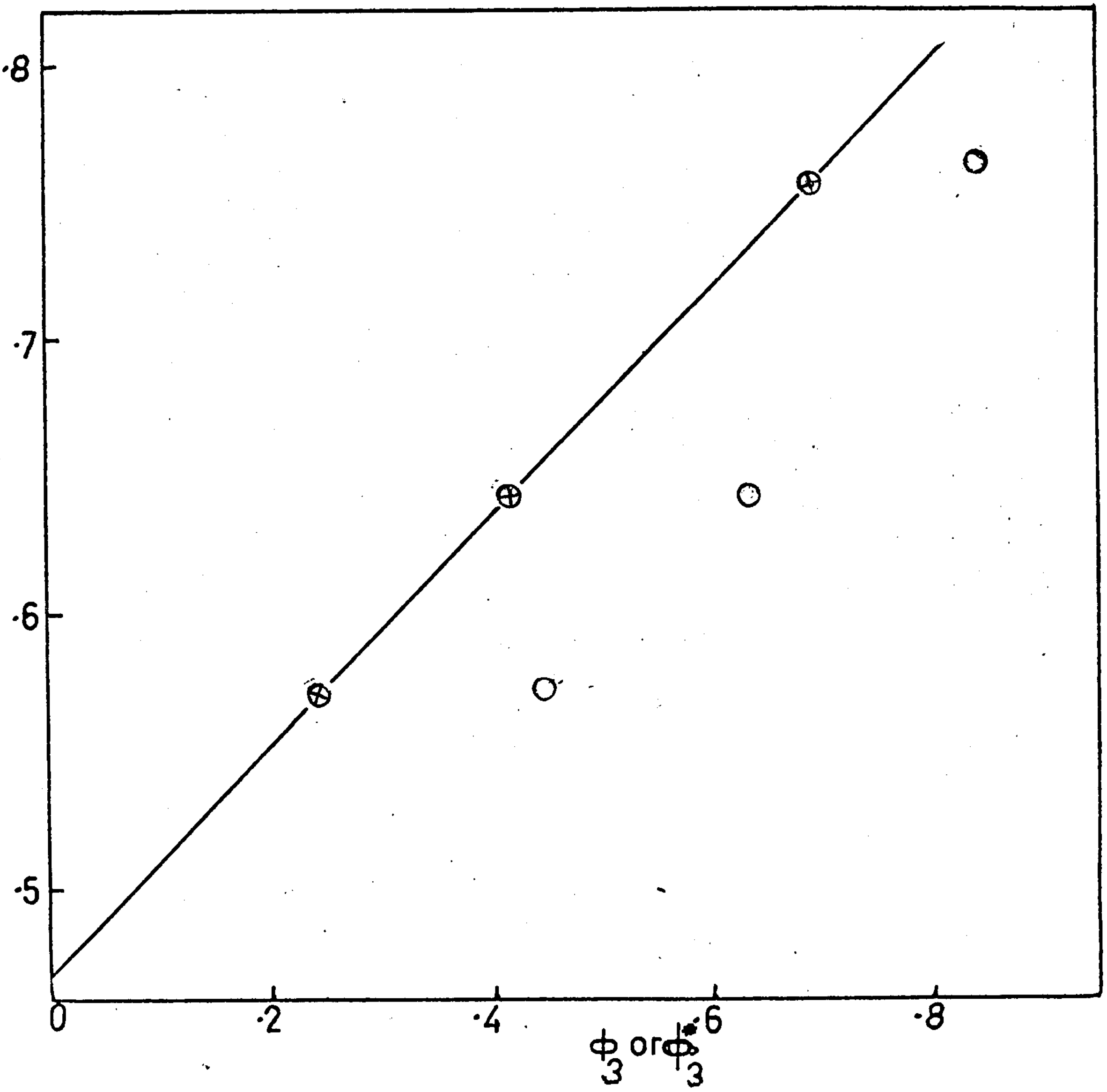


Figure II.31. Naphthalene in methylene iodide - cyclohexane mixed solvent. Y (i.e. ($\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}$) plotted as a function of volume fraction of cyclohexane (⊙) and effective volume fraction of cyclohexane (◫). In this plot it has been assumed that $\frac{\Phi_m}{\Phi_1(1,2)}$ and $\frac{\Phi_m}{\Phi_3(2,3)}$ are equal to unity. (see Table II.15 and Table II.10) All data at 25 ° C.

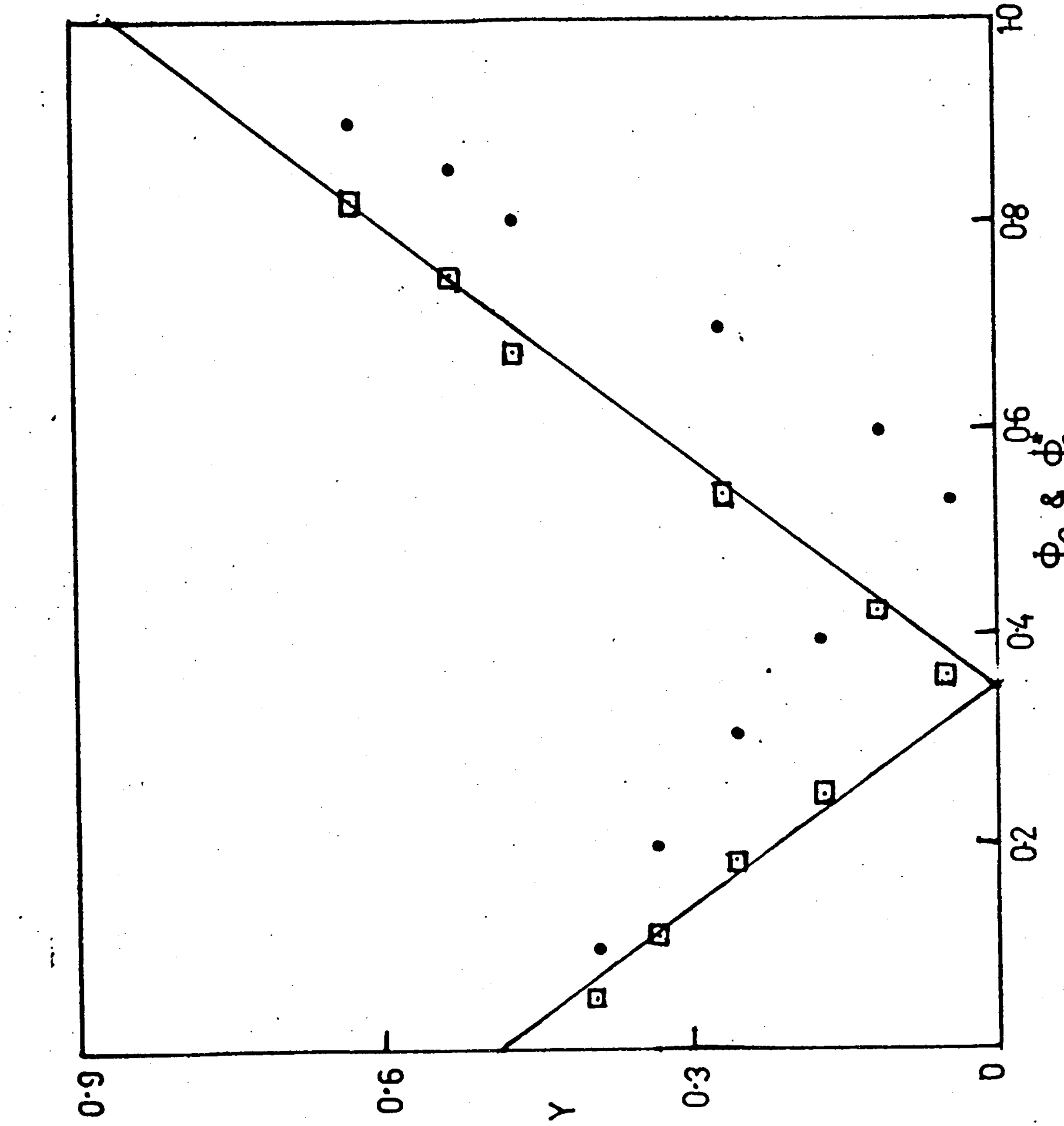


Figure II.31

Figure II.32. Naphthalene in carbon tetrachloride - cyclohexane mixed solvent. Y/Φ_m (i.e. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}/\Phi_m$) plotted as a function of volume fraction of cyclohexane (⊙) and as a function of "effective volume fraction" (⧉) of cyclohexane. Data at 25°C. (see Table II.13)

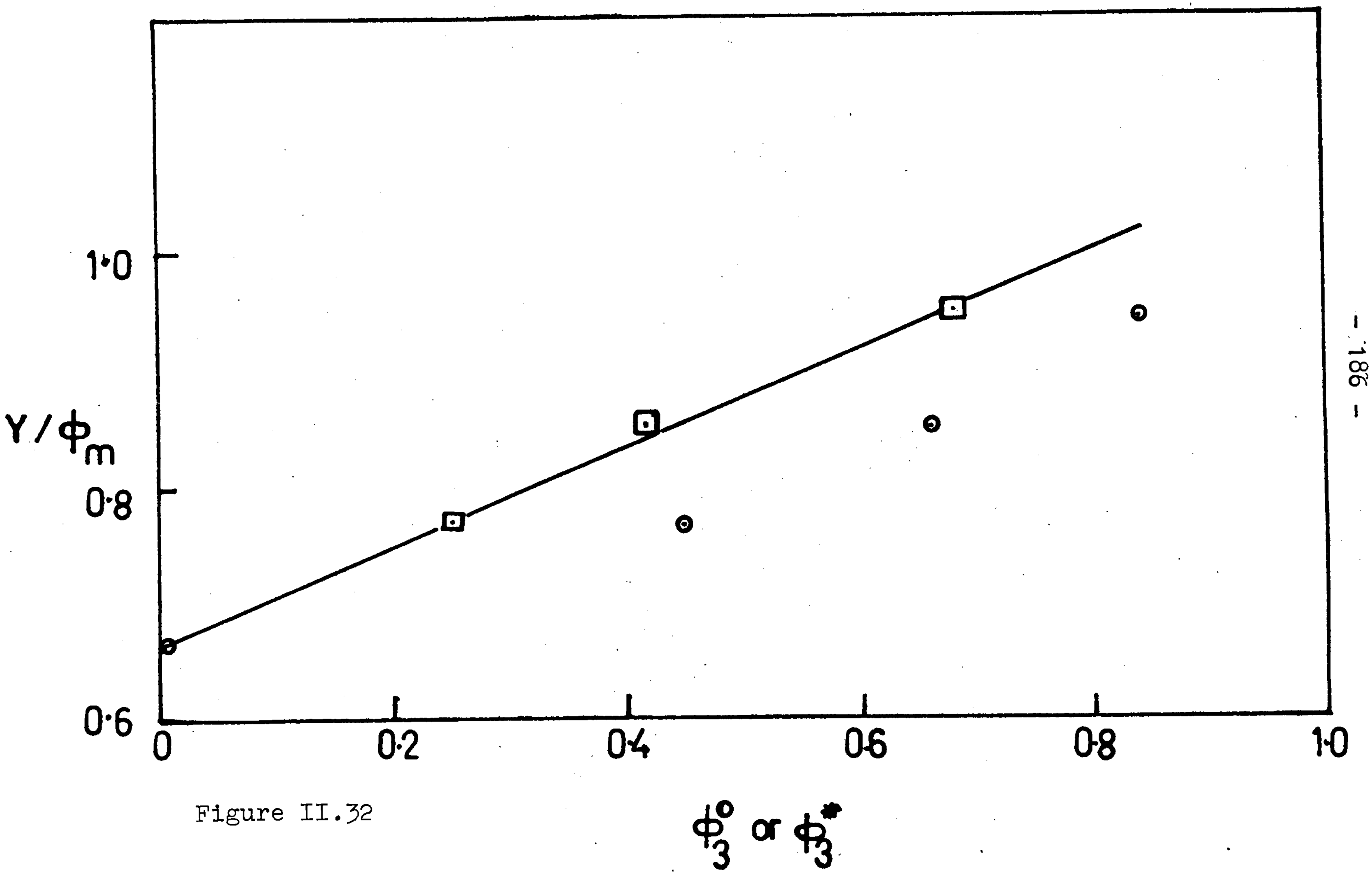
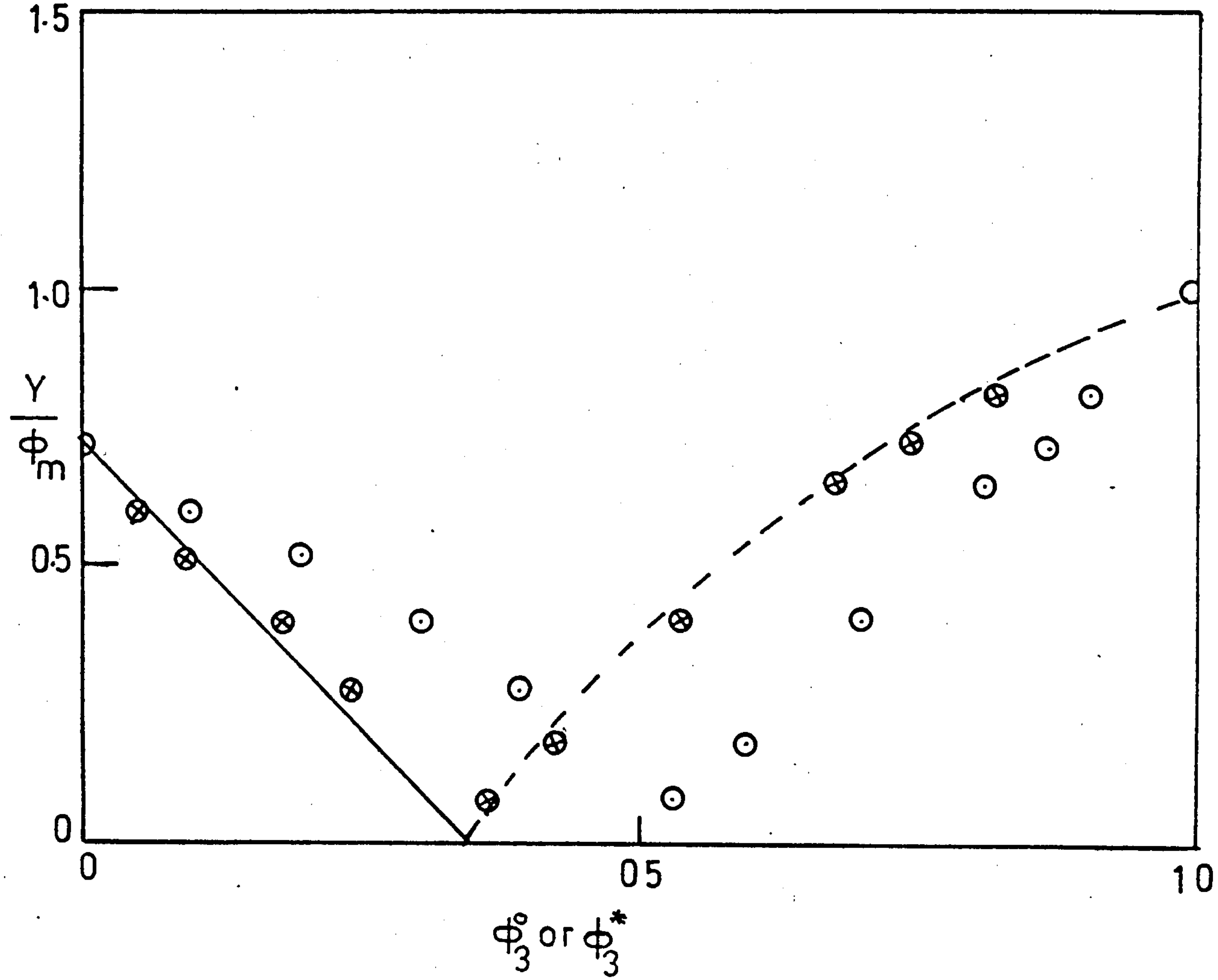


Figure II.32

Figure II.33. Naphthalene in methylene iodide - cyclohexane mixed solvent. Y/Φ_m (i.e. $(\ln a_2^i - \ln x_2^m)^{\frac{1}{2}}/\Phi_m$) plotted as a function of volume fraction of cyclohexane (○) and as a function of effective volume fraction of cyclohexane (⊗). (see Table II.15) All data at 25° C.

Figure II. 33.



Chapter - III

Calculation of Entropy of Solution from Scaled Particle Theory

The scaled particle theory of fluids is essentially an equilibrium theory concerned with the prediction of the bulk thermodynamic properties of fluids over the whole existence region of the fluid. The classical hard sphere consists of "identical" particles or molecules which are rigid spheres of diameter a , obeying classical mechanical laws. Two such molecules interact with one another only when they collide elastically. The importance of this model is due to the considerable mathematical simplification in the many-body problem resulting from its use, as well as its usefulness in describing the behaviour of real fluids under extreme conditions. Thus, at very high temperatures, when the average kinetic energy of the gas molecule is much greater than the minimum value of the intermolecular potential energy, the hard core (of diameter a) of this potential energy is important in determining the properties of the fluid. At very high density, on the other hand, the attractive part of a more realistic intermolecular potential can be thought of as a smooth average potential not greatly affecting the properties of the fluid.

The scaled particle theory was first developed by Reiss, Frisch and Lebowitz[96] in 1959 and is mainly concerned with hard spheres. Since then a number of papers and a couple of reviews have concerned themselves with various idealised systems such as hard spheres, hard discs and one dimensional systems, as well as real fluids, particularly with attempts to provide numerical results which can be compared with the experiments.

The scaled particle theory is a formal theory in the same sense as cluster theory, the radial distribution function, and the Percus-Yerick theory.[124] The scaled particle theory has been used to calculate heat of vaporization, surface tension, and heat capacities of real fluids.[97-103] Scaled particle theory can also be applied to fused salts.[104-106] Besides, scaled particle theory does not need any adjustable parameters if the hard core diameter of the molecule is known. For simple nonpolar liquids, the heat of vaporization can usually be used to calculate the hard sphere diameter. Hard sphere diameters calculated this way can be used to calculate other thermodynamic properties of real liquids and usually the calculated thermodynamic properties agree well with the experimental values when compared.

From the scaled particle theory Reiss et al.[96] obtained an expression for an equation of state for hard sphere fluids as follows:

$$P = \frac{\rho kT(1 + Y + Y^2)}{(1 - Y)^3} \tag{1}$$

where P is pressure, ρ is the number density $\frac{N}{V}$, T is temperature in absolute scale, k is Boltzmann's constant, and

$$Y = \frac{\pi a^3 \rho}{6}$$

An exactly similar equation for P (as in equation (1)) was obtained by E. Thele[108] and M. S. Wertheim[107] by simultaneous solution of the Percus-Yerik equation and the Ornstein-Zernike compressibility equation.[119] Besides, this equation is in remarkable agreement with the machine calculations of W. W. Wood and J. D. Jacobson,[120] and of B. J. Alder and T. E. Wainwright.[126] The virial development

$$P = \rho KT(1 + \sum_{n=1}^{\alpha} B_{n+1}\rho^n) \tag{2}$$

where the B_n's are the virial coefficients of equation (1) yields: (see H. L. Frisch in reference [100])

$$\frac{P}{\rho kT} = 1 + 4Y + 10Y^2 + 19Y^3 + 31Y^4 + \ldots \tag{3}$$

Equation (3) compares favourably with the exact virial series

$$\frac{P}{\rho kT} = 1 + 4Y + 10Y^2 + 18.36\ Y^3 + (28.3 \pm 1.3)Y^4 + \ldots \tag{4}$$

Comparing equation (3) with equation (4) one sees that the first three coefficients are exact in equation (3) but the fourth is in error by 3% while the fifth lies within 5% of the uncertainty[96,97]

Attempts to extend the scaled particle theory to real fluids in an effort to derive their equation of state has not met with the same success and this aspect of the theory is still under development. The most notable contribution in this field is the perturbation theory of Henderson and Barker[122-124,114,125] where they treated the soft part of the intermolecular potential of fluid molecules as a small perturbation to the hard sphere system.

Recently Lebowitz et al[112,113] obtained an expression for the equation of state for hard sphere mixtures:

$$\pi\beta P = 6\left\{\frac{\xi_0}{1-\xi_3}\right\} + 18\left\{\frac{\xi_1\xi_2}{(1-\xi_3)^2}\right\} + 18\left\{\frac{\xi_2^{\,3}}{(1-\xi_3)^3}\right\} \qquad (5)$$

ξ_ℓ's in equation (5) are defined as

$$\xi_\ell = \frac{1}{6}\,\pi\sum_{i=1}^{m} \rho_i(2R_i)^\ell \qquad (6)$$

where m is the number of components of the mixtures. R_i is the radius of the fluid particles of ith component.

The scaled particle theory as developed by Reiss and his coworkers has been used by different authors to calculate different thermodynamic properties of fluids and fluid mixtures. Pierotti[115-6] used the scaled particle theory for predicting the solubility, the heat of solution and the partial molar volume of simple gases in nonpolar solvents and in water. Yosim used the same theory to calculate the excess entropy of mixing of simple nonpolar liquids. The method used by Yosim[103] to calculate the excess entropy of mixing of two fluids was derived from the entropy of mixing of two rigid sphere fluids, each at the volume of the corresponding liquid component and the resultant mixture of the hard spheres at the volume of the mixture of two real liquids. Snider et al.[118] used Longuet-Higgins' and Widom's[117] model to calculate the excess thermodynamic functions of 10 equimolar mixtures of nonpolar liquids and found that the agreement between the calculated values and the experimental values was generally good. Longuet-Higgins' and Widom's model may be considered as an improvement of the theory developed by Reiss et al.[96] as this model has finite configurational internal energy but the effects of the configurational internal energy on the entropy change are expected to be either cancelled out or to be very small with respect to this assumption. We will use the scaled particle theory to calculate the partial molar entropy change of a solid solute dissolved in nonpolar solvents.

Method of Calculation of Partial Molal Entropy of Solution

As our interest lies in calculating the partial molal entropy change of a solid solute when dissolved in solution, i.e. $(\overline{S}_2 - S_2^s)$, we will devise a thermodynamic cycle to dissolve the solid solute in the solution. The thermodynamic cycle we will use in the following discussion consists of six steps. These steps can be described in the following manner:

Step I. Pure solid solute at room temperature is converted to supercooled liquid at that temperature. Unfortunately, we cannot use the scaled particle theory in calculating the entropy change involved in this step as it is well known that scaled particle theory can not be extended to the solid states and it does not describe correctly the melting process of solids (even in a simple case like the melting of solid argon.[107]). We decided, therefore, to use the experimental value to calculate the entropy change involved in this step. This can be calculated by the usual thermodynamic procedure. Let the entropy change involved in this step be denoted ΔS_2^I where the superscript refers to the step number, in this I because this entropy change refers to the entropy change involved due to Step I. Subscript 2 refers to the solute, our usual notation for solute.

Therefore, we see that ΔS_2^I is the entropy of fusion of the solute at room temperature. From usual thermodynamic relations we find

$$\begin{aligned}\Delta S_2^I &= n_2(\Delta S_{298}^f) \\ &= n_2\left(\Delta S_{mpt}^f - \Delta C_p^{s-\ell} \ln \frac{T_{mpt}}{298}\right) \qquad (7)\end{aligned}$$

where ΔS_{mpt}^f is the entropy of fusion at the melting point, T_{mpt} ; ΔS_{298}^f is the entropy of fusion at 298° K; $\Delta C_p^{s-\ell}$ is the difference of the heat capacities between solid and liquid solute; and n_2 is the number of moles of solid solute.

Besides the obvious problem of the nonapplicability of the scaled particle theory in describing the process of melting, there is another reason for introducing Step I. In most of the solid solubilities studies, the supercooled liquid of the solid solute extrapolated to the temperature at which the experiment was performed is the standard state for these studies and all the thermodynamic data for the solid solutes were collected with respect to this standard state.

Step II. The liquid solvent and the liquid solute created in Step I are separately "discharged" at constant volume to hard spheres.

Let the entropy change of this step be denoted by ΔS^{II} ;

$$\Delta S^{II} = -(n_1 \Delta S^{II}_{charg(1)} + n_2 \Delta S^{II}_{charg(2)}) \qquad (8)$$

where n's are the number of moles, ΔS_{charg} is the entropy change due to charging of the hard spheres to real liquids.

Step III. The hard sphere fluids produced in Step II are now vaporized at that temperature. If the vapor of the hard sphere gases at that temperature is assumed to be ideal such that $P^oV^o = RT$, then the entropy change of this step can be calculated from the scaled particle theory. Yosim obtained the entropy of vaporization of hard sphere fluids at the boiling point of the corresponding liquid as [103]

$$\Delta S^{Vap}_{bpt(i)} = n_i R \ln \frac{V^g_{bpt}}{(V^\ell_{bpt} - ca_i^3)} + \frac{3cRna_i^3(2V^\ell_{bpt} - ca_i^3)}{2(V^\ell_{bpt} - ca_i^3)} \qquad (9)$$

where V^ℓ_{bpt} is the volume of the liquid at the boiling point, C is $\frac{\pi N_o}{6}$ where N_o is Avogadro's number, a is the hard sphere diameter of the liquid, and V^g_{bpt} is the volume of the substance in the gas phase and the gas obeys the ideal gas law.

From the thermodynamic relationship, the entropy of vaporization at 298° K is given by

$$\Delta S_{Vap,298} = nR \ln \frac{V^g_{bpt(i)}}{(V^\ell_{bpt(i)} - ca_i^3)} + \frac{3cRna_i(2V^\ell_{bpt(i)} - ca_i)^3}{2(V^\ell_{bpt(i)} - ca_i)^3} - C_p^{\ell-g} \ln \frac{T_{Bpt}}{298} \qquad (10)$$

where T_B is the boiling point and $\Delta C_p^{\ell-g}$ is the difference of the heat capacities of liquid and vapor phase. In writing equation (10), we assumed that the $\Delta C_p^{\ell-g}$ is independent of the temperature.

The $\Delta C_p^{\ell-g}$ for liquids can also be calculated from the scaled particle theory of the fluids. The $\Delta C_p^{\ell-g}$ is given by[102]

$$\Delta C_p^{\ell-g} = -R + RT\alpha_\ell \frac{1 + Y_i + Y_i{}^2}{(1 - Y_i)^3} \tag{11}$$

where α_ℓ is the coefficient of thermal expansivity of the liquid, and

$$Y_i = \frac{ca_i^3}{V^\ell} \tag{12}$$

Therefore, combining equations (10) and (11),

$$\begin{aligned}
\Delta S^{III} = {} & n_1 R \ln \frac{V^g_{Bpt(1)}}{V^\ell_{Bpt(1)} - ca_1^3} + \frac{3cRn_1 a_1^3(2V^\ell_{Bpt(1)} - ca_1^3)}{2(V^\ell_{Bpt(1)} - ca_1^3)} \\
& - n_1 \Delta C^{\ell-g}_{p(1)} \ln \frac{T_{Bpt(1)}}{298} + n_2 R \ln \frac{V^g_{Bpt(2)}}{V^\ell_{Bpt(2)} - ca_2^3} \\
& + \frac{3cRn_2 a_2^3(2V^\ell_{Bpt(2)} - ca_2^3)}{2(V^\ell_{Bpt(2)} - ca_2^3)^2} - n_2 \Delta C_p^{\ell-g} \ln \frac{T_{Bpt(2)}}{298} \\
& - n_2 \Delta C^{\ell-g}_{p(2)} \ln \frac{T_{Bpt(2)}}{298}
\end{aligned} \tag{12}$$

The reason we used α_ℓ for the real liquid (i.e. the coefficient of the thermal expansivities of the liquid) and not a hard sphere liquid is due to the fact that we are calculating the heat of vaporization at the boiling point and as we are using the experimentally determined V_{Bpt} , we have to use α_ℓ to be consistent in out calculations.

Step IV. The ideal hard sphere gases produced in Step III are mixed at constant pressure. If we assume that the mixing is ideal then the entropy of this step is given by

$$\Delta S^{IV} = -n_1 R \ln x_1 - n_2 R \ln x_2 \tag{14}$$

where x's are the mole fractions.

Step V. The mixture of the hard spheres is compressed to the volume of the solution V_s^ℓ . The entropy of this step can be derived from Lebowitz's equation of state for a mixture of hard spheres and is given by (see Appendix AIII.1)

$$\begin{aligned}\Delta S^V = -R(n_1 + n_2)\Big\{ &\ln \frac{V^g_{s,298}}{V^\ell_{s,298} - c(n_1 a_1^3 + n_2 a_2^3)} \\ &- \tfrac{1}{2}\Big(c[3x_1^3 a_1^3 + x_1^2 x_2(6a_1^5 a_2 - 3a_1^4 a_2^4 + 6a_1^3 a_2) \\ &\quad + x_1 x_2^2(6a_1^3 a_2^3 - 3a_1^3 a_2^4 + 6a_1 a_2^5) + 3x^3 a_2^6] \\ &\quad - 6cV_s^\ell[x_1 a_1^3 + x_2 x_2(a_1 a_2^2 + a_1^2 a_2) + x_1 a_2^3] \\ &\quad \cdot [V^\ell_{s,298} - c(x_1 a_1^3 + x_2 a_2^3)]^{-2}\Big)\Big\}\end{aligned} \tag{15}$$

Step VI. The compressed mixtures of the rigid spheres are "recharged," i.e. the intermolecular attractive potential is brought back and the repulsive potential is changed to that of the solution. Then, the entropy change of this step is

$$\Delta S^{VI} = (n_1 + n_2)\Delta S^{VI}_{charg(1,2)}$$

Since we are interested in nonpolar liquids, it is reasonable to assume that the entropy change due to charging and discharging is very small and the difference between charging pure components and solution will be very small, or in other words we can assume

$$\Delta S^{II} - \Delta S^{IV} = -n_1\Delta S^{II}_{charg(1)} - n_2\Delta S^{II}_{charg(2)} - (n_1 + n_2)\Delta S^{VI}_{charg(1,2)} = 0 \qquad (16)$$

The excess entropy is defined as

$$\Delta S^E = \Delta S^m + \sum_{i=1}^{2} n_i R \ln x_i$$

where ΔS^m is the total entropy of mixing. Collecting all the entropy changes involved from Step I to Step VI and subtracting from then the ideal entropy of solution, one obtains the excess entropy of the mixing, ΔS^E, as

$$\Delta S^{E} = n_2 \Delta S^{I} + n_1 R \ln V^{g}_{Bpt(1)} + n_2 R \ln V^{g}_{Bpt(2)}$$

$$- n_1 R \ln (V^{\ell}_{Bpt(1)} - ca_1^3) - n_2 R \ln (V^{\ell}_{Bpt(2)} - ca_2^3)$$

$$+ \frac{3cRn_1 a_1^3 (2V^{\ell}_{Bpt(1)} - ca_1^3)}{2(V^{\ell}_{Bpt(1)} - ca_1^3)^2} - n_1 \Delta C^{\ell-g}_{p(1)} \ln \frac{T_{Bpt(1)}}{298}$$

$$+ \frac{3cRn_2 a_2^3 (2V^{\ell}_{Bpt(2)} - ca_2^3)}{2(V^{\ell}_{Bpt(2)} - ca_2^3)^2} - n_2 \Delta C^{\ell-g}_{p(1)} \ln \frac{T_{Bpt(2)}}{298}$$

$$- n_1 R \ln V^{g}_{s,298} - n_2 R \ln V^{g}_{s,298} + n_1 R \ln [V^{\ell}_{s,298} - c(n_1 a_1^3 + n_2 a_2^3)]$$

$$+ n_2 R \ln [V^{\ell}_{s,298} - c(n_1 a_1^3 + n_2 a_2^3)]$$

$$+ \frac{1}{2}(n_1 + n_2)\Big\{c[3x_1^3 a_1^3 + x_1^2 x_2 (6a_1^5 a_2 - 3a_1^4 a_2^2 + 6a_1^3 a_2^3)$$

$$+ x_1 x_2 (6a_1^3 a_2^3 - 3a_1^2 a_2^4 + 6a_1 a_2^5)] - 6cV^{\ell}_{s}[x_1^2 a_1^3 + x_1 a_2^3$$

$$+ x_2 x_1 (a_1 a_2^2 + a_1^2 a_2)]\Big\}[V^{\ell}_{s,298} - c(x_1 a_1^3 + x_2 a_2^3)]^{-2} \quad (17)$$

If the solution is dilute with respect to component 2, i.e. solute, then any term involving $x_1 x_2$ or any higher power of x_2 can be neglected and equation (17) simplifies to

$$\Delta S^{E} = n_2 \Delta S^{I} + n_1 R \ln V^{g}_{1,Bpt} + n_2 R \ln V^{g}_{2,Bpt}$$

$$- n_1 R \ln (V^{\ell}_{1,Bpt} - ca_1^3) - n_2 R \ln (V^{\ell}_{2,Bpt} - ca_2^3)$$

$$+ \frac{3n_1 cRa_1^3 (2V^{\ell}_{1,Bpt} - ca_1^3)}{2(V^{\ell}_{Bpt(1)} - ca_1^3)}$$

$$+ 3n_2 cRa_2^3 (2V^{\ell}_{Bpt(2)} - ca_2^3) - n_1 \Delta C^{\ell-s}_{p(1)} \ln \frac{T_{Bpt(1)}}{298}$$

$$- n_2 \Delta C_{p(2)}^{\ell-g} \ln \frac{T_{Bpt(2)}}{298} - (n_1 + n_2) R \ln V^{g}_{298(s)}$$

$$+ n_1 R \ln[\, V_s^{\ell} - c(n_1 a_1^3 + n_2 a_2^3) \,]$$

$$+ n_2 R \ln[\, V_s^{\ell} - c(n_1 a_1^3 + n_2 a_2^3) \,] \qquad (18)$$

Substituting $\overline{V}_s^{\ell} = n_1\overline{V}_1 + n_2\overline{V}_2$ where $\overline{V}$'s are the partial molal volume and then differentiating equation (18) with respect to n_2 and then converting the equation for 1 mole of mixture, i.e. $N_1 + N_2 = 1$, one obtains the excess partial molal entropy of component 2 as

$$\Delta\overline{S}_2^{E} = R \ln V^{g}_{Bpt(2)} - R \ln(V^{\ell}_{Bpt(2)} - ca_2^3) + \Delta\overline{S}^{I}$$

$$+ \frac{3cRa_2^3(2V^{\ell}_{Bpt(2)} - ca_2^3)}{(V^{\ell}_{Bpt(2)} - ca_2^3)^2} - \Delta C^{\ell-s}_{p(2)} \ln \frac{T_{Bpt}}{298}$$

$$- R \ln V_{298(s)} - x_1 R \frac{\overline{V}_2 - ca_2^3}{x_1\overline{V}_1 + x_2\overline{V}_2 - c(x_1a_1^3 + x_2a_2^3)}$$

$$+ x_2 R \frac{\overline{V}_2 - ca_1^3}{x_1\overline{V}_1 + x_2\overline{V}_2 - c(x_1a_1^3 + x_2a_2^3)}$$

$$+ R \ln[V_s^{\ell} - c(x_1a_1^3 + x_2a_2^3)] \qquad (19)$$

Equation (19) is further simplified for a very dilute solution as we are interested in a very dilute solution where x_2 is of the order of 10^{-3}.

For a very dilute solution, $\overline{V}_1$ or the partial molal volume of solvent in the solution can be taken as equal to V_1 or the molal volume of pure solvent at that temperature, and as dilute solution x_2 is very small, equation (19) becomes

$$\begin{aligned}\Delta\overline{S}_2^E = {} & \Delta\overline{S}^I + R\ \ln V^g_{Bpt(2)} - R\ \ln(V^\ell_{Bpt} - ca_2^3) \\ & + 3cRa_2^3(2V^\ell_{Bpt(2)} - ca_2^3)/(V^\ell_{Bpt(2)} - ca_2^3)^2 \\ & - \Delta C^{\ell-g}_{p(2)}\ \ln\frac{T_{Bpt(2)}}{298} - R\ \ln V^g_{298(s)} \\ & + R\,\frac{\overline{V}_2 - ca_1^3}{x_1V_1 + x_2V_2 - c(x_1a_1^3 + x_2a_2^3)} \\ & + R\ \ln[\,(x_1V_1 + x_2V_2) - c(x_1a_1^3 + x_2a_2^3)\,] \qquad (20)\end{aligned}$$

As we have assumed before, the vapor behaves as an ideal gas so that V^g or the volume in the gas phase can be calculated from the ideal gas law, i.e. $PV = RT$.

Equation (20) gives the entropy of solution at constant pressure. This equation was applied to calculate $\Delta\overline{S}_2^P$ or the partial molal entropy of solute at constant pressure for I_2, SnI_4, $Sn(C_6H_5)_4$ and $Sn(C_6F_5)_4$ in the following solvents: (i) CS_2, (ii) toluene, (iii) $CCl_2F.CF_2Cl$, (iv) CCl_4, (v) m-xylene, (vi) iso-octane, (vii) $C_2H_2Cl_2$.

For $Sn(C_6F_5)_4$ no experimental values for ΔS^I are known. However the difference between the experimental and theoretical ΔS_2^P values for $Sn(C_6F_5)_4$ in a range of solvents should be a constant value (i.e. the value of ΔS^I which is given by

$$(\Delta S_2^P)_{expt} - (\Delta S_2^P)_{theor} = \Delta S^I$$

The other solid solute which has been studied is tetra perfluorophenyl tin, and for this compound no literature value for boiling point is available. Also the value for entropy of fusion at room temperature is not known. For this solute we decided to calculate only $\Delta S_2^{IV} + \Delta S_2^{V}$ and subtract it from the experimental value of ΔS_2^{P}. This should give a value for $\Delta S_2^{I} + \Delta S_2^{III}$, which would be constant for a particular solute.

In Table III.2 all the calculated values for ΔS_2^{P} are compared with the experimental values.

In Table III.1 we give the values of hard sphere diameters used in this calculation.

Discussion

From the data presented in Table III.2, it can be seen that agreement between the calculated values and experimental values for I_2 and SnI_4 is extremely good. These are the only two solid solutes for which all the necessary data are available -- particularly heat of vaporization, entropy of fusion, $\Delta C_p^{\ell-s}$, i.e. the difference of heat capacities of solid and liquid state of the solute. For SnI_4, the entropy of fusion at 298° K was taken as 9.1 eu as calculated by Hildebrand et al. For iodine this value was calculated from the data given by Hildebrand et al. and found to be 8.4 eu. Hildebrand's Regular Solution theory (see Chapter I) deals with the entropy of mixing at constant volume which is related to the entropy of mixing at constant pressure (which we are interested in) by the equation

$$\Delta\overline{S}_2^V = \Delta\overline{S}_2^P - \left(\frac{\partial P}{\partial T}\right)_V \overline{V}_2^E \tag{21}$$

where ΔS_2^V is the partial molal entropy of solution at constant volume, ΔS_2^P is that at constant pressure, $\left(\frac{\partial P}{\partial T}\right)_V$ is the isochore of the solvent at constant volume, and $\overline{V}_2^E$ is the excess partial molal volume of the solute in solution.

It is clear that this method can be used to calculate ΔS_2^V because all other quantities in equation (15) are usually obtained from the experimental results. Or, if the scaled particle theory predicts ΔS_2^P correctly, then one is assured of obtaining a correct value for $\Delta\overline{S}_2^V$ as long as equation (21) is valid. In the case of iodine, it has been observed that when ΔS_2^V is plotted against $-R \ln x_2$ one obtains a straight line whose intercept is equal to 9.1 eu and slope is equal to 1.1 in comparison to the expected values 8.4 and 1.0 respectively. Or in other words, although the $\Delta\overline{S}_2^V$'s are nearly ideal for iodine as shown by J. Hildebrand et al., the excess entropy even at constant volume is not exactly zero. As mentioned earlier, we are not dealing with $\Delta\overline{S}_2^V$. In the case of iodine it is shown in Table IV.2 that the agreement between the exmixing can be applied to tetraphenyl tin - organic solvent systems. In Table III.2 we give the value of ΔS_2^I for $Sn(C_6H_5)_4$ calculated in this fashion in different organic solvents. Except for the toluene - $Sn(C_6H_5)_4$ system, $\Delta\overline{S}_2^I$ values determined in this fashion are reasonably self-consistent even though we assumed in Step IV that the entropy of mixing two ideal hard sphere gases is ideal.

The ability to predict such a large excess entropy in this case in an interesting feature of the entropy cycle we have used to calculate partial molal entropy of the solute because in this calculation the effect of the volume disparity between the solvent and solute does not need to be considered.

For $Sn(C_6F_5)_4$, as mentioned earlier, we calculated $\Delta\overline{S}_2^I + \Delta\overline{S}_2^{II}$ by subtracting $\Delta S^{III} + \Delta S_2^{IV} + \Delta S_2^V + \Delta S_2^{VI}$ from the experimental $\Delta\overline{S}_2^P$. The calculated values for $\Delta\overline{S}_2^I + \Delta\overline{S}_2^{II}$ for $Sn(C_6F_5)_4$ in different solvents are also given in Table III.2. As before, $\Delta\overline{S}_2^I + \Delta\overline{S}_2^{II}$ for a solute should be constant irrespective of the solvents. This is observed in the case of $Sn(C_6F_5)_4$ for different organic solvents as shown in Table III.2.

Considering that no allowance for volume difference on the entropy of mixing was made in this calculation, it is interesting to note that the entropy cycle we used here may be applied successfully in cases where the ratio of the solute-solvent molar volume is as large as five. Considering the success of applying this entropy cycle in predicting such a large excess entropy, it seems that for spherical molecules the large excess entropy of mixing may not be due to molar volume differences alone.

Going back to Table III.2 again, we can see that for tetraphenyl tin the ΔS_2^I calculated by the procedure described above is reasonably constant except for toluene, where the calculated excess entropy is much larger than the experimental one. We have no definite idea as to why the toluene - $SnPh_4$ system deviates to such a large extent. It has been suggested[129] that $SnPh_4$ forms a complex with benzene, although no such studies have been reported for the toluene - $SnPh_4$ system; it may be that $SnPh_4$ also forms a complex with toluene. In that case these calculations do not have any meaningful significance because they are based on the assumption that molecules interact according to the hard sphere potential and the "charging" and "discharging" processes have almost negligible effect on the entropy of the solution. This is not the case where more specific interactions are present.

For tetra perfluorophenyl tin the situation becomes more complicated. As mentioned earlier the entropy change for $\Delta S_{298}^f + \Delta S_2^{III}$ is not known. So we looked for a constant value of $\Delta S_{298}^f + \Delta S_2^{III}$ for $SnPf_4$ by the method described earlier. The calculated perimental $\Delta\overline{S}_2^P$ and the $\Delta\overline{S}_2^P$ calculated from the scaled particle theory are in good agreement, it is clear from equation (15) that $\Delta\overline{S}_2^V$'s have to be in good agreement, provided equation (15) is valid.

The difference between the method described here to calculate the entropy of the mixing and Regular Solution theory is that in this method we assumed that the entropy of mixing is ideal when two ideal hard sphere gases are mixed, whereas in Regular Solution theory it was assumed that the entropy of mixing is ideal when two liquids are mixed. As mentioned earlier, the two solid solutes which have been studied extensively in terms of the Regular Solution theory do seem to have a very small excess entropy.

But for tetraphenyl tin, the excess entropy of mixing is quite large and as shown by Vitoria and Walkley,[54] the Regular Solution theory breaks down for tetraphenyl tin - organic solvent systems due to the large excess entropy of mixing. We were unable to calculate the $\Delta\overline{S}_2^P$ for $Sn(C_6H_5)_4$ in different solvents due to the unavailability of necessary data to calculate the entropy of fusion for $Sn(C_6H_5)_4$ at 298° K, i.e. $\Delta\overline{S}_2^I$. But as $\Delta\overline{S}_2^I$ is constant for the solute irrespective of the solvents, we shall be able to calculate $\Delta\overline{S}_2^I$ by subtracting $(\Delta\overline{S}_2^{II} + \Delta\overline{S}_2^{III} + \Delta\overline{S}^{IV} + \Delta\overline{S}_2^V + \Delta\overline{S}_2^{VI})$ from the experimental $\Delta\overline{S}_2^P$ -- and this value for $\Delta\overline{S}_2^I$ should be a constant if this method of calculating entropy of values of $\Delta S^{f}_{298} + \Delta S^{III}_{2}$ come to be constant within a few per cent (which can be cosidered to be good). But as there is exact method by which ΔS^{f}_{298} can be seperated from $\Delta S^{f}_{298} + \Delta S^{III}_{2}$, this procedure is not very helpful in calculating the excess partial molal entropy of mixing of $Sn(C_6F_5)_4$ in organic solvent.

Conclusion

In this chapter we showed that the scaled particle theory can be used in calculating the partial molal entropy of mixing of a solute and we also showed that the calculated values of $\Delta\bar{S}^{P}_{2}$ are in good agreement with the experimental values. But as the major contributions in calculating $\Delta\bar{S}^{P}_{2}$ come from ΔS^{f}_{298} (the entropy of fusion at 289°K) and from ΔS^{IV}_{2} $(-R \ln x_2)$, a more critical test of the method of calculation will be the comparision of calculated and experimental values of excess partial molal entropies. For solids , we shall compare the calculated and the experimental values of $[\Delta\bar{S}^{P}_{2}]_{excess}$ where $[\Delta\bar{S}^{P}_{2}]_{excess}$ is define as $\Delta\bar{S}^{P}_{2} + R \ln x_2$. We subtracted ΔS^{f}_{298} from $[\Delta\bar{S}^{P}_{2}]_{excess}$ because ΔS^{I}_{298} cannot be calculated from the scaled particle theory and moreover its contribution to $\Delta\bar{S}^{P}_{2}$ is quite large (approximately 8 eu.). In table III.3, we give both calculated and experimental values for $[\bar{S}_2^P]_{excess} - S^f_{298}$ for I_2 and SnI_4. It can be seen from Table III.3 that the calculated values are not widely different from the experimental values. Within the limits of the assumption of a hard sphere interaction potential and the uncertainty involved in calculating hard sphere diameters[115], the results can be considered to be good. These results could probably be improved by using a more realistic interaction potential. Until a rigorous method is developed using the scaled particle theory approach for a realistic interacting potential allowing the equation state to be formulated, no real improvement is possible.[118]

After completion of this work, a paper was published by Benson et al[126], where they used the perturbation theory as developed by Barker and Henderson[29] to calculate the heat of mixing and the entropy of mixing for nonelectrolyte solutions. They showed that the perturbation of hard sphere potential does not affect the entropy of mixing, i.e. the entropy of mixing of two nonelectrolyte liquids in absence of any specific interactions is equal to the entropy of two hard sphere fluids -- a conclusion similar to our assumption that the entropy change during the "charging" and "discharging" processes cancel out each other.

Table III.1

Hard sphere diameters of different solvents and solutes:

(see Appendix AIV.1 for the methods of calculation)

	$a \times 10^{-8}$ values used in this calculation	$a_{\Delta H_V}$ $\times 10^{-8}$ cm	a_α $\times 10^{-8}$ cm	a_β $\times 10^{-8}$ cm
I_2	4.61	4.61		-
SnI_4	5.34	5.34		-
$Sn(C_6H_5)_4$	9.039	-	9.039	-
$Sn(C_6F_5)_4$	9.37	-	9.37	
C_6H_6	5.089	5.089	-	4.99
$c\text{-}C_6H_{12}$	5.45	5.45	-	5.37
CCl_4	5.23	5.23		5.14
$CCl_2F.CF_2Cl$	5.55	5.55		5.47
$C_2H_4Cl_2$	4.89	4.89		4.83
$i\text{-}C_8H_{18}$	6.295	6.295		6.23
CH_2Cl_2	4.48	4.48		4.31
toluene	5.46	5.46		5.42
m-xylene	5.77	5.77		5.75
CS_2	4.42	4.42		4.33

($a_{\Delta V}$'s are the hard sphere diameters calculated from the heat of vaporization data by Snider-Harrington's equation; a_α are the hard sphere diameters calculated from thermal expansivities data; a_β 's are the hard sphere diameters calculated from the coefficient of isothermal compressibility data)

Table III.2

ΔS_2^P for different nonpolar binary mixtures:

System	ΔS_2^P(calc'd)	ΔS_2^P(exp)
c-C_6H_{12} - I_2	22.28	22.2[110]
CCl_4 - I_2	21.2	21.9[110]
$CCl_2F.CF_2Cl$ - I_2	24.99	24.4[110]
CS_2 - I_2	18.09	18.8[110]
i-octane - I_2	23.45	23.3[110]
CCl_4 - SnI_4	18.85	19.17[52]
toluene - SnI_4	18.4	17.4[52]
$CCl_2F.CF_2Cl$ - SnI_4	24.77	25.4[52]
c-C_6H_{12} - $SnPh_4$	ΔS^f_{298} + 23.07	32.87[54] (i.e. S^f_{298} = 9.8)
CCl_4 - $SnPh_4$	" + 19.59	26.77[54] (S^f_{298} = 7.2)
toluene - $SnPh_4$	" + 19.45	16.48[54]
$CCl_2F.CF_2Cl$ - $SnPh_4$	" + 25.0	33.27[54] (S^f_{298} = 8.2)
CCl_4 - $SnPf_4$	$\Delta S^I+\Delta S^{III}$ + 4.04	28.38 ($\Delta S^I+\Delta S^{III}$ = 24.34)
c-C_6H_{12} - $SnPf_4$	" + " + 9.31	33.41 ($\Delta S^I+\Delta S^{III}$ = 24.10)
toluene - $SnPf_4$	" + " + 5.55	30.22 ($\Delta S^I+\Delta S^{III}$ = 24.65)
isooctane - $SnPf_4$	" + " + 5.8	29.0 ($\Delta S^I+\Delta S^{III}$ = 23.2)

Table - III.3

A comparision of excess partial molal entropy of solution for solid solue calculated by means of equation-(20) of chapter III with those determined experimntally.

System	$-R \ln x_2$	$[\Delta \bar{S}_2^P]_{excess}$ $- \Delta S_I^{298}$ (calc'd)	$[\Delta \bar{S}_2^P]_{excess}$ $- \Delta S_I^{298}$ (experimental)
I_2 - CCl_4	8.46[110]	4.34	5.04[110]
I_2 - c-C_6H_{12}	9.38	4.50	4.42[110]
I_2 - CCl_2FCClF_2	10.76[110]	5.79	5.24[110]
I_2 - CS_2	5.74[110]	3.95	4.66[110]
I_2 - isooctane	10.19[110]	4.71	4.86[110]
SnI_4- CCl_4	8.50 [52]	1.35	1.67[52]
SnI_4- toluene	7.33 [52]	1.97	0.97[52]
SnI_4- CCl_2FCClF_2	13.25[52]	2.42	3.05[52]

Table III.4

Saturation solubility of $Sn(C_6F_5)_4$ at different temperature.

Solvent	T^oK	x_2 $x10^{-4}$	$-R \ln x_2$
CCl_4	308	66.13	
	298	46.63	10.6628
	293	39.23	
$c-C_6H_{12}$	308	8.18	
	298	4.067	15.5082
	293	3.22	
toluene	308	81.0	
	298	47.57	10.6234
	293	40.36	
isooctane	308	17.63	
	298	11.55	13.4348
	293	9.322	

Table III.5

Values of $\overline{V}_2$ and $\Delta\,\overline{S}_2^P$ for $Sn(C_6F_5)_4$ - organic solvent systems:

Solvent	$\overline{V}_2$ in cc.mole^{-1}	$\Delta\,\overline{S}_2^P$
CCl_4	-	28.38
c-C_6H_{12}	408.5	33.41
toluene		30.22
isooctane	415.5	29.0

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Appendix AI.1

Important Thermodynamic Relations

$C_V \equiv$ heat capacity at constant volume

$$= \left(\frac{\partial E}{\partial T}\right)_V \qquad \text{(AI.1.1)}$$

$C_p \equiv$ heat capacity at constant pressure

$$= \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{(AI.1.2)}$$

$\alpha \equiv$ coefficient of thermal expansion

$$= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(AI.1.3)}$$

$\beta \equiv$ coefficient of isothermal compressibility

$$= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{(AI.1.4)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha}{\beta} \qquad \text{(AI.1.5)}$$

We also used the term "fugacity" designated by f. The fugacity in two states A and B is related to the molal free energy in these states by the equation

$$F_B - F_A = RT \ln \frac{f_B}{f_A} \qquad \text{(AI.1.6)}$$

A summary of relations between thermodynamic functions is given in Table AI.1.1.

Table AI.1.1

A Summary of Relations between Thermodynamic Functions.

X=	F	H	S	E	A
$\left(\frac{\partial X}{\partial T}\right)_V =$	$V\left(\frac{\partial P}{\partial T}\right)_V - S$	$C_v + V\left(\frac{\partial P}{\partial T}\right)_V$	C_v / T	$C_v = C_p - T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$	$-S = \frac{A-E}{T}$
$\left(\frac{\partial X}{\partial T}\right)_P =$	$-S = \frac{F-H}{T}$	$C_p = C_v + T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$	C_p / T	$C_p / T\left(\frac{\partial V}{\partial T}\right)_P$	$-P\left(\frac{\partial V}{\partial T}\right)_P - S$
$\left(\frac{\partial X}{\partial V}\right)_T =$	$V / \left(\frac{\partial V}{\partial P}\right)_T = -1/\beta$	$T\left(\frac{\partial P}{\partial T}\right)_V + V / \left(\frac{\partial V}{\partial P}\right)_T$	$\left(\frac{\partial P}{\partial T}\right)_V$	$T\left(\frac{\partial P}{\partial T}\right)_V - P$	$-P$
$\left(\frac{\partial X}{\partial P}\right)_T =$	V	$V - T\left(\frac{\partial V}{\partial T}\right)_P$	$-\left(\frac{\partial V}{\partial T}\right)_P$	$-T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$	$-P\left(\frac{\partial V}{\partial P}\right)_T$
$\left(\frac{\partial X}{\partial P}\right)_V =$	$V - S / \left(\frac{\partial P}{\partial T}\right)_V$	$V + C_v / \left(\frac{\partial P}{\partial T}\right)_V$	$C_v / T\left(\frac{\partial P}{\partial T}\right)_V$	$C_v / \left(\frac{\partial P}{\partial T}\right)_V$	$-S / \left(\frac{\partial P}{\partial T}\right)_V$
$\left(\frac{\partial X}{\partial V}\right)_P =$	$-S / \left(\frac{\partial V}{\partial T}\right)_P$	$C_p / \left(\frac{\partial V}{\partial T}\right)_P$	$C_p / T\left(\frac{\partial V}{\partial T}\right)_P$	$C_p / \left(\frac{\partial V}{\partial T}\right)_P - P$	$\frac{-S}{\left(\frac{\partial V}{\partial T}\right)_P} - P$

Activity and Choice of Standard State

The other important thermodynamic quantity we have used is the activity, designated as a. The activity a of a substance in a particular solution is the ratio of its fugacity in that solution to its fugacity in some arbitrarily chosen standard state which in this theory is always pure liquid. For standard state $a^o = 1$ while in any other state it is given by .

$$RT \ln a = \mu - \mu^o = \overline{F} - \overline{F}^o$$

$$= RT \ln (f / f^o) \qquad (AI.1.7)$$

where superscript o denotes standard state and μ is the chemical potential in any given state.

Any state can be chosen as the standard state. Thus for aqueous solution electrolytes the infinite dilute solution of the electrolyte is usually selected as standard state. But in this work, only the pure liquid will be considered as the standard state. For solid, the standard state is the pure hypothetical liquid supercooled below the melting point. This standard state was accepted by Hildebrand[24]

The advantage of this convention is that it yields equations of same form for all components and avoids a distinction between solvent and solute. To distinguish the solute, Hildebrand[24] used subscript 2. In this work, some notations will be used to distinguish solute in a solution -- irrespective of whether it is a binary or ternary mixture.

Activity of Solids

As solid solute is used in all experiments mentioned in this work, and as the pure liquid has been taken as the standard state, one needs to know the activity of a solid substance which is given by

$$a^S = \frac{f^S}{f^O} \qquad \text{(AI.1.8)}$$

In dealing with the solubility of solids, sometimes it is important to know its activity referred to the hypothetical liquid supercooled below the melting point. The thermodynamic relationship

$$\left(\frac{\partial \ln a^S}{\partial T}\right)_P = \left\{\frac{\partial (F^S - F^O)/RT}{\partial T}\right\}_P = \frac{H^O - H^S}{RT^2} = \frac{\Delta H^F}{RT^2} \qquad \text{(AI.1.9)}$$

(where ΔH^F is the heat of fusion at that temperature T) can be integrated from temperature T to the melting point T_m under the assumption that the heat of fusion is constant, giving

$$\ln a^S = - \frac{\Delta H^F}{R} \frac{T_m - T}{TT_m} \qquad \text{(AI.1.10)}$$

where the difference between the molal heat capacities of liquid and solid are known then

$$C_p^{\ell} - C_p^{s} = \Delta C_p \quad \text{amd} \quad \Delta H^F = \Delta H_m^F - \Delta C_p(T_m - T) \qquad \text{(AI.1.11)}$$

where ΔH_m^F is the heat of fusion of the melting point;

C_p^{ℓ} is the heat capacity of liquid;

C_p^{s} is the heat capacity of the solid.

Substitution of equation (AI.1.11) in equation (AI.1.9) and integration of equation (90) yields

$$\ln a^s = \frac{-\Delta H_m^F}{R}\,\frac{T_m - T}{T_m T} + \frac{\Delta C_p}{R}\,\frac{T_m - T}{T} - \frac{\Delta C_p}{R}\ln\frac{T_m}{T} \qquad \text{(AI.1.12)}$$

Equation (AI.1.12) reduces to equation (AI.1.11) when ΔC_p is zero, or in other words, the heat of fusion is constant, the assumption which has been invoked in deriving equation (AI.1.10).

Again rewriting equation (AI.1.10), one obtains

$$\ln a^s = -\frac{\Delta H^F}{R}\left\{\frac{1}{T} - \frac{1}{T_m}\right\}$$

or it ΔC_p is zero, then plotting of $\ln a^s$ versus $1/T$ should give a straight line.

However, if ΔC_p is not zero and for other purpose which will be explained later, it is advantageous to plot $\log a^s$ (or $\log x_2$) versus $\log T$. The linearity of such a curve can be tested in the following manner:

The equation (AI.1.10) is rewritten as

$$\left(\frac{\partial \ln a^{s}}{\partial \ln T}\right)_{P} = \frac{\Delta H^{F}}{RT} \qquad \text{(AI.1.13)}$$

Then taking the second derivative with respect to T one obtains

$$\left\{\frac{\partial^{2} \ln a^{s}}{(\partial \ln T)^{2}}\right\}_{P} = T\left\{\frac{\partial}{\partial T}\left(\frac{\Delta H^{F}}{RT}\right)\right\}_{P} = \frac{\Delta C_{p}}{R} - \frac{\Delta H^{F}}{RT}. \qquad \text{(AI.1.14)}$$

At the melting point, T_m , $\Delta H^{F}_{m} = T\Delta S^{F}_{m}$, so the second derivative would be zero (and the curve straight, at least at this point) if ΔS^{F}_{m} is equal to ΔC_p . Table AI.1.2 compares ΔC_p and ΔS^{F}_{m} for a group of solid solutes. The ratio of ΔC_p to ΔS^{F}_{m} ranges from 0.4 to 2.1, which does not support the assumption $\Delta C_p = \Delta S^{F}_{m}$, but certainly this assumption is better than assuming $\Delta C_p = 0$. So assuming

$$\Delta H^{F} \approx T\Delta S^{F}_{m} \approx T\Delta C_{p}$$

$$\text{or} \quad \left(\frac{\partial \ln a^{s}}{\partial \ln T}\right) \approx \frac{\Delta H^{F}_{m}}{RT_{m}} = \frac{\Delta S^{F}_{m}}{R} \quad \text{and} \quad \ln a^{s} \approx \frac{\Delta S^{F}_{m}}{R} \ln\frac{T}{T_{m}} \qquad \text{(AI.1.15)}$$

Table AI.1.2

Thermodynamic Functions for Fusion[24]

Substance	ΔS_m^F (cal/ deg)	ΔC_p (cal/ deg)	$\Delta C_p / \Delta S_m^F$
H_2	2.0	1.9	0.95
A	3.35	2.16	0.65
I_2	9.67	3.9	0.40
S_8	0.75	1.6	2.1
P_4	0.47	0.5	1.0
SnI_4	10.73	5.7	0.53
S_2	9.63	5.6	0.59
CCl_4	2.4	1.1	0.5

Consequently, log T instead of $\frac{1}{T}$ was used by Hildebrand et al. for graphs but the a^s is corrected if ΔC_p is known. In this derivation, it has been assumed that ΔC_p is constant which is not an exact condition and thus even if ΔC_p is known, the values for a_2^s are subjected to a certain degree of uncertainty particularly at a temperature far below the melting point. But it has been observed that a plot of $\log x_2$ versus log T gives straight lines in the region $x_2 < 0.1$ whereas $\log x_2$ versus $\frac{1}{T}$ curved lines throughout.[24]

Table AI.1.2

Thermodynamic Functions for Fusion[24]

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Measures of Composition

The composition of a solution can be expressed in a variety of ways, e.g.

(1) concentration in grams or moles per unit volume;

(2) the ratio of the number of moles of one component of a binary solution to the number of moles of the second component, i.e. $\frac{n_1}{n_2}$;

(3) mole fraction, which is the most extensively used unit of expressing the solubility of nonelectrolytes in solution. The mole fraction x_i of any component i in solution is defined as

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots + n_i} \qquad \text{(AI.1.16)}$$

evidently $x_1 + x_2 + \ldots + x_i = 1$ (AI.1.17)

or in the case of binary solution,

$$x_1 + x_2 = 1$$

and $dx_1 = -dx_2$ (AI.1.18)

(4) volume fraction Φ . The Φ_i , volume fraction of any component, is given by

$$\Phi_i = \frac{V_i}{V_1 + V_2 + \ldots + V_i} \qquad \text{(AI.1.19)}$$

As mentioned earlier, the volume of a solution is not equal to the sum of the volumes of its components but it is the fraction sum of its partial molar volumes. Thus

$$\Phi_i = \frac{n_i\overline{V}_i}{n_1\overline{V}_1 + n_2\overline{V}_2 + \dots + n_i\overline{V}_i}$$

$$= \frac{x_i\overline{V}_i}{x_1\overline{V}_1 + x_2\overline{V}_2 + \dots + x_i\overline{V}_i} \qquad \text{(AI.1.20)}$$

If one assumes that volume change due to mixing is small, the volume fraction Φ_i of the ith component is given by

$$\Phi_i = \frac{x_i V_i^o}{x_1 V_1^o + x_2 V_2^o + \dots + x_i V_i^o} \qquad \text{(AI.1.21)}$$

where V_i^o is the molar volume of pure liquid components.

Throughout this work volume fraction as defined by equation (AI.1.21) will be used instead of the volume fraction defined in terms of partial molal volumes as in equation (AI.1.20). The advantage of using the volume fraction as the measure of composition of a mixture is that the unit of volume fraction takes care of the difference in molar volumes of different components.

Since the different liquids may have different coefficients of thermal expansion, the volume fraction will be slightly dependent on the temperature, but this dependence will be neglected in this work because the temperature range used in this work is very small.

Appendix AI.2

Repulsive Forces

As mentioned earlier, the intermolecular potential may be written as

$$U(r) = j/r^n - k/r^6 \tag{AI.2.1}$$

It is well known that potential energy of a molecular pair passes through a minimum at which $\frac{dU}{dr} = 0$. This condition may be used to define a distance r_o and a minimum (negative) energy ε_o . Differentiation of equation (AI,2,1) with respect to r gives

$$\frac{dU}{dr} = -\frac{nj}{r^{n+1}} + \frac{6k}{r^7} \tag{AI.2.2}$$

If one sets the derivative equal to zero, the resulting equations for r_o and ε_o are

$$r_o^{n-6} = \frac{nj}{6k} \tag{AI.2.3}$$

$$\varepsilon_o = \frac{j}{r_o^{\;n}} - \frac{k}{r_o^{-6}} = (n-6)\left\{\frac{6^6k^n}{n^nj^6}\right\}^{\frac{1}{n-6}} \tag{AI.2.4}$$

which is the equation used in the text for ε_o .

Appendix AII.1

Derivation of Excess Volume of Mixing, $\Delta V_2^{E,M}$

We defined

$$\Delta_V^i = \frac{\overline{V}_2^i - V_2^o}{V_2^o}$$

$$= n_i \beta_i (\delta_2 - \delta_i)^2 \qquad \text{(AII.1.1)}$$

Similarly,

$$\Delta_V^M = \frac{\overline{V}_2^m - V_2^o}{V_2^o}$$

$$= n_m \beta_m (\delta_2 - \delta_m)^2 \qquad \text{(AII.1.2)}$$

or

$$V_2^o \Delta_V^M = V_2^o n_m \beta_m (\delta_2 - \delta_m)^2$$

$$= \overline{V}_2^m - V_2^o \qquad \text{(AII.1.3)}$$

or

$$V_2^m = V_2^o + V_2^o \Delta_V^M$$

$$= V_2^o + V_2^o n_m \beta_m (\delta_2 - \delta_m)^2 \qquad \text{(AII.1.4)}$$

Again if we write a term $\overline{V}_2^{M,1,3}$ such that

$$\overline{V}_2^{M,1,3} = \Phi_1 \overline{V}_2^1 + \Phi_3 \overline{V}_2^3$$

$$= \Phi_1 \overline{V}_2^1 + \Phi_3 \overline{V}_2^3 + V_2^o(\Phi_1 \Delta_V^1 + \Phi_3 \Delta_V^3)$$

$$= V_2^o + V_2^o(\Phi_1 \Delta_V^1 + \Phi_3 \Delta_V^3) \qquad \text{(AII.1.5)}$$

Or from (AII.1.5),

$$\begin{aligned}\overline{V}_2^{M,1,3} - V_2^o &= V_2^o(\Phi_1\Delta_V^1 + \Phi_3\Delta_V^3)\\ &= V_2^o[n_1\beta_1(\delta_2 - \delta_1)^2\Phi_1 + n_3\beta_3(\delta_2 - \delta_3)^2\Phi_3]\\ &= V_2^o[(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_2^{\,2}\\ &\quad - 2\delta_2(\Phi_1 n_1\beta_1\delta_1 + \Phi_3 n_3\beta_3\delta_3)\\ &\quad + (\Phi_1 n_1\beta_1\delta_1^{\,2} + \Phi_3 n_3\beta_3\delta_3^{\,2})] \qquad \text{(AII.1.6)}\end{aligned}$$

Similarly from the equation (AII.1.4),

$$\begin{aligned}\overline{V}_2^M - V_2^o = V_2^o(n_m\beta_m\delta_2^{\,2} - 2\delta_2 n_m\beta_m\delta_m\\ + n_m\beta_m\delta_m^{\,2}) \qquad \text{(AII.1.7)}\end{aligned}$$

Again we define $\Delta\overline{V}_2^{E,M}$ i.e. the excess term in the text as

$$\begin{aligned}\overline{V}_2^{E,M} &= \overline{V}_2^{M,1,3} - \overline{V}_2^M\\ &= -V_2^o[\Delta_V^M - (\Phi_1\Delta_V^1 + \Phi_3\Delta_V^3 \qquad \text{(AII.1.8)}\end{aligned}$$

Denoting $\Phi_1\Delta_V^1 + \Phi_3\Delta_V^3 = \Delta_V^{M,1,3}$ we obtain equation (56) in the text. Substituting equation (AII.1.6) and (AII.1.7) in equation (AII.1.8) we obtain

$$\begin{aligned}\Delta\overline{V}_2^{E,M} = V_2^o[&(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_2^{\,2}\\ &- 2\delta_2(\Phi_1 n_1\beta_1\delta_1 + \Phi_3 n_3\beta_3\delta_3) - n_m\beta_m\delta_2^{\,2}\\ &+ (\Phi_1 n_1\beta_1\delta_1^{\,2} + \Phi_3 n_3\beta_3\delta_3^{\,2})\\ &+ 2n_m\beta_m\delta_m - n_m\beta_m\delta_m^{\,2}] \qquad \text{(AII.1.9)}\end{aligned}$$

Writing

$$n_m\beta_m = \Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3 \qquad \text{(AII.1.10)}$$

and substituting (AII.1.10) in equation (AII.1.9),

$$\begin{aligned}
\Delta V_2^{E,M} = V_2^o[& (\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_2^{\;2} \\
& - 2\delta_2(\Phi_1 n_1\beta_1\delta_1 + \Phi_3 n_3\beta_3\delta_3) \\
& - (\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_2^{\;2} \\
& + 2(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_2\delta_m \\
& - (\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_m^{\;2} \\
& + (\Phi_1 n_1\beta_1\delta_1^{\;2} + \Phi_3 n_3\beta_3\delta_3^{\;2})] \\
= V_2^o \Big\{ & 2\delta_2[(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)\delta_m \\
& \quad - (\Phi_1 n_1\beta_1\delta_1 + \Phi_3 n_3\beta_3\delta_3)] \\
& + (\Phi_1 n_1\beta_1\delta_1^{\;2} + \Phi_3 n_3\beta_3\delta_3^{\;2}) \\
& - \delta_m(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3) \Big\} \qquad \text{(AII.1.11)}
\end{aligned}$$

The equation (AII.1.11) is equivalent to equation (65) in the text. Now if we assume that

$$n_m\beta_m\delta_m^{\;2} = n_1\beta_1\delta_1^{\;2} + n_3\beta_3\delta_3^{\;2}$$

then along with the assumption made in equation (AII.1.10), the equation (AII.1.9) reduces to

$$\Delta\overline{V}_2^{E,M} = V_2^o[2\delta_2\delta_m(\Phi_1 n_1\beta_1 + \Phi_3 n_3\beta_3)$$

$$- 2\delta_2(\Phi_1 n_1\beta_1\delta_1 + \Phi_3 n_3\beta_3\delta_3)] \qquad \text{(AII.1.12)}$$

Again writing

$$n_i\beta_i\delta_i^{\,2} = \alpha_i T$$

or

$$n_i\beta_i\delta_i = \frac{\alpha_i T}{\delta_i} \qquad \text{(AII.1.13)}$$

and then substituting equation (AII.1.13) in equation (AII.1.12) we obtain

$$\Delta\overline{V}_2^{E,M} = 2V_2^o\delta_2 T\left\{\frac{\alpha_m}{\delta_m} - \Phi_1\frac{\alpha_1}{\delta_1} + \Phi_3\frac{\alpha_2}{\delta_2}\right\} \qquad \text{(AII.1.14)}$$

The equation (AII.1.14) is equivalent to equation (64) in the text.

Appendix AII.2

Derivation of $\Phi_1(\max)$ for $(1/A)\Delta^*(\ln x_2^m)$

$$\frac{1}{A}\,\Delta^*(\ln x_2^m) = \Phi_1^*(1 - \Phi_1^*)(\delta_2 - \delta_3)^2 \qquad \text{(AII.2.1)}$$

Again,

$$\frac{\Phi_1^*}{\Phi_3^*} = \frac{\Phi_1^o}{\Phi_3^o}\,\frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2} \qquad \text{(AII.2.2)}$$

and

$$\Phi_1^* + \Phi_3^* = 1 \qquad \text{(AII.2.3)}$$

or

$$\frac{\Phi_1^*}{1 - \Phi_1^*} = \frac{\Phi_1^o}{1 - \Phi_1^o}\,\frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2} \qquad \text{(AII.2.4)}$$

Adding 1 in both the sides of the equation (AII.2.4) we obtain

$$1 + \frac{\Phi_1^*}{1 - \Phi_1^*} = 1 + \frac{\Phi_1^o}{1 - \Phi_1^o}\,\frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2}$$

or

$$\frac{1}{1 - \Phi_1^*} = \frac{(1 - \Phi_1^o)(\delta_2 - \delta_1)^2 + \Phi_1^o(\delta_2 - \delta_3)^2}{(1 - \Phi_1^o)(\delta_2 - \delta_1)^2} \qquad \text{(AII.2.5)}$$

Dividing (AII.2.4) by (AII.2.5),

$$\Phi_1^* = \frac{\Phi_1^o(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2 - \Phi_1[(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2]} \qquad \text{(AII.2.6)}$$

Again by differentiating equation (AII.2.1) with respect to Φ_1^*, we see that the maximum value for $\frac{1}{A}\Delta^*(\ln x_2^m)$ will occur at

$$\frac{\partial[\frac{1}{A}\Delta^*(\ln x_2^m)]}{\partial \Phi_1^*} = 0 = (1 - 2\Phi_1^*) \qquad \text{(AII.2.7)}$$

at $\Phi_1^*(\max)$, or

$$\Phi_1^*(\max) = \frac{1}{2} \qquad \text{(AII.2.8)}$$

Substituting equation (AII.2.6) in the equation (AII.2.8) we obtain

$$\begin{aligned}(\delta_2 - \delta_1)^2 &= \Phi_1^o[(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2] \\ &= 2\Phi_1^o(\delta_2 - \delta_3)^2 \qquad \text{(AII.2.9)}\end{aligned}$$

Rearranging the equation (AII.2.9),

$$\begin{aligned}\Phi_1(\max) &= \frac{(\delta_2 - \delta_1)^2}{(\delta_2 - \delta_3)^2 + (\delta_2 - \delta_1)^2} \\ &= \left\{ \frac{(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2} + 1 \right\}^{-1} \qquad \text{(AII.2.10)}\end{aligned}$$

Appendix AII.3

The solubility equation can be written as

$$\ln x_2^m = \ln a_2^i - \frac{V_2^o}{RT}(\delta_2 - \delta_m)^2 \qquad \text{(AII.3.1)}$$

writing

$$\delta_m = \Phi_1^o\delta_1 + \Phi_3^o\delta_3 \qquad \text{(AII.3.2)}$$

such that

$$\Phi_1^o + \Phi_3^o = 1$$

or

$$\Phi_3^o = 1 - \Phi_1^o \qquad \text{(AII.3.3)}$$

Substituting equation (AII.3.3) in the equation (AII.3.2) we obtain

$$\delta_m = \Phi_1^o(\delta_1 - \delta_3) + \delta_3 \qquad \text{(AII.3.4)}$$

Substituting equation (AII.3.4) in equation (AII.3.1),

$$\ln x_2^m = \ln a_2^i - \frac{V_2^o}{RT}\left\{(\delta_2 - \delta_3) - \Phi_1^o(\delta_1 - \delta_3)\right\}^2$$

$$= \ln a_2^i - \frac{V_2^o}{RT}\left\{(\delta_2 - \delta_3)^2 - 2\Phi_1^o(\delta_1 - \delta_3)(\delta_2 - \delta_3) + \Phi_1^{o2}(\delta_1 - \delta_3)^2\right\} \qquad \text{(AII.3.5)}$$

Differentiating $\ln x_2^m$ with respect to Φ_1^o and then writing the condition for maximum, we obtain

$$\frac{\partial \ln x_2^m}{\partial \Phi_1^o} = 0 = \frac{V_2^o}{RT}\left[2(\delta_1 - \delta_2)(\delta_2 - \delta_3) - 2\Phi_1^o(\delta_1 - \delta_3)^2\right]$$

or

$$\Phi_1^{max} = \frac{\delta_2 - \delta_3}{\delta_1 - \delta_3} \qquad \text{(AII.3.6)}$$

Similarly, if one writes δ_m in terms of Φ_1^*, then

$$\Phi_1^{*,max} = \frac{\delta_2 - \delta_3}{\delta_1 - \delta_3} \qquad \text{(AII.3.7)}$$

Recalling the relationship between Φ_1^* and Φ_1^o, i.e.

$$\Phi_1^* = \frac{\Phi_1^o(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2 - \Phi_1^o[(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2]} \qquad \text{(AII.3.8)}$$

we obtain

$$\Phi_1^{*,max} = \frac{\Phi_1^o(\delta_2 - \delta_3)^2}{(\delta_2 - \delta_1)^2 - \Phi_1^o[(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2}$$

$$= \frac{\delta_2 - \delta_3}{\delta_1 - \delta_3} \qquad \text{(AII.3.9)}$$

or $$\Phi_1^o(\delta_2 - \delta_3)(\delta_1 - \delta_3) = (\delta_2 - \delta_1)^2 - \Phi_1^o[(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2]$$

or $$\Phi_1^o \{(\delta_2 - \delta_3)(\delta_1 - \delta_3) + [(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2]\} = (\delta_2 - \delta_1)^2$$

or $$\Phi_1^o(\delta_1 - \delta_3)(\delta_2 - \delta_1) = (\delta_2 - \delta_1)^2$$

or

$$\Phi_1^{o,\max} = \frac{\delta_2 - \delta_1}{\delta_1 - \delta_3} \qquad \text{(AII.3.10)}$$

Φ_1^{o}'s in equation (AII.3.8) to (AII.3.10) are the corresponding Φ_1^{o} value of $\Phi_1^{*,\max}$.

Appendix AIII.1

Entropy of Compressing a Mixture of Rigid Spheres

For a binary mixture of hard spheres Lebowitz, Helfand and Praestgaard[112] derived the following equation of state from the scaled particle theory:

$$\frac{P}{kT} = \Big\{ (\rho_1 + \rho_2)(1 + \xi + \xi^2) - \frac{18}{\pi} [Y_1 Y_2 (a_2 - a_1)^2]$$

$$\cdot [a_1 + a_2 + a_1 a_2 (Y_1 a_1^3 + Y_2 a_2^3)] \Big\} (1 - \xi)^{-3} \quad \text{(AIII.1.1)}$$

where

$$Y_i = \frac{\pi N_i}{6V} \quad \text{(AIII.1.2)}$$

and

$$\xi = \pi(N_1 a_1^3 + N_2 a_2^3) / 6V \quad \text{(AIII.1.3)}$$

In the above equations, P is the pressure at temperature T and volume V, k is Boltzmann's constant, ρ_i is the number density N_i / V and a_i is the hard sphere diameter of i .

If equations AIII.1.2 and A.III.3 are substituted in equation A.III.1.1 and then, multiplying numerator and denominator by V^3 , one obtains

$$P = kT(BV^2 + CV + D) / (V - A)^3 \quad \text{(AIII.1.4)}$$

where

$$A = \pi(N_1 a_1^3 + N_2 a_2^3) / 6$$

$$B = N_1 + N_2$$

$$C = \frac{\pi}{6} [N_1 a_1^3 + N_1 N_2 (-2a_1^3 - 2a_2^3 + 3a_1 a_2^2$$

$$+ 3a_1^2 a_2) + N_2^2 a_2^3]$$

$$D = \frac{\pi^2}{36}[N_1^3 a_1^6 + N_1^2 N_2(a_1^6 - 3a_1^5 a_2 + 6a_1^4 a_2^2 - a_1^3 a_2^3) + N_1 N_2^2(-a_1^3 a_2^3 + 6a_1^2 a_2^4 - 3a_1 a_2^5 + a_2^6) - N_2^3 a_2^6]$$

Thus the entropy of the compression is given by

$$\Delta S_{comp} = \int_{V_1}^{V_2} \frac{P}{T}\, dV \qquad \text{(A.III.1.5)}$$

Substitution of equation AIII.1.4 in equation AIII.1.5 followed by integration yields

$$\Delta S_{expan} = R\left\{ B \ln \frac{V_2 - A}{V_1 - A} + [D - CA - 3BA^2 + (2C + 4BA)V_1]/2(V_1 - a)^2 - [(D - CA - 3BA^2) + (2C + BA)V_2]/2(V_2 - a)^2\right\} \qquad \text{(AIII.1.6)}$$

The constants $D - CA + 3BA^2$ and $2C + 4BA$ are:

$$D - CA - 3BA^2 = \frac{\pi^2}{36}[-3\pi^2 a_1^6 - N_1 N_2(6a_1^5 a_2 - 3a_1^4 a_2^2 + 6a_1^3 a_2^3) - N_1 N_2(6a_1^3 a_2^3 - 3a_1^2 a_2^4 + 6a_1 a_2^5) - 3N_2^3 a_2^6] \qquad \text{(AIII.1.7)}$$

and $2C + 4AB = \pi[N_1^2 a_1^3 + N_1 N_2(a_1 a_2^3 + a_1^2 a_2) + N_2^2 a_2^3]$ AIII.1.8)

The compression is carried out from the volume of the gaseous solution $V_1 = V_s^g$ to the volume of the liquid solution $V_2 = V_s^\ell$. As V_1 is large, the second term in equation AIII.1.6 can be neglected. Further, in the first term $A \ll V_s^g$. Equation AIII.1.6 can be converted to mole quantities if one writes down

$$N_i = N_o x_i(n_1 + n_2)$$

where N_o is Avogadro's number, x's are the mole fractions, and n's are the number of moles.

Appendix AIII.2

Calculation of Hard Sphere Diameter

The most important part in any theory on hard sphere fluids is the choice of a meaningful value for hard sphere diameter. In earlier calculations, workers have used the equilibrium distance calculated for Lennard-Jones potential as the hard sphere diameter which is actually a bad choice because of the fact that the repulsive part of Lennard-Jones 6:12 potential is not as steep as the hard sphere potential and the equilibrium distance in that case can not be equated with the hard sphere potential.

Reiss[99] has used hard sphere diameter calculated from surface tension, the coefficient of isothermal compressibility and the coefficient of thermal expansivity of liquids. Pierotti[115] and Snider[118] calculated hard sphere diameter from the heat of vaporization of the liquids.

From scaled particle theory, the coefficient of isothermal compressibility β_ℓ of a liquid is given by

$$\beta_\ell = V^\ell(1 - Y)^4 / RT(1 + 2Y)^2 \qquad \text{(AIII.2.1)}$$

Similarly the coefficient of thermal expansivity of a liquid is given by

$$\alpha_\ell = (1 - Y^3) / T(1 + 2Y)^2 \qquad \text{(AIII.2.2)}$$

whereas Snider et al.[118] calculated heat of vaporization of normal liquid from Longuet-Higgins' model and derived an expression

$$\frac{\Delta H_V^o}{NkT} = \frac{1 + Y + Y^2}{(1 - Y)^3} + 1 \qquad \text{(AIII.2.3)}$$

The surface tension σ of a liquid is related to Y as

$$\sigma = aRT(2 + Y)/\,4V^{\ell}(1 - Y)^2 \qquad \text{(AIII.2.4)}$$

The hard sphere diameter has also been calculated from the viscosity of the dilute gas, $(\eta_i)_{gas}$ as

$$(\eta_i)_{gas} = 1.0165 \frac{5}{16a_{ii}^2} (m_i kT/\,\pi)^{\frac{1}{2}} \qquad \text{(AIII.2.5)}$$

where a is the hard sphere diameter, m is the mass and k is Boltzmann's constant.

In this connection it seems that the choice of the coefficient of thermal expansivity of real liquids will be a bad choice because the attractive forces are not considered in the scaled particle theory of Reiss, Frisch and Lebowitz[96] but they enter into the theory in the density and the thermal expansivity of the liquid.[101] This raises a point which was mentioned earlier, that in the scaled particle theory, the equation of state of a real liquid is not known. Hence the coefficient of thermal expansivity and the density of the liquid can not be calculated but have to be measured.

For the remaining three methods, there is no reason for supposing that any particular one gives the best a value. But if these derivations are correct, then a's determined by these three methods should not be very different from each other. Next the problem lies with the nonspherical molecules and the physical meaning of a in that case. Reiss et al. suggested that if the molecules are not too badly nonspherical, due to the effect of rotational averaging it is possible to have a meaningful value of a .

Another aspect that has to be emphasized is that in the scaled particle theory, a is treated as constant and does not vary with the temperature. This assumption leads to an incorrect temperature dependence for α_ℓ .[102] Besides, Stillinger calculated the effective value of a from the compressibility and densities of the molten salts and observed that a decreases with temperature. Mayer[128] noted that the surface tension equation derived by Reiss et al.[96] also has an incorrect temperature dependence. He suggested that a ought to decrease with temperature rather than remain constant. This decrease of a with temperature originates from the fact that with increasing temperature, the ability of the molecules to penetrate one another's repulsive field is more effectively due to the increase in the average thermal energy. A real molecule has, in fact, a 'soft', not a 'hard' repulsive potential.

But the problem still remains what numerical values can be accepted for a as a reasonable value. We chose to calculate a values from the heat of vaporization at the boiling point where the value for heat of vaporization is known by means of the equation of Snider et al.[118] Also we have calculated a values from β_ℓ.

But as we are interested in those solutes which are solid at room temperature and in most of the cases, β_ℓ for the molten solids are not known, for the sake of consistency we preferred a values calculated from the heat of vaporization calculated from equation AIII. 2.3 . In the case of solutes, where heat of vaporization data are not known, we are forced to use a calculated from the α_ℓ of the molten solid above melting point.

In the case where a values are available for both heat of vaporization and the coefficient of isothermal compressibility, it can be seen in the table below that a values determined by both the methods are comparable. So in all the following calculations we used a values calculated from the heats of vaporization for both solvent and solute except in such cases as tetraphenyl tin and tetrakis pentafluoro phenyl tin when a values are calculated from the α_ℓ . The a values in these calculations are assumed to be independent of the temperature because a 's are involved directly but they are involved as Y and any change in a will have a very small effect on Y .

Also, in this calculation, we used the experimental values for V^{ℓ} and α_{ℓ} instead of the calculated values due to reasons mentioned earlier.

We have rejected the method of determining a by viscosity due to the fact that the viscosity data gives some very unreasonable values for a .