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PREDICTION AND CORRELATION
OF THE SALT-EFFECT
IN VAPOR-LIQUID EQUILIBRIUM

BY

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A THESIS
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To My Wife

For Her Love and Understanding

ABSTRACT

The feasibility of developing a method of correlation and prediction for mixtures of two solvents containing a dissolved salt has been studied. The procedure consisted of arriving at the interaction parameters for the three binary systems (solvent 1-solvent 2, solvent 1-salt, solvent 2-salt) and using these to calculate the ternary results. Attempts to generate interaction parameters for the solvent-salt binaries by means of the Wilson equation were unsuccessful, whereas, use of the NRTL equation resulted in a very good fit of the binary data.

In correlating the ternary results, it became necessary to redefine the liquid phase mole fractions and activity coefficients for the binary and ternary systems, by the assumption of full dissociation of the salt in solution. A further assumption led to a simplification of the procedure and an improvement of the results for some of the ternary systems: for certain binaries in which the activity coefficient of the solvent did not deviate from unity by more than 10%, the parameters were assumed to equal 0.0 and the binary to behave ideal.

A study was made of the effect of α_{12} on the ternary fit. Prediction of the ternary behavior from binary data appears possible but additional experimental data is needed for the development of guidelines for the choice of the appropriate value of α for the solvent-solvent binary.

For the system MeOH-H_2O-LiCl the results are better than those of the Broul and Hala correlation. Good results were also

obtained for MeOH-H_2O-potassium acetate and MeOH-H_2O-$CaCl_2$. The Johnson and Furter equation fails to correlate the potassium acetate system. For two additional systems of questionable experimental accuracy, erroneous predictions were made.

The method of correlation is easier to apply than the Broul and Hala technique. All other methods of correlation - Broul and Hala excepted - have dealt only with systems saturated with salt. The method presented here can be applied for any salt concentration. The method can be applied to either isobaric or isothermal data.

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INTRODUCTION

The change that occurs on the relative volatility of a system consisting of two solvents when a salt is introduced into the system is called the "salt effect".

In aqueous solutions, if the introduction of the salt results in a higher concentration of the non- aqueous solvent in the vapor phase, the effect is called "salting out". If the reverse is true, the salt is said to have a "salting in" effect on the system.

The magnitude of the salt effect is related to the concentration of the salt. Thus, the maximum salt effect is obtained at saturation. For this reason a large number of experimental studies on the salt effect are conducted on solvent mixtures saturated with salt.

Other studies have been conducted using either constant salt concentration or variable salt concentration. Systems containing fixed quantities of salt however, can be more directly applied to industrial processes.

In order to more directly compare the effect of different salts on the vapor-liquid equilibrium of a solvent mixture, some investigators have reported their findings on a salt-free basis. In correlating salt-effect data these investigators have opted to treat the systems as pseudo-binaries. To account for the presence of the salt an empirical coefficient is incorporated into the correlating equation or the standard state for the activity coefficient is redefined.

Departing from the traditional treatment of salt-effect data, Hala (9) has opted to treat such systems as ternaries. The effect of the salt on each individual solvent is expressed algebraically and is then incorporated into the correlating equation.

Jaques and Furter (15) have offered the only reported method that permits the calculation of the vapor phase composition of isobaric systems that contain a salt at saturation. However, this method of calculation requires measurement of the temperature, pressure and liquid composition of the solvent-salt mixture.

The theories of the salt effect most commonly encountered in the literature are hydration theories, electrostatic theories, van der Waals forces and internal pressure concept. These theories are reviewed by Long and McDevitt (21). Furter and Cook have reviewed the literature on the salt effect with particular emphasis on the use of the salt effect in extractive distillation (6). Tsiparis has published a comprehensive work on data of the salt effect on vapor-liquid equilibrium (46). Hala and co-workers have included systems containing salts in their general bibliographies on vapor-liquid equilibrium (10).

SCOPE

The object of this work is to develop a method by which the vapor-liquid equilibrium of systems consisting of two solvents and a salt can be predicted from data on the three binary pairs with little or no knowledge of the ternary behavior.

Although vapor-liquid equilibrium data on the salt-effect has been growing in recent years, data on the effect of the salt on the vapor pressure or boiling point of individual solvents is scarce. In addition, since many of the studies on the salt effect are carried out at saturation, data on the solubility of the salt in the solvent mixtures of these studies is not always available.

Because of these limitations, the findings of this work will need to be confirmed or rejected when more data becomes available. Nevertheless, the five cases studied cover a broad spectrum of systems which makes the findings applicable to a wide variety of cases (See Appendix A).

One isothermal and four isobaric systems are examined. Two of the five systems exhibit a "salting-in" effect. Four systems contain inorganic salts while the fifth contains an organic salt. One system contains a salt with comparable miscibility in both solvents, while the other four have preferential solubility to one of the solvents.

I. BASIC PRINCIPLES.

Theoretical principles which are used in the remainder of this work are defined and discussed in this section. All the equations that are cited in following sections are stated herein.

The general discussion of vapor-liquid equilibrium and of correlating equations is based on material contained in the works of Hougen, et al. (12), and Marina (22). The works of Wilson (48) and Renon and Prausnitz (34) are used to supplement the discussion on the Wilson and NRTL equations. The discussion on theories of the salt effect is based on the reviews by Long and McDevitt (21) and Cook and Furter (6).

A) DEFINITIONS.

The term solution refers to a homogeneous mixture of two or more components. The properties of a solution are not, in general, the sum of the properties of the pure components. Properties that are mass dependent, such as volume, are called extensive properties. The actual contribution of a component to an extensive property is designated as its partial molal property. The partial molal property of a given component in solution is defined as the differential change in that property relative to a differential change in the amount of the same component under conditions of constant pressure and temperature, and a constant number of moles of all other components. The partial molal volume of components is given by:

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_j \neq i} \qquad \text{(I-1)}$$

where,

$\bar{v}_i$ = partial molal volume of component i

V = total volume

P = total pressure

T = temperature

n_i = number of moles of component i

n_j = number of moles of component j

The partial molal properties of all other extensive properties may be expressed in a similar fashion.

A system is said to be in equilibrium when it cannot undergo spontaneous or unassisted changes. Such a state can exist only when all forces or potentials that tend to promote change are absent or when they are exactly balanced against similar forces or potentials. When such a condition exists between the vapor and liquid phases of a solution, the system is said to be at vapor-liquid equilibrium.

The most useful quantity in the study of vapor-liquid equilibrium is the Gibbs free energy, G. At constant temperature and pressure, equilibrium is achieved when the total Gibbs free energy change is zero if no means of performing work are present. This can be expressed as follows:

$$\bar{G}_i' = \bar{G}_i'' \qquad \text{(I-2)}$$

Equation (I-2) expresses the criterion for equilibrium. The partial molal free energy of component i must be the same in both phases (phase' and phase").

The chemical potential μ_i is a quantity related to the Gibbs free energy of the solution. It can be shown that the chemical potential of a component is equal to the partial molal free energy, $\mu_i = \bar{G}_i$.

The fugacity of a component in solution is defined in terms of its partial molal free energy, or chemical potential, as follows:

$$(d\bar{G}_i = d\mu_i = RTd\ln f_i)_T \qquad (I-3)$$

Where, f_i = fugacity of component i in solution

R = Idial gas constant

T = Temperature

and $\lim_{x_i \to 0} \frac{f_i}{x_i P} = 1$

Equation (I-2) describing the criteria of equilibrium can be rewritten in terms of the chemical potential or the fugacity as follows:

$$\mu'_i = \mu''_i \qquad (I-4)$$

$$f'_i = f''_i \qquad (I-5)$$

The chemical potentials of any given component are identical in all phases. The fugacity criterion as expressed in equation (I-5) is a more useful expression as fugacities can be expressed in absolute values. At vapor-liquid equilibrium the fugacity of component i in the vapor phase is identical to its fugacity in the liquid phase.

An ideal solution is defined as a solution in which the fugacity of each component i is equal to the product of its mole fraction and the fugacity f_i^o of the pure component at the same temperature and pressure as the solution. This can be expressed as follows:

$$(f_i = N_i f_i^o)_{T,P} \qquad (I-6)$$

where Ni is the mole fraction of component i in the same phase. This expression agrees with Raoult's Law for liquid ideal solutions and Dalton's Law for ideal gas mixtures.

An ideal liquid solution implies that when the components are mixed mutual solubility results, that no chemical interaction occurs, that molecular diameters are the same and that the intermolecular forces of attraction and repulsion are the same between, unlike as between like molecules.

The ratio of fugacities of component i in any state to its standard state fugacity at the same temperature is designated as its activity a_i. The activity can, therefore, be directly related to ideal solution behavior. To describe the departure of a solution from ideal behavior, an empirical correction factor termed the activity coefficient (γ) is used. The activity coefficient is the ratio of the activity to a numerical expression of the composition. The numerical value of the activity coefficient has no significance unless the standard state and the units for the composition are specified. In terms of mole fractions the activity coefficients for the liquid and vapor phases are defined as follows:

$$\gamma_{iL} = \frac{a_{iV}}{x_i} : f_i \;/\; (f_i^{o} x_i) \qquad \text{(I-7)}$$

and,

$$\gamma_{iV} = \frac{a_{iv}}{y_i} = f_i \;/ (f_i^{o}\, y_i) \qquad \text{(I-8)}$$

where,

x_i = liquid phase mole fraction on component i

y_i = vapor phase mole fraction of component i.

At atmospheric pressure or below the activity coefficients of the components in the gas phase are nearly unity; i.e. the vapor phase behaves ideally.

Under these conditions the standard state fugacity of each component in the liquid state equals the saturated vapor pressure of the component and the fugacity equals the partial pressure. That is,

$$f^{\circ}_{iL} = P^{\circ}_i \qquad \text{(I-9)}$$

and

$$f_i = \bar{P}_i = y P_T \qquad \text{(I-10)}$$

where PT equals the total pressure on the system. For low pressure vapor-liquid equilibrium the vapor phase activity coefficient can be assumed to equal unity and the liquid phase activity coefficients become

$$\gamma_{iL} = \frac{y_i P_T}{x_i P^{\circ}_i} \qquad \text{(I-11)}$$

If the liquid phase behaves ideally, the activity coefficient γ_{iL} equals unity and equation (11) reduces to the well known Raoult's Law for ideal solutions.

Equation (I-11) is used in the remainder of this work since all systems studied were reported at pressures not exceeding atmospheric pressure.

For ideal solutions the relative volatility (α_{ij}) of component i relative to j is given by the ratios of the vapor pressures. For systems that obey Raoult's Law the relative volatility is independent of composition.

For non-ideal solutions the relative volatility is not constant but varies with composition. The ratio of the vapor pressures is multiplied by the ratio of the activity coefficients which varies with composition. Non-ideal solutions exhibit temperature - composition curves substantially different from those of ideal solutions. An azetropic system is a solution that exhibits at least one point where the vapor composition and the liquid composition are identical. At this point the mixture continues to vaporize at a single temperature, as does a pure liquid. No further change in the composition of the azeotrope occurs. This characteristic is undesirable if a separation of the mixture into its constituents by distillation is necessary.

B. THE GIBBS-DUHEM EQUATION.

The Gibbs-Duhem equation is a rigorous thermodynamic relation that is valid for conditions at constant temperature and pressure. This equation, in its various forms, is useful in minimizing the number of experimental data necessary to evaluate the properties of a system. The equation has also been used to detect inconsistent or erroneous measurements.

The Gibbs-Duhem equation expresses the relationship of the partial molal free energy of a component in solution to the partial molal free energy of the other components and to the composition. For a multicomponent system, the Gibbs-Duhem equation can be expressed in terms of fugacity as follows:

$$\left[x_1\left(\frac{\partial \ln f_1}{\partial x_1}\right) + x_2\left(\frac{\partial \ln f_2}{\partial x_2}\right) + x_3\left(\frac{\partial \ln f_3}{\partial x_3}\right) + \ldots = 0\right]_{P,T} \qquad (I\text{-}12)$$

For a binary solution, equation (12) becomes

$$\left[x_1\left(\frac{\partial \ln f_1}{\partial x_1}\right)\right]_{P,T} = -\left[x_2\left(\frac{\partial \ln f_2}{\partial x_2}\right)\right]_{P,T} \qquad (I\text{-}13)$$

Equation (13) can also be expressed in terms of activity coefficients as follows:

$$\left[x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)\right]_{P,T} = -\left[x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)\right]_{P,T} \qquad (I\text{-}14)$$

C. THE CONCEPT OF EXCESS PROPERTIES.

To describe the degree of departure of a real mixture from ideal behavior the concept of excess properties is used. An excess property is defined as the difference between the value of this property in the real mixture and the value this property would have should the mixture behave ideally. The excess free energy of a mixture is defined by

$$G^E = G^M - G^M_* \qquad \text{(I-15)}$$

where,

G^E = Excess Gibbs free energy

G^M = Gibbs energy of mixing

G^M_* = Gibbs energy of mixing for an ideal solution.

The excess Gibbs free energy can be expressed in terms of the activity coefficients and mole fractions by

$$G^E = RT \sum_{i=1}^{n} x_i \ln \gamma_i \qquad \text{(I-16)}$$

The partial molal excess Gibbs energy is defined by

$$\bar{G}_i^E = RT \ln \gamma_i \qquad \text{(I-17)}$$

This equation offers a convenient way of relating the activity coefficients to the excess properties. The partial molal excess free energy can be related to the total excess Gibbs energy by

$$\bar{G}_i^E = RT \ln \gamma_i = G^E - \sum_{\substack{i=1 \\ i \neq j}}^{n} x_i \frac{\partial G^E}{\partial x_i} \qquad \text{(I-18)}$$

Throughout the years, correlations for the vapor liquid equilibrium have made use of the excess free energy concept to derive algebraic relationships describing the non-ideal behavior as a function of composition. Equation (I-18) is used to obtain from experimental data the parameters of such correlations. Some of these correlations will be described in the following section.

D. CORRELATIONS FOR THE ACTIVITY COEFFICIENTS.

The concept of excess free energy includes all the effects that contribute to non-ideal solution behavior, such as differences in intermolecular forces, polarity, chemical structure, and molecular size. Because of this, the excess free energy has been empirically expressed as a function of composition by many correlating equations for vapor-liquid equilibrium.

It is the purpose of this section to present some of these correlating equations, particularly those that have been applied to systems containing a salt.

1. The Wohl Three-Suffix Equation.

The general Wohl equation expresses the excess free energy as a function of composition, effective molal volume and effective volumetric fraction Z_i of the separate components. The equation permits the use of as many terms as are needed to describe the complexity of a solution being restricted only by the precision of the experimental data.

For binary systems, the Wohl equation in its three suffix form is given by

$$\frac{G^E}{RT} = \left(x_1 + \frac{q_2}{q_1} x_2\right) Z_1 Z_2 \left[Z_1 q_1 \left(2a_{12}+3a_{112}\right) + Z_2 q_1 \left(2a_{12}+3a_{112}\right)\right] \qquad \text{(I-19)}$$

when,

q_1, q_2 = effective molal volume of components 1 and 2

Z_1, Z_2 = effective volume fractions of components 1 and 2

a_{12}, a_{112}, a_{22} = empirical constants.

The effective volume fractions Z_1 and Z_2 are given by

$$Z_i = \frac{X_i}{X_i + \sum_{i \neq j} \frac{q_j X_j}{q_i}} \qquad \text{(I-20)}$$

By using equations (I-18) and (I-19) the expressions for the activity coefficients are obtained.

$$\log \gamma_1 = Z_2{}^2 \left[A + Z \left(B \frac{q_1}{q_2} - A\right) Z_1\right] \qquad \text{(I-21)}$$

$$\log \gamma_2 = Z_1{}^2 \left[B + 2 \left(A \frac{q_2}{q_1} - B\right) Z_2\right] \qquad \text{(I-22)}$$

where $A = 2.303 \left[q_1 \left(2a_{12} + 3a_{122}\right)\right]$

and $B = 2.303 \left[q_2 \left(2a_{12} + 3a_{112}\right)\right]$.

The constants A, B and q_1/q_2 are characteristic of each binary system.

2. The Margules Three-Suffix Equation.

The Margules three-suffix equation as modified by Carlson and Colburn can be obtained from the Wohl's equations for the activity coefficients by setting q_2/q_1 equal to unity. Thus,

$$\log \gamma_1 = x_2^2 \left[A+2(B-A)x_1\right] = (2B-A)x_2^2+2(A-B)x_2^3 \quad \text{(I-23)}$$

$$\log \gamma_2 = x_1^2 \quad B+2(A-B)x_1^2+2(B-A)x_1^2+2(B-A)x_1^3 \quad \text{(I-24)}$$

Where these equations hold, A is the value of log γ_1 at $x_1 = 0$ and B is the value of log γ_2 at $x_2 = 0$.

The Margules three-suffix equation is suited for symmetrical systems where the constants A and B are nearly the same. For systems where A and B can be taken as identical, the Margules two-suffix equation results:

$$\log \gamma_1 = A\,x_2^2 \quad \text{(I-25)}$$

$$\log \gamma_2 = A\,x_1^2 \quad \text{(I-26)}$$

3. The van Laar Equation.

The Wohl equation reduces to the van Laar two-suffix equation if q_1/q_2 is set equal to A/B. Thus,

$$\log \gamma_1 = Az_2^2 = \frac{A x_2^2}{[(A/B)\, x_1 + x_2]^2} \qquad \text{(I-27)}$$

$$\log \gamma_2 = Bz_1^2 = \frac{B x_1^2}{[x_1 + (B/A)\, x_2]^2} \qquad \text{(I-28)}$$

The van Laar equation may be used for unsymmetrical solutions where the ratio A/B does not exceed 2. The equation cannot be used where maxima or minima values of $\log \gamma$ occur.

Determination of γ_1 and γ_2 at a single known composition permits the evaluation of the entire activity coefficient-composition curves by using the van Laar equation. The constants A and B can be calculated from the measured values of the activity coefficients.

4. The Redlich-Kister Equation.

The Redlich-Kister equation relates the excess free energy to composition, at constant temperature and pressure, by a series fuction using terms sufficient to fit the experimental data. The excess free energy for a binary system is given by

$$G^E = RTx_1x_2\left[B+C(x_1-x_2) + D(x_1-x_2)^2+\ldots\right]_{P,T} \qquad \text{(I-29)}$$

The individual activity coefficients are obtained by differentiation of equation. Thus,

$$\ln\gamma_1 = x_1x_2\left[B+C(x_1-x_2)+D(x_1-x_2)^2+\ldots\right]+x_2\left[B(x_2-x_1) +C(6x_1x_2-1)+D(x_1-x_2)(8x_1x_2-1)+\ldots\right] \qquad \text{(I-30)}$$

$$\ln\gamma_2 = x_1x_2\left[B+C(x_1-x_2)+D(x_1-x_2)^2+\ldots\right]-x_1\left[B(x_2-x_1) +C(6x_1x_2-1)+D(x_1-x_2)(8x_1x_2-1)+\ldots\right] \qquad \text{(I-31)}$$

Equations (I-30) and (I-31) can be combined into a single equation by subtracting the latter from the former to give

$$\ln\gamma_1/\gamma_2 = B(x_2-x_1)+C(6x_1x_2-1)+D(x_2-x_1)(1-8x_1x_2)+\ldots \qquad \text{(I-32).}$$

5. The Wilson Equation.

A great advancement in the semi-empirical correlation of vapor-liquid systems was made by the introduction of the Wilson equation (48). This equation can be readily expanded to multicomponent systems and prediction of multicomponent vapor-liquid equilibrium may be obtained from binary data alone.

The excess free energy is given by Wilson as

$$\frac{G^E}{RT} = -\sum_i x_i \ln\left(1-\sum_j x_j \Lambda_{ij}\right) \qquad (I\text{-}33)$$

where

$$\Lambda_{ji} = 1-\frac{v_j}{v_i}\left(e^{-(\lambda_{ji}-\lambda_{ii})/RT}\right) \qquad (I\text{-}33\,b)$$

v_j = pure component molar volume of component j

v_i = pure component molar volume of component i

λ_{ji} = constant proportional to the energy of interaction between component i and j

λ_{ii} = constant proportional to the energy of interaction between molecules of component ii.

The two parameter Wilson equation represents with great accuracy vapor-liquid of miscible systems. However, the equation fails to correlate systems exhibiting partial miscibility. Unlike the previously discussed equations, the Wilson equation contains parameters with a degree of built-in temperature dependency.

6. The Renon-Prausnitz Equation (NRTL).

Renon modified the Wilson equation by introducing the constant α as a third parameter. The resulting expression for the excess Gibbs free energy is given by

$$\frac{G^E}{RT} = \frac{x_1 x_2}{RT}\left[\frac{(g_{21}-g_{11})\ \exp[-\alpha(g_{21}-g_{11})/RT]}{x_1+x_2\ \ \exp[-\alpha(g_{21}-g_{11})/RT]} + \frac{(g_{12}-g_{22})\ \exp[-\alpha(g_{12}-g_{22})/RT]}{x_2+x_1\ \ \exp[-\alpha(g_{12}-g_{22})/RT]}\right] \qquad \text{(I-34)}$$

where

g_{ij} = residual Gibb energies

x_1, x_2 = mole fractions of components 1 and 2.

The terms (g_{ij} - g_{jj}) are fitted to the data and the third parameter, α, may either be fitted to the data or may be set at a value corresponding to the nature of the system. Renon suggested a classification of binary system into eight categories from considerations on the polarity and self association characteristics of the pure components and the value of the excess free energy of the mixture. The values of α suggested for these eight types vary in the range from 0.2 to 0.47. These rules, however, constitute an approximation and curve fitting with a variable value of α generally gives more accurate correlations.

In general, this equation correlates binary data and multicomponent phase equilibria with good accuracy. The NRTL equation, although a 3 parameter equation, represents an improvement over the Wilson equation because it can be applied to systems exhibiting partial miscibility.

Because of the physical significance attributed to the parameter α_{ij} in the original derivation of the NRTL equation, the value of this parameter was restricted to the range $0 < \alpha_{ij} < 1$. Renon and Prausnitz recommended guidelines for assigning values of α_{ij} to reflect the type of system under consideration. However, in recent years the NRTL has often been used as an empirical parameter. Marina (23) for instance has shown that pre-setting the value of α to -1.00 yields equal or better predictions for the equilibria of multicomponent systems than those obtained by the recommended α values. Other authors have opted for variable or regressed values of (8, 27, 42).

Expressed in terms of the activity coefficients, equation (I-34) becomes:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{kj} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{l=1}^{n} x_l \tau_{lj} G_{lj}}{\sum_{k=1}^{n} G_{kj} x_k} \right) \quad \text{(I-34-b)}$$

where,

$$\tau_{ji} = (g_{ji} - g_{ii})/RT$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$$

$$\alpha_{ij} = \alpha_{ji} \quad \text{and} \quad g_{ij} = g_{ji}.$$

E. Theories on the Salt-Effect.

Several theories have been offered to attempt to explain the complex interactions that occur in solvent mixtures containing a salt. These have been classified into four types: hydration, internal pressure, electrostatic and van der Waal's forces theories. This section offers a summary of these theories. A more detailed description can be found in the reviews of Long and McDevit (21) and Cook and Furter (6).

The discussion uses the nomenclature generally used in salt-effect theory. The non-aqueous solvent is referred to as the nonelectrolyte; water is called the solvent and salt is referred to as the electrolyte.

According to the hydration theories, the salting-out effect results from the effective removal of water molecules from their solvent role due to the hydration of ions.

Long and McDevit found this theory to be inadequate in that it does not consider the effect of the salt on the rest of the solvent or of the nonelectrolyte. This theory indicates that hydration numbers should be independent of the species of nonelectrolyte, which they are not. In addition, the theory does not allow for the occurrence of salting-in and the order of ion effectiveness does not correspond to the observed order.

The theory of "internal pressure", which Long and McDevit found to hold only for strictly non-polar nonelectrolytes, relates volume contraction to the salt-effect. The "effective pressure" of a salt is defined as the external pressure that would have to be applied to cause a volume contraction equal to that caused by the salt. This parameter has been found to correspond roughly to the magnitude of the salt effect.

The electrostatic theories relate salt effect to the influence of the nonelectrolyte on the dielectric constant of the solvent. The amount of work necessary to discharge the ions in pure solvent and to recharge them in a solution containing the nonelectrolyte, thus yielding the electrical contribution to the free energy, and hence to the activity coefficient, of the nonelectrolyte is calculated. These theories consider only departures from ideality due to the electrostatic interactions arising from the ionic charges. The resulting equations are limiting laws since they are derived for infinite dilution. Attempts to extend these theories to finite electrolyte concentrations have been largely unsuccessful.

The van der Waals forces theory attempts to explain why a given nonelectrolyte may be salted-in by some electrolytes and salted-out by others in the same solvent. The theory holds that at finite concentrations short range dispersion forces may also be appreciable in determining the salt-effect. In the presence of large ions having weak electrostatic fields, or in the presence of relatively undissociated salts, the highly polar water molecules may tend to associate much more strongly with each other than with the salt, forcing the salt into the vicinity of the less polar nonelectrolyte molecules with which it associates resulting in the salting-in of the nonelectrolyte.

Attempts to apply this theory quantitatively have thus far been inconclusive.

None of the theories that have been formulated thus far to explain the salt-effect have been successful in representing the phenomenon. It is hoped that by taking an empirical approach, it may be possible to correlate the salt-effect by obtaining the binary interaction parameters from data on the constituent binaries (solvent-salt, nonelectrolyte-salt and solvent-nonelectrolyte).

II. LITERATURE REVIEW

As previously mentioned, the theory and experimental work on the salt effect have been the subject of comprehensive reviews by Furter and Cook (6) and Long and Mc Devitt (21). This section will serve to give emphasis to the methods of correlation found in the literature and to cite the more recent publications on the subject.

With the exception of the papers by Rius Miro and coworkers (37 - 41), only articles written in English or translated into English were reviewed.

A. Methods of Correlation.

Ruis Miro, and others, have correlated with partial success systems consisting of ethanol, water and a dissolved salt by means of the Van Laar equations as modified by Carlson and Colburn (37 , 38).

In attempting to correlate systems in which the salt is considerably more soluble in water than in ethanol (NaCl, KCl and KNO_3), Rius Miro found that although the calculated activity coefficients for ethanol were in good agreement with experimental values, the activity coefficients for water deviated from the experimental values by an average of 22%. Ruis Miro concluded that the Van Laar equation does not satisfactorily correlate systems saturated with a salt.

To correlate systems in which the salt is soluble in both solvents, Rius Miro and coworkers have modified the Van Laar equation by introduction of two empirical parameters, k_1 and k_2. Thus,

$$\log \gamma_1 k_1 = \frac{A}{\left(1+\frac{A}{B}\frac{x_1}{x_2}\right)^2} \qquad \text{(II-1a)}$$

$$\log \gamma_2 k_2 = \frac{B}{\left(1+\frac{B}{A}\frac{x_2}{x_1}\right)^2} \qquad \text{(II-1b)}$$

The parameters k_1 and k_2 are used to normalize the values of the activity coefficients. If the values of the activity coefficient for one component are all greater than unity, or all smaller than unity, the value of the constant k for that component is set at k=1. If, on the other hand, some values of the activity coefficient are greater than unity while others are lower than unity, the value of k for that component is equated to the reciprocal of the lowest value of the activity coefficient. Assigning such a value to k has the effect of making the γk all equal to or greater than unity.

This modification is also said to improve the results of systems in which the salt is soluble only in water. However, only the values of the parameters are reported and not the fit of the correlation. The method failed to correlate the data for the system containing KBr.

In a later study, Rius Miro and his coworkers plotted the ratio of the fugacity of the solvent in the solvent-salt ternary to the fugacity of the solvent in its standard state (saturated with salt against the ratio of the fugacities in the absence of salts). The plots were linear except when two liquid phases occur. The data was correlated by the following equation:

$$\frac{\Delta\mu^E}{2.3RT} \doteq \log\left(\frac{f_i}{f_i^o}\right) - \log\left(\frac{f_{io}}{f_{io}^o}\right) = k_s C_s \qquad \text{(II-2)}$$

where,

f_i = fugacity of component i in the ternary system

f_i^o = standard state fugacity of component i saturated with salt

f_{io} = fugacity of component i, salt free

f_{io}^o = standard state fugacity of component i, salt free (pure component)

k_s = solvent interaction constant

Cs = salt concentration (moles of salt/moles of component i)

For the system ethanol-water calcium nitrate Ruis Miro and coworkers developed a correlation based on solvation theory. This correlation method, however, cannot be extended to other systems.

Johnson and Furter have developed from electrostatic theories a relation that is similar to equation (**II-2**):

$$\Delta\mu^E = RT \log \frac{\alpha_s}{\alpha} = f\ (x_3) \qquad \text{(II-3)}$$

where,

α_s = relative volatility in the presence of salt

α = relative volatility in the absence of salt

x_3 = mole fractions of salt.

By assuming constant temperature and a linear relationship between the excess chemical potential and the concentration, equation

$$\log \frac{\alpha_s}{\alpha} = k_3 x_3 \qquad \text{(II-4)}$$

where,

k_3 = salt effect parameter.

Johnson and Furter showed for 9 systems in which the salt concentration was experimentally determined the parameter k_3 was independent of the solvent concentration, x_2. These results were extended to a total of 24 systems. For these systems it was found that the vapor phase composition could be calculated to within 1 mole per-cent from a single experimental determination of k_3. This method provides a simple means of correlating salt effect data provided that the parameter, k_3, is approximately constant throughout the solvent concentration range.

Meranda and Furter found that large variations of k_3 with x_2 exist for some alcohol-water-acetate salt systems (24). In addition, Yoshida found that for acetic acid-water-salt systems the data is correlated with smaller deviations by:

$$\log y/y_o = k_m M \qquad \text{(II-5)}$$

where,

y = mole fraction of organic solvent vapor

y_o = mole fraction of organic solvent vapor in salt free mixture

k_m = correlation parameter

M = concentration of salt (g-moles/kg of solvent)

Yoshida's equation, however, cannot be used to correlate alcohol-water-salt systems.

To improve the correlations obtained from equation (II-4), Jacques and Furter have superimposed the Redlich-Kister equation for the solvent-solvent interactions to the power series expression quoted by MacDevitt and Long (21):

$$\log \gamma_i = \sum_{n,m}^{\infty} K_{nm} Cs^n Ci^m \qquad \text{(II-6)}$$

where,

γ_i = activity coefficient of component

Cs = salt concentration

Ci = concentration of component i

K_{nm} = interaction parameter.

Substituting x for Ci and z for Cs and expanding for n+m 3, Jacques and Furter obtained:

$$\log \gamma = k_0 + k_{01}x + k_{10}z + k_{02}x^2 + k_{11}Xz + k_{20}Z^2 + k_{03}x^3 + k_{12}X^2Z + k_{21}Xz^2 + k_{30}Z^3 \qquad \text{(II-7)}$$

The Redlich-Kister equation can be re-written in the terms of equation (II-7) to give:

$$\log \gamma = k_0 + k_{01}x + k_{02}x^2 + k_{03}x^3 \qquad \text{(II-8)}$$

Equation (II-8) represents the variation of the activity coefficient with solvent concentration in the absence of salt. If equation (II-8) is subtracted from equation (II-7), the resultant expression is a measure of the salt effect. The excess chemical potential is given by Jacques and Furter as:

$$\Delta\mu^E = C_1z + C_2xz + C_3z^2 + C_4x^2z + C_5xz^2 + C_6z^3 \qquad \text{(II-9)}$$

Jacques and Furter reported that equation (II-9) gave considerably improved results over equation (II-4) when applied to 12 systems consisting of ethanol-water-inorganic salt (13)

Rousseau, Ashcraft and Shoenborn(42) correlated the alcohol-water-salt data of Johnson and Furter by means of the Van Laar (11), the Wilson (48) and the Renon (34,35) equations. The activity coefficients of the volatile components were calculated by using a modified reference fugacity that takes into account the vapor pressure lowering due to the salt. Because most salts are more soluble in water and data on the vapor depression of the alcohols was unavailable to these workers, the effects of the salts on the reference liquid fugacity of the alcohol was neglected. The activity coefficients were then calculated by using the depressed vapor pressure of water as the reference liquid fugacity for water, while the pure alcohol vapor pressure is used as the reference fugacity for the alcohol. In applying the Renon (NRTL) equation to these systems, Rousseau and coworkers used a variable value of the parameter α_{12}.

Jacques and Furter(15) took a similar approach to that of Rousseau and coworkers in developing a method of calculation of the vapor composition in isobaric systems containing ethanol, water and an inorganic salt. The method permits the calculation of the vapor composition from data on the boiling point, total pressure and liquid phase composition by means of the Wilson equation.

Jacques and Furter, like Rousseau and coworkers, based their liquid component activity coefficients on the standard state of the liquid saturated with the salt. Jacques and Furter, however, corrected for the lack of data on the vapor depression of ethanol by multiplying the pure liquid vapor pressure by the ratio of the vapor pressure of ethanol saturated with salt to the vapor pressure of pure ethanol at the same temperature. This ratio is assumed to be independent of temperature.

The depressed vapor pressure of the alcohol used in the activity coefficient calculations is then given by

$$P_1'(T_2) = P_1^{o}(T_2) \times \frac{P_1'(T_1)}{P_1^{o}(T_1)} \tag{II-10}$$

where,

$P_1'(T_2)$ = Calculated depressed vapor pressure of ethanol saturated with salt at temperature T_2

$P_1^{o}(T_2)$ = Vapor pressure of pure ethanol at temperature T_2

$P_1'(T_1)$ = Observed depressed vapor pressure of ethanol saturated with salt at temperature T_1.

$P_1^{o}(T_1)$ = Vapor pressure of pure ethanol at temperature T_2.

The total pressure is expressed as follows:

$$P_T = x_1 P_1' \cdot \gamma_1 + (1-x_1)\gamma_2 P_2' \tag{II-11}$$

where,

P_T = total pressure, calculated

P_1' , P_2' = vapor pressures saturated with salt.

By fitting equation (II-11) with the observed total pressure, the best parameters of the Wilson equation can be found. The vapor phase mole fractions can then be calculated from these parameters. For systems exhibiting partial miscibility, Jacques and Furter used the three constant form of the Wilson equation.

Hala(9) has developed a method for correlating the salt effect from data on the vapor depression of the solvents. The method makes use of the assumption of full dissociation of the salt to calculate the solvent-salt interaction parameters. The depressed vapor pressure is expressed as follows:

$$P_1' = P_1^\circ \cdot X_{1\pm} \cdot \gamma_{1\pm} \qquad \text{(II-12)}$$

where,

P_1' = dpressed vapor pressure

P_1° = vapor pressure of pure solvent

$X_{1\pm}$ = mean mole fraction of solvent

$\gamma_{1\pm}$ = mean rational activity coefficients.

The mean quantities are evaluated with the assumption of full dissociation of the salt. The mean mole fraction $X_{1\pm}$ is defined as follows:

$$x_{1\pm} = \frac{x_1}{x_1 + \nu x_3} \qquad \text{(II-13)}$$

where,

x_1 = analytical mole fraction of solvent

x_3 = analytical mole fraction of salt

ν = total number of ions in one mole of salt.

The mean rational activity coefficient is defined in terms of the mean mole fraction with the assumption of ideal vapor phase by equation. (II-12)

Hala superposed the term $-1/2\, c x_3^{3/2}$ to the Margules three-suffix equation to account for the coloumbic interactions. The constant C is evaluated along with the Margules parameters. The resulting expression is given by

$$\log \gamma_{1\pm} = -1/2 c x_3^{3/2} + x_3^2 \left[A_{13} + 2x_1 (A_{31}x_1 - A_{13})\right] \quad \text{(II-14)}$$

where,

c = constant representing coloumbic interactions

A_{13}, A_{31} = Margules parameters.

To simplify the ternary correlation, Hala suggested setting the constant C to be the same value for the two solvent-salt pairs. By combining equations (II-12) and (II-14), the binary parameters for the solvent-salt pairs are obtained. The Margules parameters for the solvent-solvent pair are obtained in the conventional manner.

To correlate the ternary data from the binary parameters, the following expressions are used:

$$\log\left(\frac{\gamma_{1\pm}}{\gamma_{2\pm}}\right) = x_2^{2}A_{12} - x_1^{2}A_{21} - 2x_1x_2\ (A_{12}-A_{21})$$
$$- x_3\Big(2A_{32}x_2-2A_{31}x_1 + x_3\ (A_{23}-A_{13}) + (x_1-x_2)$$
$$\Big[1/2\ (A_{12} + A_{21} + A_{13} + A_{31} + A_{23} + A_{32})$$
$$- C_{123}\Big]\Big) \qquad \text{(II-15)}$$

$$\beta_{12} = \frac{(\gamma_{1\pm})\cdot P_1^{\circ}}{(\gamma_{2\pm})\cdot P_2^{\circ}} \qquad \text{(II-16)}$$

$$y_1 = \frac{\beta_{12}\ (x_1/x_2)}{[1 + \beta_{12}\ (x_1/x_2)]} \qquad \text{(II-17)}$$

where,

β_{12} = generalized relative volatility

A_{ij} = binary parameters

C_{123} = ternary constant.

Hala's method differs in approach from previous methods of correlation in that it considers the systems as true ternaries rather than pseudo-binaries, making use of binary interactions to correlate the ternary behavior. His method is easily modified to correlate different types of mixtures of electrolytes and nonelectrolytes. For all types of mixtures, both the coloumbic and non-columbic interactions are taken into account (9 , 10).

Sada and Morisue (43) have presented a series of equations to rigorously describe the salt effect for systems containing two volatile components and a non-volatile salt. These authors have generalized the Gibbs-Duhem equation to satisfy such systems. An expression for the salt effect is derived from this generalized Gibbs-Duhem equation. Unfortunately, these authors have not applied their equations to any real systems nor shown how these rather complex expressions can be practically applied.

Jacques and Furter have presented a method of testing the thermodynamic consistency of data for the ethanol-water system saturated with inorganic salts (14).

The methods of correlation mentioned above cannot be used to predict vapor-liquid equilibria in the absence of ternary data. The method of Hala provides a foundation for a predictive method; however, Hala in his correlation makes use of a ternary constant.

It is the objective of this study to develop a method of correlation that may be used as tool for the prediction of the salt effect. Such a method would permit calculation of the vapor phase composition in a ternary solvent-solvent-salt system from binary data alone. The method would not be restricted to salt saturated systems but would permit calculations of y for salt concentrations below saturation as well.

B. Experimental Work.

Broul has reported data on the system methanol-water-lithium chloride at 60°C. His correlation based on Hala's theories gave an average deviation in the vapor phase mole fraction of 0.0191 (2).

Chen and Thompson reported data on the system glycerol-water-sodium chloride (3). The salt was shown to have a pronounced effect on the activity coefficient of glycerol.

Johnson and Furter presented data for 24 systems consisting of an alcohol (methanol, ethanol or n-propanol), water and a salt present in the liquid phase at saturated concentrations (17).

Cook and Furter reported a series of experimental runs on a pilot plant scale where aqueous ethanol was fractionated in a 12 tray column using potassium acetate as the separating agent (4). Small concentrations of salt were sufficient to destroy the azeotrope. The overhead product was completely free of the separating agent.

Johnson, Ward and Furter reported isobaric data on the system n-octane-propionic acid-sodium propionate (18). The salt was found to enhance the relative volatility.

Kato, Sato and Hirata reported isobaric data for the systems methanol-ethanol-calcium chloride and iso-propanol-water-calcium chloride (19). The authors proposed a new analytical technique based on bubble point and condensation point measurements.

Lindberg and Tassios reported isothermal data on the systems n-hexane-ethanol and hexene-1-ethanol saturated by lithium bromide and potassium acetate (20). These authors found that the salts cannot be used as extractive agents for these systems since they do not destroy the azeotrope.

The system ethanol-water saturated by potassium acetate is reported by Meranda and Furter (24). The data was not satisfactorily correlated by the Johnson and Furter equation. in a subsequent publication, this study was extended to 7 other ethanol-water-acetate salt and methanol-water-acetate salts (25). The methanol-water-potassium acetate exhibited an even larger deviation from the Johnson and Furter equation.

Meranda and Furter also investigated the effects of halide salts in the vapor-liquid equilibrium of alcohol-water systems (26). The synergistic effects of halide salt mixtures were investigated.

Ohe and others reported the effect of calcium chloride on the methanol-ethyl acetate system (29). From the data these authors conclude that a solvate is formed between the alcohol and the salt.

Prausnitz and Targovnik reported data on the salt effects of various salts on the systems water-pyridine, water-dioxane and water-isopropyl alcohol (32). They explain their findings in terms of the various theories of the salt effect.

Ciparis and Smorigaite reported data on the effects of KI, KBr, KCl and $CaCl_2$ on the equilibrium of the system water-acetic acid (47). The salting-out of acetic acid was characterized in terms of concentration, the nature of the ions and the temperature.

Yoshida and others measured the effect of various salts on the vapor-liquid equilibrium of water-methanol and water-acetic acid systems (49). These authors determined the order of effectiveness of the ions present. They also found that for the system water-acetic acid-salt the Johnson and Furter equation does not correlate the data with sufficient accuracy.

III. PROCEDURE

The system methanol-water-lithium chloride was chosen for the initial analysis for two reasons. First, the system is isothermal which eliminates the problem of temperature dependency of the parameters. Second, the ternary data is extensive and the binary data is readily available.

The Wilson equation was used to correlate the binary data. Since the parameters of this equation have a degree of built-in temperature dependence which makes it ideal for use in isobaric systems where the temperature range is broad.

The parameters of this equation for the systems MeOH-LiCl and H_2O-LiCl were first approximated by a method similar to that of Baker. This method will be explained in a later section.

The approximate solutions revealed that at least one of the two parameters is negative. In order to confirm this finding a least-squares subroutine was used to attempt to find the roots of the Wilson equation. The subroutine failed to converge for the normal starting values for the parameters. However, when the approximate roots developed by the first technique were used, the iteration converged to a set of parameters where one of the parameters is negative. This confirmed the initial findings.

Since the use of the ternary form of the Wilson equation requires a set of positive parameters, the study of the Wilson equation was discontinued. The NRTL equation developed by Renon and Prausnitz was chosen for further study since it does not contain logarithmic terms.

The Renon and Prausnitz parameter, α, was regressed for the three binary pairs. In addition, the binary data was fitted by using various preset values of α and regressing the other NRTL parameters A and B. The ternary data was then fitted solely by the use of the binary parameter thus derived.

An adaptation of Hala's method of correlation was also examined. Hala's term, $-1/2\ c\chi_3^{3/2}$, describing the coloumbic interactions, was superposed on the NRTL equation. This procedure results in a four parameter equation for the binary solvent-salt systems. Since the same value of the parameter, c, is used for both binary solvent-salt pairs, its value cancels out and the original ternary form of the NRTL equation is retained. The parameters obtained by this technique are different in value from those obtained by the previous method. The use of a four parameter equation can only be justified where the number of binary data points is large.

To correlate the isobaric systems, a bubble point subroutine was incorporated into the computer program. This subroutine was found to converge only when full dissociation of the salt was assumed in the definition of the mole fractions and activity coefficients. The activity coefficient of the solvent calculated by the assumption of full dissociation of the salt was called the ionic activity coefficient, while the mole fractions of the solvent and salt calculated by this assumption were called ionic mole fractions. These ionic quantities are strictly defined in a later section.

For certain binaries it was observed that the ionic activity coefficients were approximately unity throughout the solubility range. In order to determine whether the accuracy of the ternary predictions would be reduced by assuming such binaries to be ideal, the parameters for such binaries were preset at 0.0. When the ternary results obtained by this assumption were compared to the results obtained without the assumption, it was observed that the results were comparable or better.

To obtain the value of α_{12} that would best fit all the ternary systems, the value of α_{12} was pre-set at incremental values in the range from -1.0 to 1.0. The values of α_{13} and α_{23} were pre-set at either 0.30 or 0.0 depending on whether the assumption of ideality in the respective binaries had reasonable validity.

The more extensive isothermal data of Broul for the system methanol-water-lithium chloride was then examined by using the ionic quantities defined for the isobaric systems.

A study was carried out to determine the type of ternary fit that would be obtained from two different sets of binary solvent-solvent data.

For the system methanol-water-potassium acetate, which exhibits large temperature variations, a study was carried out to determine if the use of temperature dependent parameters would result in an improved correlation of the ternary results.

RESULTS

I. The Wilson Equation.

The system methanol-water-lithium chloride was first examined by using a parametric method adapted from Baker's technique (1). It was hoped that this method would provide a graphical means of studying the behavior of the roots of the Wilson equation for the binaries methanol-lithium chloride and water-lithium chloride. The method of Baker uses the Wilson equation for both activity coefficients, but since the Wilson equation cannot correlate the activity coefficients of the salt in the binaries in question, only the activity coefficients of the solvents are considered here. The complete derivation of the modified technique is given in the Appendix, a brief summary of the derivation and its use follows.

The Wilson equation is solved for one of its parameters Λ_{21} in terms of the other, Λ_{12}, the mole fractions X_1 and X_2 and the activity coefficient of one data point γ_1. The final expression gives

$$\Lambda_{21} = \frac{x_2 (- \frac{\Lambda_{12}}{T} - \frac{\ln \gamma_1 T}{x_2}}{1 - x_1 (- \frac{\Lambda_{12}}{T} + \frac{\ln \gamma_1 T}{x_2})} \qquad \text{(IV-1)}$$

where, $T = x_1 + \Lambda_{12} x_2$

The substitution of the expression to the right of the equal sign in equation (IV-1) for Λ_{21} in the Wilson equation results in an expression for the activity coefficient, γ_1^2, for a subsequent data point in terms of the parameter Λ_{12}

and the activity coefficient for the previous data point. Thus, from knowledge of one observed activity coefficient, a curve of activity coefficients against Λ_{12} is generated for each solvent-salt pair.

The family of curves thus obtained show a minimum point in the range from $\Lambda_{12} = 10$ to $\Lambda_{21} = 20$. When a horizontal line is traced from the value of the observed activity coefficient to the curve, two roots to the Wilson equation are found - one root on each side of the minimum point of the curve. However, both of these roots resulted in negative values for the dependent parameter, Λ_{21}.

The curves show a point of discontinuity at high values of Λ_{12}. The existence of this discontinuity can be predicted from the parametric expression derivation as shown in the appendix. The existence of this discontinuity presented the possibility of a set of positive roots to be found in areas where Λ_{21} is very large. However, a systematic search for such a set of roots failed to find them. The branch of the family of curves to the right of the point of discontinuity leveled off and did not approach the values of the observed activity coefficients.

Negative parameters of the Wilson equation are considered to be physically impossible. Because of this difficulty, it was necessary to examine the system by a more powerful method. Marina has used a non-linear least squares regression subroutine to arrive at the roots of the NRTL equation for a wide variety of systems. (22).

In using a regression subroutine different solutions of the correlating equation can be found if different starting values for the parameters are used. Silverman and Tassios (44) have shown that for negative deviations of Raoult's law, three sets of parameters can be obtained for the Wilson equation as a function of the starting values of the regression subroutine.

An initial trial was made using $\Lambda_{12} = \Lambda_{21} = 0.00$ as starting values for the solvent-salt binaries, but this choice resulted in a failure of the computer program to work. This failure occurred because Λ_{12} is contained within a logarithmic term and by using $\Lambda_{12} = 0.0$ as the starting value the subroutine attempted to assign a negative value to Λ_{12}. To prevent this problem from occurring, a restraint was used to force the regression to positive values of Λ_{12}. Whenever the subroutine returned a negative value of Λ_{12}, the minimizing function was arbitrarily set at a very large value and the activity coefficient calculation by-passed.

This procedure prevented a premature break down of the program but did not assure convergence; in fact, it resulted in a poor fit of the data for the starting values of $\Lambda_{12} = \Lambda_{21} = 0.0$. A change in the starting values to $\Lambda_{12} = 20.0$ and $\Lambda_{21} = 0.0$ resulted in a dramatic improvement in the fit of the data. A further improvement was obtained when Λ_{12} was initially set at 20.0 and Λ_{21} was set at -10.0. The regressed roots for this last set of starting values agreed well with the findings of the parametric technique.

The inability to find sets of positive roots for the Wilson equation prevented the use of this equation for correlating the ternary data from the binary parameters. The binary results are tabulated in Tables 1 and 2.

The only set of positive parameters was obtained when the starting values were set at $\Lambda_{12} = \Lambda_{21} = 1000$ for the methanol-lithium chloride binary. However, the fit obtained was poor and when the same procedure was applied to the water-lithium chloride binary, a negative value of Λ_{12} was obtained with a poor fit of the data. At this point it became necessary to abandon the Wilson equation and to examine the Renon & Prausnitz (NRTL) equation.

Table 1

System Methanol-Lithium Chloride
Correlated by the Wilson Equation

Λ_{12} Start	Λ_{21} Start	Λ_{12} Regr.	Λ_{21} Regr.	Restraint	Max.% Error in γ	Sum of Squares
0.0	0.0	-2.9	24641.	YYn=YYold	24	0.225
0.0	0.0	-2.9	56454.	YYn=2YYold	24	0.225
0.0	0.0	-2.9	56454.	YYn=100	24	0.225
20.0	0.0	18.9	-.163	YYn=2*YYold	18	0.08
20.0	-10.0	9.3	-.40	YYn=2*YYold	5	0.007
1000.	1000.	13.2	1288.8	YYn=2*YYold	15	0.060

YYn= Arbitrary new value of sum of squares. Used whenever subroutine returns negative value of Λ_{12}.

YYold = Old value of sum of squares.

Table 2

System Water-Lithium Chloride

Correlated by the Wilson Equation.

Λ_{12} Start	Λ_{21} Start	Λ_{12} Regr.	Λ_{21} Regr.	Restraint	Max. % Error in γ	Sum of Squares
0.0	0.0	-3.13	9996	YYn=2*YYold	24	0.26
20.0	0.0	20.6	-0.011	YYn=2*YYold	25	0.11
20.0	-10.0	10.4	-0.34	YYn=2*YYold	3	0.003
1000	1000	-34.5	1298.2	YYn=2*YYold	109.6	0.16

YYn = Arbitrary new value of sum of squares. Used whenever subroutine returns negative value of Λ_{12}.

YYold = Old value of sum of squares.

II. The NRTL Equation.

Due to the difficulties encountered in correlating the binary solvent-salt data with the Wilson equation, it was necessary to take a different approach. The NRTL equation seemed a reasonable alternative as its parameter can be either positive or negative. This equation derived by Renon and Prausnitz has been shown to correlate a wide variety of binary systems and can serve to predict vapor-liquid equilibrium in ternary systems from the three sets of binary parameters (34). The equation as initially conceived consists of two regressed parameters and a constant parameter α which is set at a value determined by the nature of the binary system.

In all the work with the NRTL equation, the starting values of the parameters were set at 0.0 as suggested by Marina for the NRTL equation. Figures 1 and 2 show the plot of the sum of the squares (the value of the minimized function against α for the solvent-salt binaries). It can be observed from these plots that the fit resulting from Marina's recommendation of α = -1.00 is very poor. Marina, however, did not investigate systems containing salts.

What is the specific minimization function used?

Prausnitz and Renon have not investigated the application of their equation to systems containing a salt. No precedent exists for assigning a value to α. Renon and Prausnitz have suggested a value of α of 0.30 for systems that exhibit small deviations from ideality. Since the activity coefficient for the solvent-salt binaries varied from 0.50 to 1.0, this suggestion was tested. It can be seen from figures 1 and 2 that the fit for α = 0.3 is much better than for α = -1.00. However, both binary systems were correlated best by values of α close to 0.0. The minima of the curves corresponded to the regressed values of α. Therefore, the first attempts to fit the ternary data were made by using the regressed values of α for the solvent-salt pairs. It must be noted though that using the value of α that gives the best binary fit does not always result in a good ternary fit.

Three possibilities initially existed regarding the value of α for the solvent-solvent binary: $\alpha_{12} = 0.30$, $\alpha_{12} = -1.00$ and α_{12} regressed. It was observed that the error in calculating ternary γ_1 were large positive errors (largest 85%) for the case $\alpha_{12} = -1.00$. The errors in calculating γ_1 for the cases $\alpha_{12} = 0.30$ and α_{12} regressed were large negative errors (largest: -59% and -38%, respectively). As other values of α_{12} were tried, the pattern seemed to indicate that a better fit existed in the range $-1.00 < \alpha_{12} < -0.15$. By trial and error it was found that $\alpha_{12} = -0.40$ resulted in an extremely good fit for γ_1. Figure 3 shows the plot of the average absolute error in γ_1 plotted against α_{12}. As shown in Table 3, the error in the calculated vapor phase mole fraction (y_1) is lowest for $\alpha_{12} = -0.40$. The error in y_1 for the case α_{12} regressed is considered to be acceptable. For the cases $\alpha_{12} = 0.30$ and $\alpha_{12} = -1.00$ the errors are high.

The activity coefficient and vapor phase mole fraction of methanol appear to be very sensitive to the value of α_{12}. The activity coefficient for water, on the other hand, appears to be insensitive to the value of α_{12} and the error in calculating this coefficient is small regardless of the value of α_{12}.

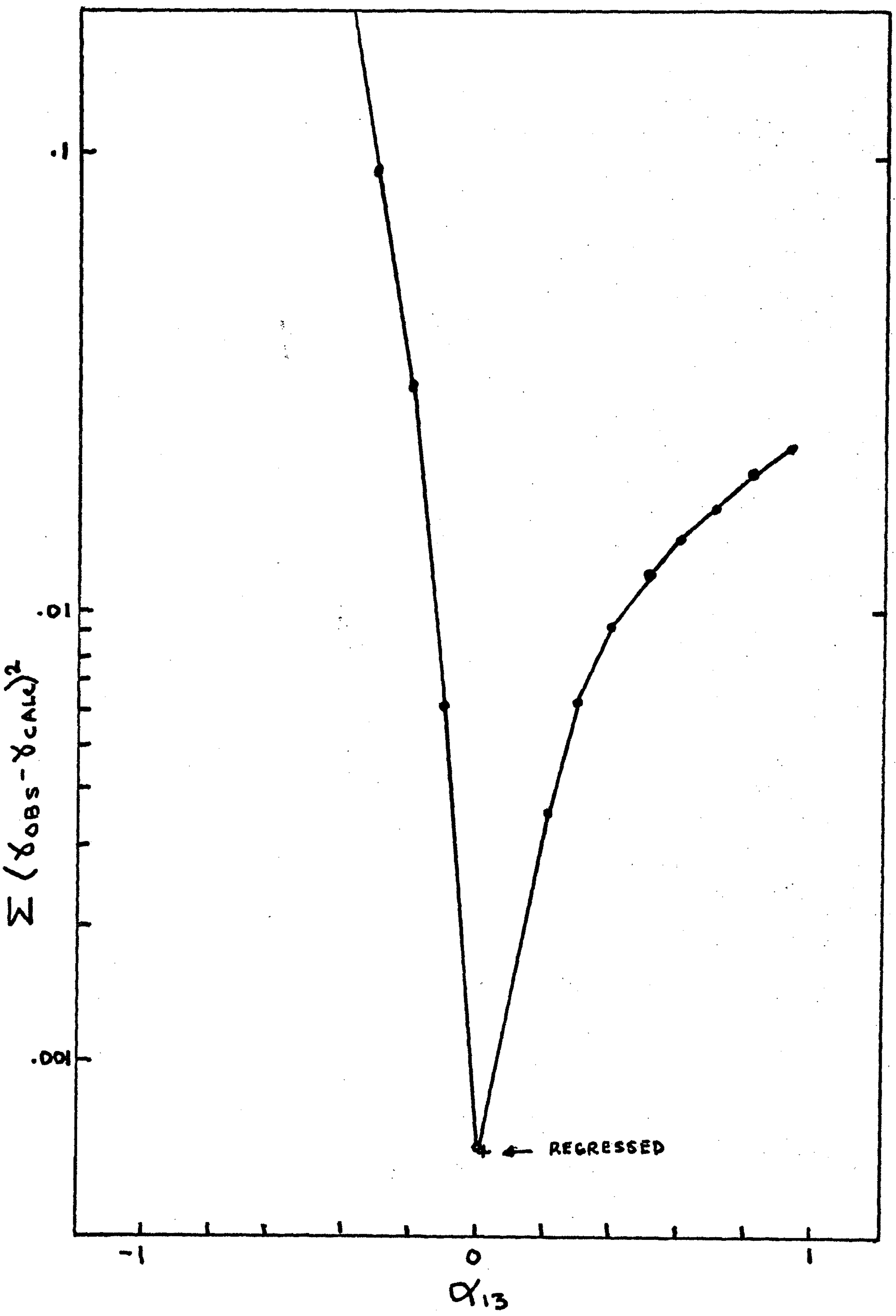
Throughout this work, the ternary vapor phase mole fraction is calculated in terms of the ratio of the calculated activity coefficients (γ_1/γ_2).

As mentioned earlier, in this section the regressed values of α_{13} and α_{23} were used. This procedure however, can only be justified where sufficient data points exist to permit the regression of three parameters. In later sections it will be found more convenient to use preset values of α for the solvent-salt pairs.

From the work in this section the possibility of correlating vapor-liquid equilibrium data for systems containing a dissolved salt by means of the NRTL equation has been demonstrated.

The next section will consider the possibility of adapting Hala's superposition method to the NRTL equation. The same sets of data used in this section will be used in the next.

MeOH - LiCl Figure 1



H₂O - LiCl Figure 2

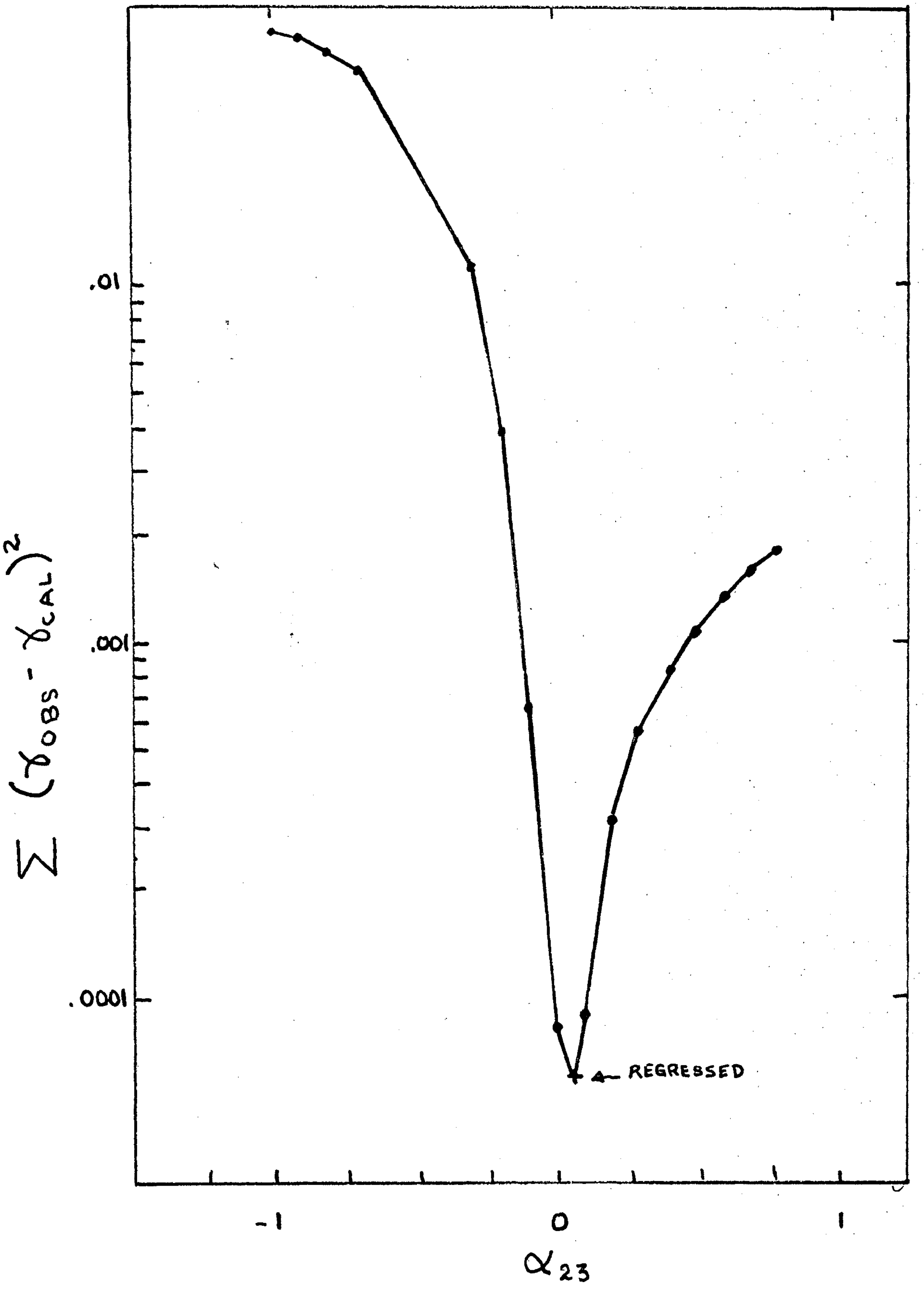


Table 3

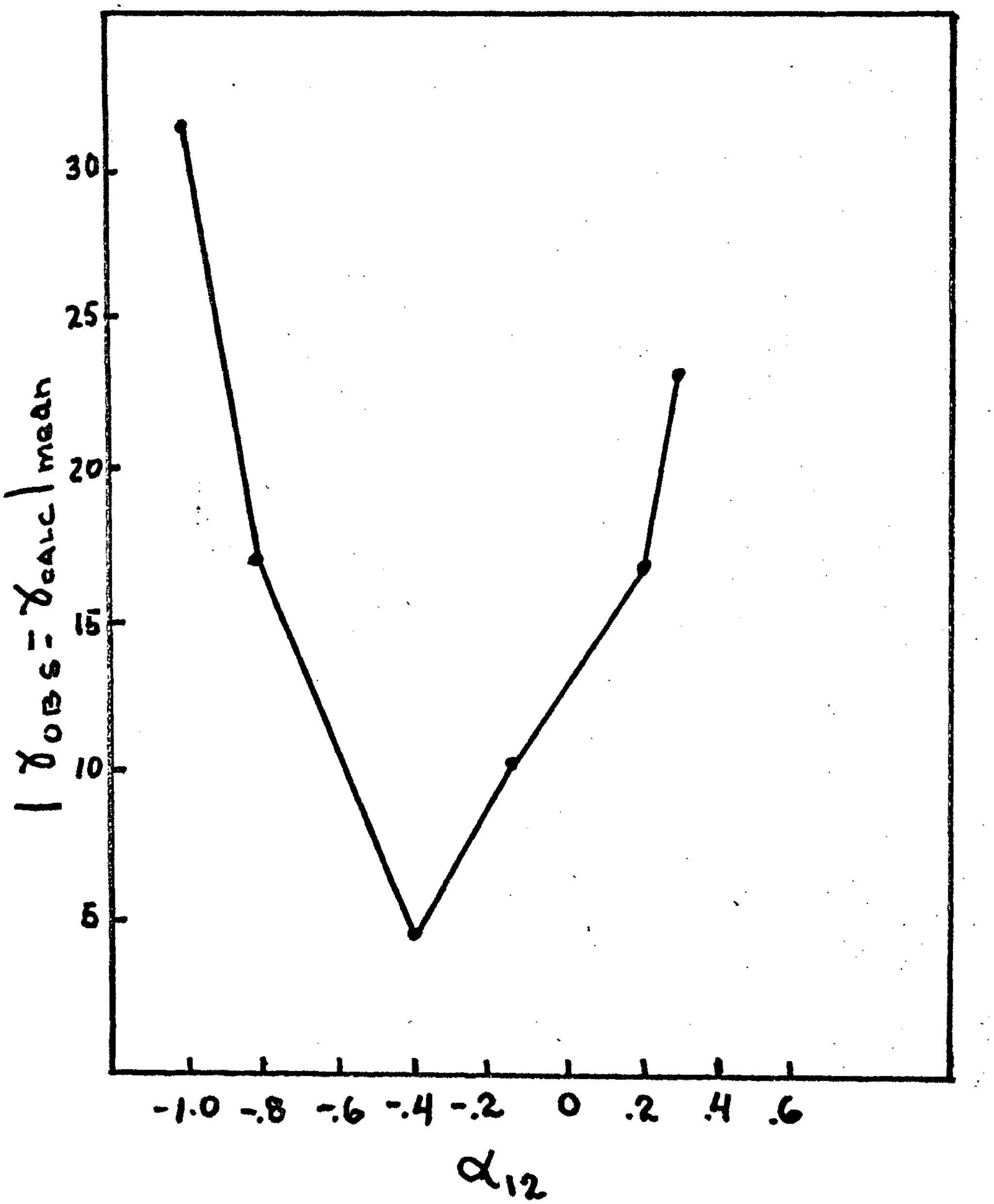
Ternary Results NRTL Equation for
Methanol (1)- Water (2) - Lithium Chloride (3).

α_{12}	$\alpha_{23}{}^{*}$	$\alpha_{31}{}^{*}$	$\Sigma\lvert\Delta y\rvert/n$
0.30**	0.01	0.05	0.054
-1.00**	0.01	0.05	0.078
-0.15*	0.01	0.05	0.021
-0.40**	0.01	0.05	0.0076
-0.50**	0.01	0.05	0.0119

* = Regressed

** = Pre-set

MeOH-H_2O-LiCl
Figure 3



III. Modification of the NRTL Equation by the Hala Technique.

As previously mentioned, Hala has correlated the system methanol-water-lithium chloride by superposing an expression for the columbic interactions on the Margules equation. An analogous method was used in this study. The expression for the coloumbic interactions on the NRTL equation.

The mean rational activity coefficient as defined by Hala is:

$$\gamma_{1\pm} = \frac{P_T}{(x_{1\pm} \cdot P_1^o)} \qquad \text{(IV-2)}$$

where,

P_T = total pressure

P_1^o = pure solvent vapor pressure

$x_{1\pm} = \frac{x_1}{x_1 + \nu x_3}$, mean rational mole fraction of solvent

x_1 = analytical mole fraction of solvent

x_3 = analytical mole fraction of salt

ν = number of ions in one mole of salt, for LiCl, $\nu = 2$.

The coloumbic interactions for a solvent-salt system in which the salt consists of two ions are represented by a function

$$C = -1/2\, c\, x_2^{\,3/2} \qquad \text{(IV-3)}$$

where x_2 is the analytical mole fraction of the salt and c is a constant. By adding this expression to the NRTL equation and fitting the modified equation to the observed mean rational activity

TABLE 4

Ternary Results by Modified NRTL Equation by the Addition of Hala Term for Methanol (1) - Water (2) - Lithium Chloride (3).

α_{12}	α_{23}	α_{31}	Δy max	$\frac{\sum \lvert\Delta y\rvert}{N}$
-1.00	-1.00	-1.00	0.23	.057
0.20	0.20	0.20	0.24	.051
0.30	0.30	0.30	0.28	.058
0.30	0.00	0.00	0.11	.029
0.00	0.00	0.00	0.028	.008
-1.00	0.00	0.00	0.24	.112

coefficients ($\gamma_{1\pm}$) defined by equation 2 it was hoped to obtain an improved correlation.

Hala recommended for the sake of simplicity that the same value of c be used for both solvent-salt pairs. This procedure has the effect of eliminating two parameters, c_{13} and c_{23}, from the ternary expression. This recommendation was followed in this study.

The binary methanol-lithium chloride was fit using a pre-set value of α and three variable parameters, A_{13}, A_{31} and c. Using the same value of α and the regressed value of c, the water-lithium chloride system was fit to obtain the regressed values of A_{23} and A_{32}.

For the binary methanol-water, the value of α was pre-set at four different values, -1.00, 0.30, 0.20 and 0.0. Using the regressed values of the parameters, the ratio γ_1/γ_2 is calculated for the ternary data and from this ratio the calculated values of the vapor phase mole fraction are derived. Since the parameter c cancels out in this expression, the ternary form of the NRTL equation remains intact in form and only the values of the binary parameters are affected by this treatment. However, if the fit of the activity coefficients is of interest, the terms including c_{13} and c_{23} must be retained in the ternary form of the NRTL equation.

The results obtained for this method are tabulated in Table 4. It can be seen that the fit of the vapor phase mole fraction was very sensitive to the pre-set values of the α's.

The best results were obtained for the case $\alpha_{12} = \alpha_{13} = \alpha_{23} = 0.0$. However, acceptable results were also obtained for the case $\alpha_{12} = 0.30$, $\alpha_{13} = \alpha_{23} = 0.0$.

At this point the study of this method was discontinued because the superposition of the Hala correction did not provide better results, as a comparison between Tables 3 and 4 indicates. In addition, in the currently available sets of data, the number of points for the solvent-salt pairs is seldom large enough to justify the regression of more than two parameters.

The remainder of the work in this study concentrated on the use of the NRTL equation for the type of systems under consideration. The next section will deal with several isobaric systems.

Further work on the isothermal methonal water-lithium chloride system was carried out at the conclusion of the investigation on isobaric systems. This work is reported in a later section.

IV. The NRTL Equation for Isobaric Systems.

A) Methanol-Water-Calcium Chloride.

To investigate the applicability of the NRTL equation to isobaric systems containing a salt, the system methanol-water-calcium chloride was studied. The binary parameters of the NRTL equation were derived as before and the Antoine equation was used to find the vapor pressure of the pure solvent at the various temperatures. The Antoine constants are given in the Appendix.

The first attempt was to use the NRTL equation with regressed α's. However, it was found that the regressed α for the solvent-solvent binary was very sensitive to the particular set of data used. Omission of one data point resulted in a completely different value of α_{12}. For this reason, the regression of α was discarded in favor of the method of pre-setting α at a specific value while regressing the other parameters.

The value of α was initially pre-set at three values 0.0, -1.00 and 0.30. The parameters generated were used to attempt to fit the ternary data. A bubble-point subroutine was incorporated into the computer program for the ternary system. The bubble point calculation was based on the analytical mole fractions as follows:

$$\gamma_1 x_1 P_1^o + \gamma_2 x_2 P_2^o = Q \qquad \text{(IV-4)}$$

The value of the temperature was iterated until the function $(Q - P_T)$ where P_T = total pressure reached a value of less than 1 mm Hg. The bisection iteration method was used in this subroutine. This method assumes convergence of the iteration provided that the function has a root within the interval chosen.

It was found, however, that the errors in the activity coefficients were so large as to make the function ($Q-P_T$) always a large positive number for a broad temperature range (0-200°C).

The second approach taken was far more successful. The salt was assumed to fully dissociate in the binaries and ternary systems. The ionic mole fractions were defined for the binary systems as follows:

$$x_1' = \frac{x_1}{x_1 + \nu x_2} \qquad \text{(IV-5)}$$

$$x_2' = 1 - x_1' \qquad \text{(IV-6)}$$

where,

x_1' = ionic mole fraction of solvent in liquid

x_2' = ionic mole fraction of salt in liquid

x_1 = analytical mole fraction of solvent in liquid

x_2 = analytical mole fraction of salt in liquid

ν = number of ions resulting from dissociation of one molecule of salt.

The activity coefficient of the solvent in the binary was defined as follows:

$$\gamma_1' = P_T / (x_1' \cdot P_1^\circ) \qquad \text{(IV-7)}$$

where,

γ_1' = ionic activity coefficient

P_T = total pressure

x_1' = ionic mole fraction of solvent

P_1° = pure solvent vapor pressure at the temperature of system

The observed ionic activity coefficients as defined by equation (IV-7) were fit by the NRTL expression for γ_1 using the ionic mole fractions instead of the analytical mole fractions. The parameters generated were used to fit the ternary ionic activity coefficients which are defined by

$$\gamma_1' = y_1 P_T / (x_1' \cdot P_1^o) \qquad \text{(IV-8)a}$$

and

$$x_1' = \frac{x_1}{x_1 + x_2 + \nu x_3}$$

$$\gamma_2' = y_2 P_T / (x_2' \cdot P_2^o) \qquad \text{(IV-8)b}$$

$$x_2' = \frac{x_2}{x_1 + x_2 + \nu x_3}$$

where,

γ_1', γ_2' = ionic activity coefficients of solvents
y_1, y_2 = vapor phase mole fractions of solvents
P_T = total pressure
x_1', x_2' = ionic liquid phase mole fraction of solvents 1 and 2
P_1^o, P_2^o = vapor pressure of the pure solvents 1 and 2 at temperature of system.

The ionic mole fraction of the salt is defined by

$$x_3' = 1 - x_1' - x_2' \qquad \text{(IV-9)}$$

The ionic mole fractions are used to generate the calculated values of γ_{1i} and γ_{2i} with the NRTL equation. The bubble point is calculated by

$$\gamma_1' x_1' P_1^o + \gamma_2' x_2' P_2^o = Q \qquad \text{(IV-10)}$$

This method resulted in convergence for all data points. However, the average error in the vapor phase mole fraction was large for all the parameters tried. For $\alpha_{12} = -0.10$ the mean error in y_1 was acceptable but the maximum error in y_1 was 0.09 mole which was thought to be unacceptable. Table 5 summarizes these results.

In the previous section, the regressed values of α for the two solvent-salt pairs were used. However, since for most solvent-salt pairs the number of data points would not justify the regression of three parameters, the decision was made to pre-set the values of α_{13} and α_{23}. Table 5 shows a comparison of the results obtained by setting the values of α for the solvent-salt pairs at 0.30 and 0.0. The value of $\alpha = 0.30$ gave considerable better results. This value was arbitrarily assigned to α_{13} and α_{23} to arrive at the other values on Table 5. No attempt was made to arrive at optimum values of α for the solvent-salt pairs.

By examining the variation of the activity coefficient in the methanol-calcium chloride binary, it was proposed that this binary could be treated as an ideal solution and its parameters set to 0.0. The values of γ_1 varied from 1.009 to 1.046. The assumption of ideality, although not strictly valid, is acceptable for this particular case. In effect, this assumption is similar to the treatment given by Rousseau and co-workers in neglecting the effect of the salt on the vapor pressure of the alcohol for water-alcohol-salt solutions.

With the assumption of ideality for the methanol-calcium chloride binary, the ternary system was examined for values of α_{12} in the range -1.00 to 1.50. The results are tabulated in Table 6. A comparison of Tables 5 and 6 indicates that for this system better results are obtained by assuming the methanol-calcium chloride binary to behave ideally.

Table 5

Non-Ideal Treatment of the Methanol-$CaCl_2$ Binary in the System Methanol-Water-Calcium Chloride *.

α_{12}	α_{13}	α_{23}	$\lvert\Delta y_1\rvert_{mean}$
0.30	0.00	0.00	.142
0.30	0.30	0.30	.065
0.60	0.30	0.30	.085
-0.40	0.30	0.30	.088
-0.10	0.30	0.30	.039

* The values of α were pre-set while all other binary parameters were regressed. Data for 1-2 binary from Perry (31).

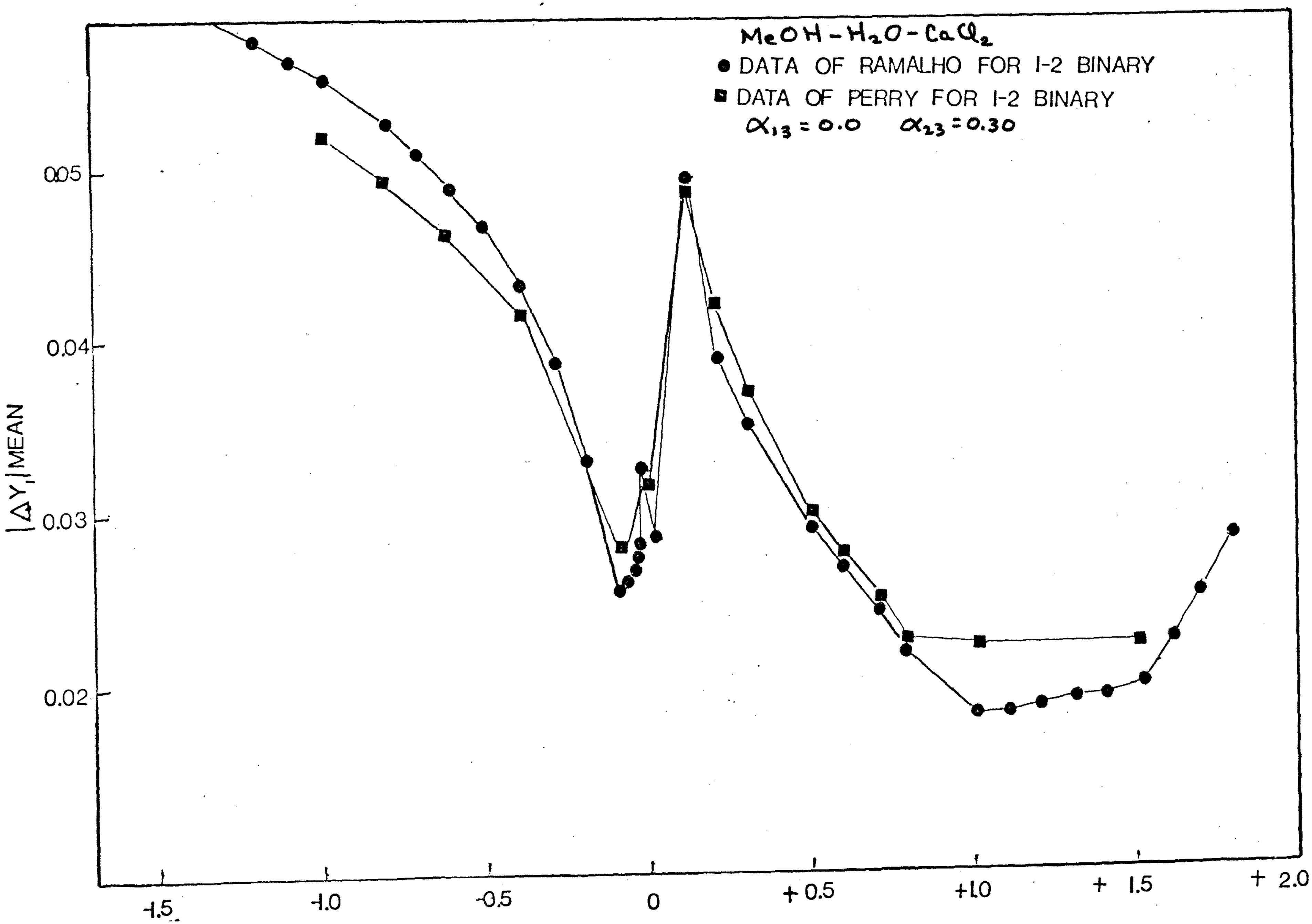
Table 6

Results for Methanol-Water-Calcium Chloride Assuming Ideal Behavior for the Methanol-Calcium Chloride Binary*.

($\alpha_{13} = 0.0$, $\alpha_{23} = 0.30$)

α_{12}	$\lvert\Delta y_1\rvert$ mean	Max. Error in y_1	Max. Temp. Error	Max. Error in γ_1	Max. Error in γ_2
-1.00	.053	.068	10.2	53.7	15.3
-0.80	.050	.100	10.1	52.6	15.5
-0.60	.047	.091	9.9	51.3	15.7
-0.40	.043	.081	9.6	49.8	15.9
-0.10	.029	.048	8.6	44.3	17.0
0.00	.033	.051	9.2	47.9	16.2
0.10	.050	.100	10.0	52.5	15.3
0.20	.043	.080	9.4	48.9	15.8
0.30	.037	.070	9.1	47.0	16.1
0.40	.033	.066	8.9	45.5	16.4
0.50	.031	.056	8.6	44.2	16.4
0.60	.028	.049	8.0	42.8	16.6
0.70	.025	.044	7.6	41.5	16.7
0.80	.023	.045	8.0	40.2	16.9
0.90	.023	.044	7.7	38.7	17.0
1.00	.023	.043	7.5	37.3	17.1
1.50	.023	.054	5.8	28.4	17.8

* Data for the 1-2 binary from Perry (31).


MeOH - H₂O - CaCl₂
● DATA OF RAMALHO FOR 1-2 BINARY
■ DATA OF PERRY FOR 1-2 BINARY
$\alpha_{13} = 0.0$ $\alpha_{23} = 0.30$
$|\Delta Y_1|$ MEAN
0.05
0.04
0.03
0.02
-1.5
-1.0
-0.5
0
+ 0.5
+1.0
+ 1.5
+ 2.0

METHANOL- WATER -CALCIUM CHLORIDE

$\alpha_{13} = 0.0 \quad \alpha_{23} = 0.30$

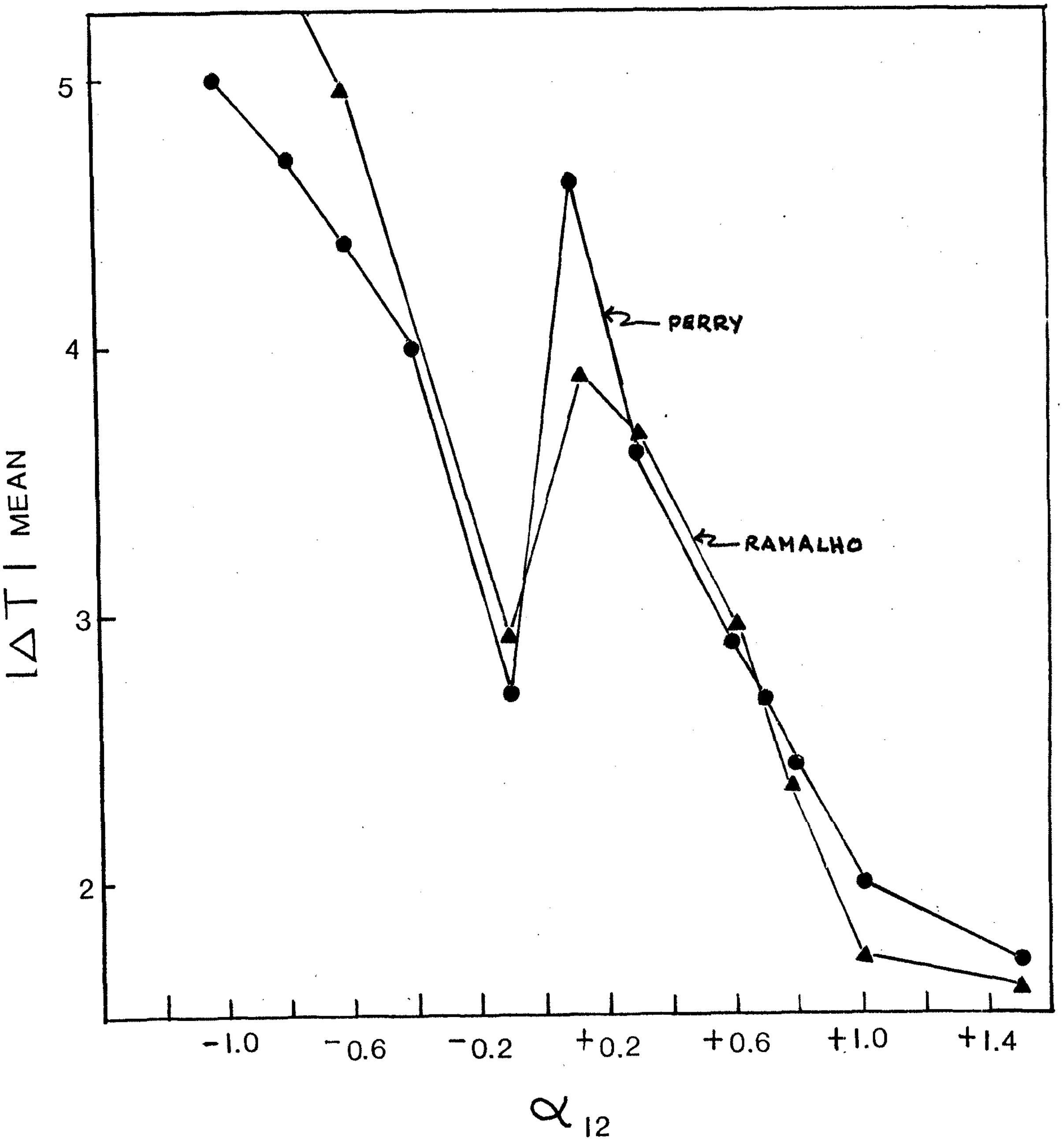


Figure 5.

METHANOL-WATER-CALCIUM CHLORIDE

$\alpha_{12} = 1.0$

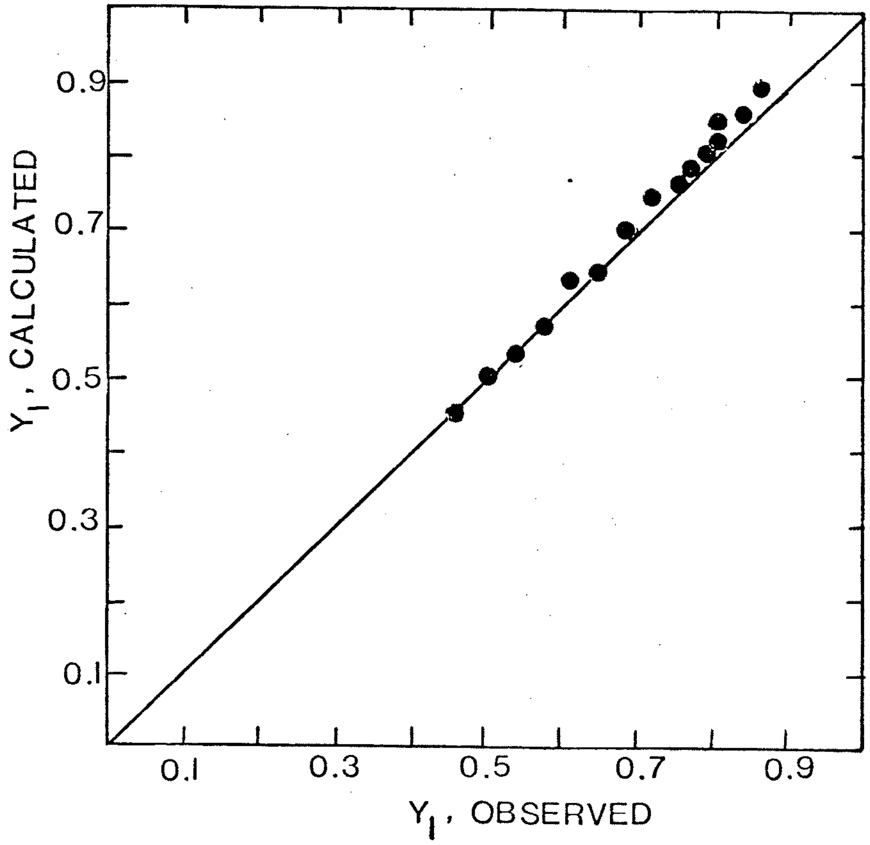


Figure 6

The errors for the vapor phase mole fractions were considered acceptable for α_{12} = -0.10 and α_{12} in the range 0.60 to 1.00. The error in calculating the activity coefficients is high. The maximum error in the temperature calculation for these values of α_{12} is high (7.5-8.6°C). The error in temperature, however, is less than 5° C for 13 out of the 15 data points for these values of α_{12}.

To test the effect that different sets of binary solvent-solvent data will have on the correlation of the ternary data, the data of Ramalho et al. (33) for the methanol-water system was compared to the previously used data of Perry (31). Figure 4 shows the plot of $|\Delta y_1|$mean vs. α_{12} for the ternary results obtained using both sets of finary data. Figure 5 gives the error in temperature calculation against α_{12} for both sets of data. It can be seen from these figures that the two sets of binary data result in very similar ternary results. The more accurate data of Ramalho, however, gives improved errors in the mole fraction calculation.

Figure 6 gives the plot of $y_{1_{cal}}$ against $y_{1_{obs}}$ for α_{12} = 1.0 using the binary data of Ramalho. It can be seen from this plot that the correlation for this system is very good.

A final trial was made by assuming that the salt dissociates fully in the ternary system and in water-calcium chloride binary system but does not dissociate at all in the methanol-calcium chloride binary. Although this assumption is reasonable, it yielded very poor ternary results.

The assumptions made in this section will be tested for three other isobaric systems in the sections that follow. The redefinition of the mole fraction and activity coefficient undertaken in this section will also be tested for the isothermal system methanol-water-lithium chloride discussed in the previous section.

B) Methanol-Water-Potassium Acetate.

To investigate the validity of the preliminary conclusions reached for the system methanol-water-calcium chloride, the system methanol-water-potassium acetate was studied.

The first trial was made using the analytical mole fractions. The same difficulty was encountered in the bubble-point calculation as with the methanol-water-calcium chloride system. The subroutine failed to converge due to the large values of the function $(Q-P_T)$ for values of α_{12} of -1.00, and 0.30.

A second trial was made using the ionic mole fraction as defined in tha last section. This method was tried for two values of α_{12}, 0.30 and -0.10 while setting $\alpha_{13} = \alpha_{23} = 0.30$. Although convergence was obtained in the bubble-point subroutine, the errors in calculating the activity coefficients were very large. The corresponding errors in the bubble-point temperatures were also very large. An explanation for the large errors encountered in this system is offered in the discussion section. The results are given in Table 7.

It was observed that the ionic activity coefficients for the water-potassium acetate binary varied from 0.65 to 1.00, while the ionic activity coefficients for the methanol-potassium acetate binary varied from 1.014 to 1.065 throughout the solubility range. Although the departure from unity of the activity coefficients for the methanol-potassium acetate system was greater than in the methanol-$CaCl_2$ system discussed in the last section, it was decided to investigate the predictions that would occur

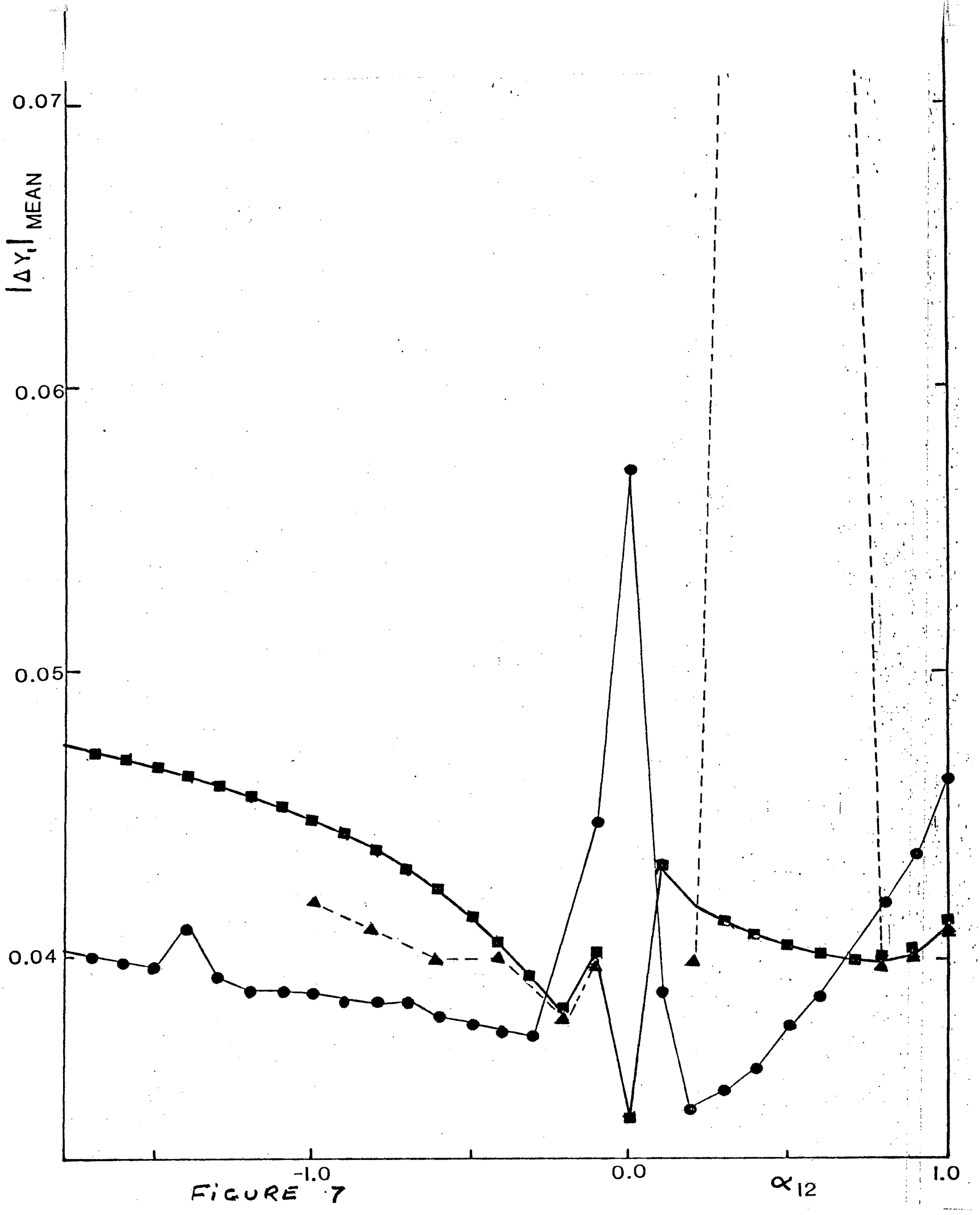


FIGURE 7

METHANOL -WATER- POTASIUM ACETATE

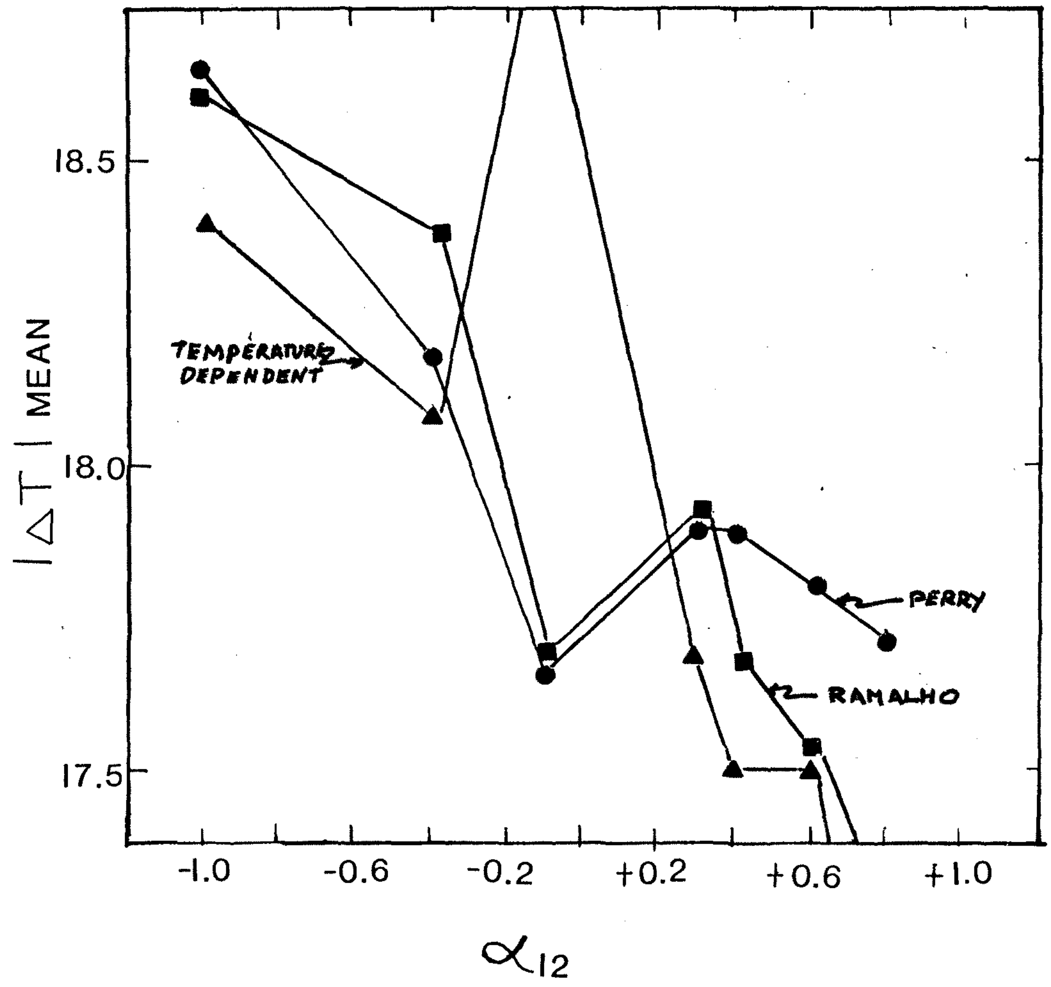


FIGURE 8

METHANOL-WATER- POTASSIUM ACETATE

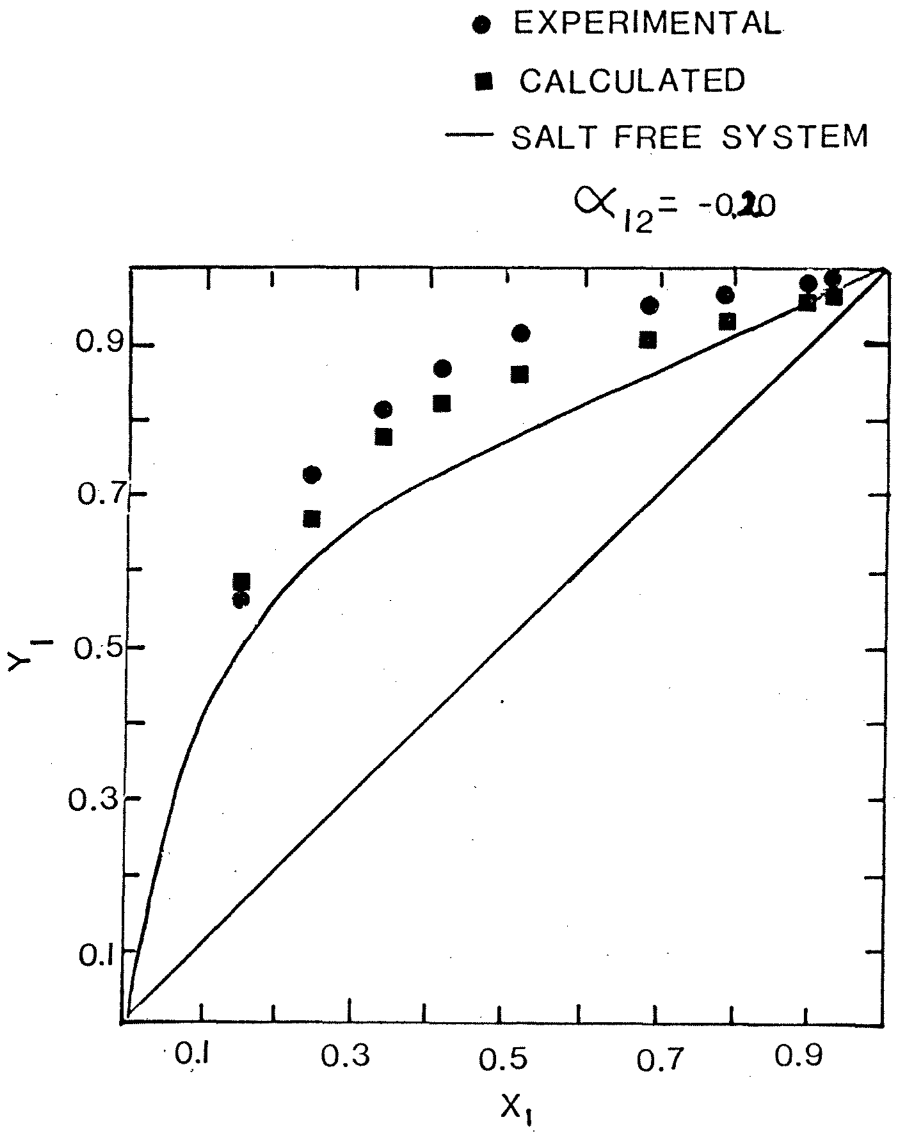
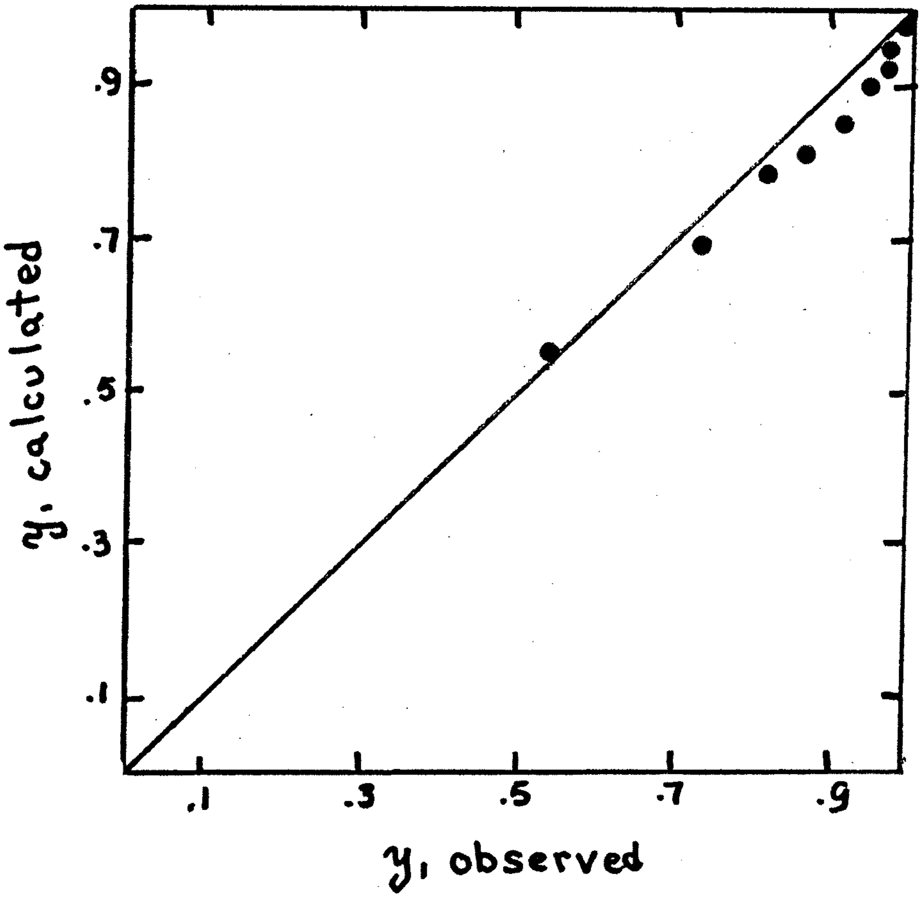


FIGURE 9

Fig 10

MeOH - H_2O - POTASSIUM ACETATE

$\alpha_{12} = -0.20$



if the methanol-potassium acetate binary was considered ideal.

Setting all the parameters of the methanol-potassium acetate binary equal to 0.0 and $\alpha_{23} = 0.30$ the value of α_{12} was varied between -1.0 and +1.0. The results are given in Table 8. It can be observed when comparing the values of Table 8 to those of Table 7 that assuming the methanol-potassium acetate binary to behave ideally results in a reduction in the maximum error in y_1.

As evidenced by Table 8, large errors were encountered in the calculation of the temperature for this system. A possible explanation for these errors is offered in the discussion section. An attempt was made to improve these errors by use of parameters that were linear functions of temperature, to account for the large temperature variations encountered in the three binary and the ternary systems (up to 61°C). These functions are described in the Appendix. This approach failed to yield an improvement in the temperature error.

Figure 7 shows the plot of $|\Delta y_1|_{mean}$ vs. α_{12} for the temperature dependent parameters as well as for temperature independent parameters using the binary data of Perry and Ramalho. Figure 8 shows the plot of $|\Delta T|_{mean}$ vs. α_{12}.

Figure 9 shows the plot of y_1 vs. x_1 for $\alpha_{12} = -0.20$. It can be seen from this plot that in spite of the large temperature errors observed, the NRTL can correlate the vapor phase mole fraction with good accuracy. Figure 10 shows the plot of $y_{1\,cal}$ vs. y_{1obs} for $\alpha_{12} = -0.20$.

Two additional isobaric systems will be examined next.

Table 7

Non-Ideal Treatment of the Methanol-Potassium Acetate Binary in the System Methanol-Water-Potassium Acetate ($\alpha_{13} = \alpha_{23} = 0.30$).

α_{12}	$\lvert\Delta y_1\rvert$mean	Max.Error in y_1	Max.Error in γ_1	Max.Error in γ_2	Max.Error in Temp.
-0.10	.026	.085	234.6	285.0	36.6
0.30	.056	.264	625.7	329.1	32.2

Table 8

Results for Methanol-Water-Potassium Acetate Assuming Ideal Behavior for the Methanol-Potassium Acetate Binary*(α_{13} = 0.0, α_{23} = 0.30).

α_{12}	$\lvert\Delta y_1 \text{ mean}\rvert$	Max.Error in y_1	Max.Error in γ_1	Max.Error in γ_2	Max.Error in Temp.
-1.00	0.042	0.077	211	374	35.4
-0.80	0.041	0.076	201	370	34.9
-0.60	0.040	0.076	190	365	34.2
-0.40	0.040	0.075	178	360	33.5
-0.20	0.036	0.072	154	355	31.9
0.00	0.036	0.066	147	357	31.4
0.30	0.074	0.133	144	418	35.9
0.40	0.074	0.135	142	416	35.7
0.50	0.075	0.139	139	415	35.4
0.60	0.075	0.139	135	412	35.4
0.70	0.076	0.142	132	410	35.2
0.80	0.040	0.073	137	327	30.9
0.90	0.041	0.075	132	323	30.4
1.00	0.042	0.073	127	318	30.1

* Data of Perry (31) for the 1-2 binary.

C) Methanol-Water-Mercuric Chloride.

The method developed for the previous isobaric systems was also tried for this system. Certain reservations exist regarding the accuracy of the binary data used for the correlation of this ternary system. These reservations will be the subject of later discussion.

Because of the low solubility of mercuric chloride in water theis solvent-salt pair was assumed to behave ideally. Full dissociation of the salt in methanol and in the mixed solvent was assumed. The parameter α_{13} was pre-set at 0.30 while α_{12} was varied in the range from -1.00 to 0.80. The results are given in Table 9.

Figure 11 compares the behavior of $|\Delta y_1|_{mean}$ vs. α_{12} using the data of Ramalho for the 1-2 binary to that obtained. The more accurate data of Ramalho gives a minimum near $\alpha_{12} = -1.00$. Figure 12 shows the same comparison for the behavior of $|\Delta T|_{mean}$ against α_{12}. A minimum is observed for this curve near $\alpha_{12} = -0.10$.

Figure 13 shows a plot of $y_{1\,obs}$ vs. x_1 for $\alpha_{12} = -1.00$ using the parameters developed from the binary data of Ramalho. Figure 14 shows a plot of $y_{1\,cal}$ vs. $y_{1\,obs}$ for the same value of α_{12}. Figure 13 shows a failure of the method to predict the salt-effect for this system.

Table 9

Results for Methanol-Water-Mercuric Chloride Assuming Ideality for the Water-Mercuric Chloride Binary* ($\alpha_{13} = 0.30$).

α_{12}	$\lvert \Delta y_1 \rvert$ mean	Max.Error in y_1	Max.Error in γ_1	Max.Error in γ_2	Max.Error in Temp.
-1.00	0.043	0.0716	14.5	71.7	4.0
-0.80	0.043	0.0720	13.9	72.1	4.0
-0.60	0.042	0.0722	13.5	72.3	4.1
-0.40	0.042	0.0717	13.9	72.1	4.1
-0.30	0.043	0.0695	15.5	70.7	4.0
-0.20	0.042	0.0689	15.0	69.6	3.8
-0.10	0.047	0.0679	14.8	67.4	3.4
0.00	0.044	0.0761	7.3	71.8	3.5
0.10	0.041	0.0832	13.7	78.0	5.2
0.20	0.040	0.0810	11.8	77.5	4.6
0.30	0.040	0.0804	11.4	77.1	5.0
0.40	0.040	0.0802	11.4	76.9	4.7
0.50	0.040	0.0804	11.7	77.0	4.9
0.60	0.041	0.0804	11.6	77.0	4.9
0.70	0.041	0.0811	12.6	77.2	4.8
0.80	0.041	0.0816	13.2	77.3	4.8

* Data of Perry (31) for the 1-2 binary.

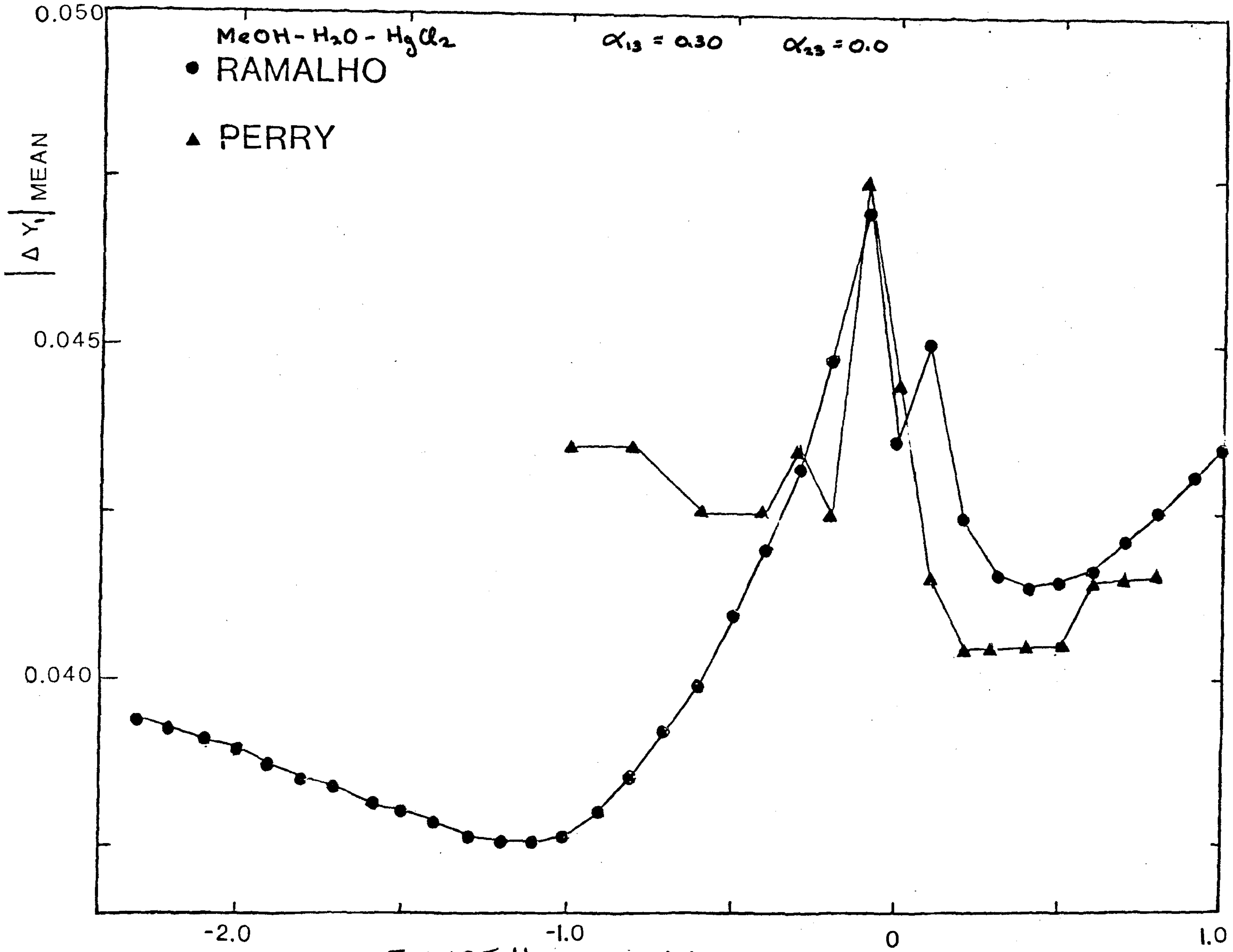

MeOH - H$_2$O - HgCl$_2$
$\alpha_{13} = 0.30$
$\alpha_{23} = 0.0$
● RAMALHO
▲ PERRY
$|\Delta Y_1|_{MEAN}$
0.050
0.045
0.040
-2.0
-1.0
0
1.0
α_{12}

FIGURE 11

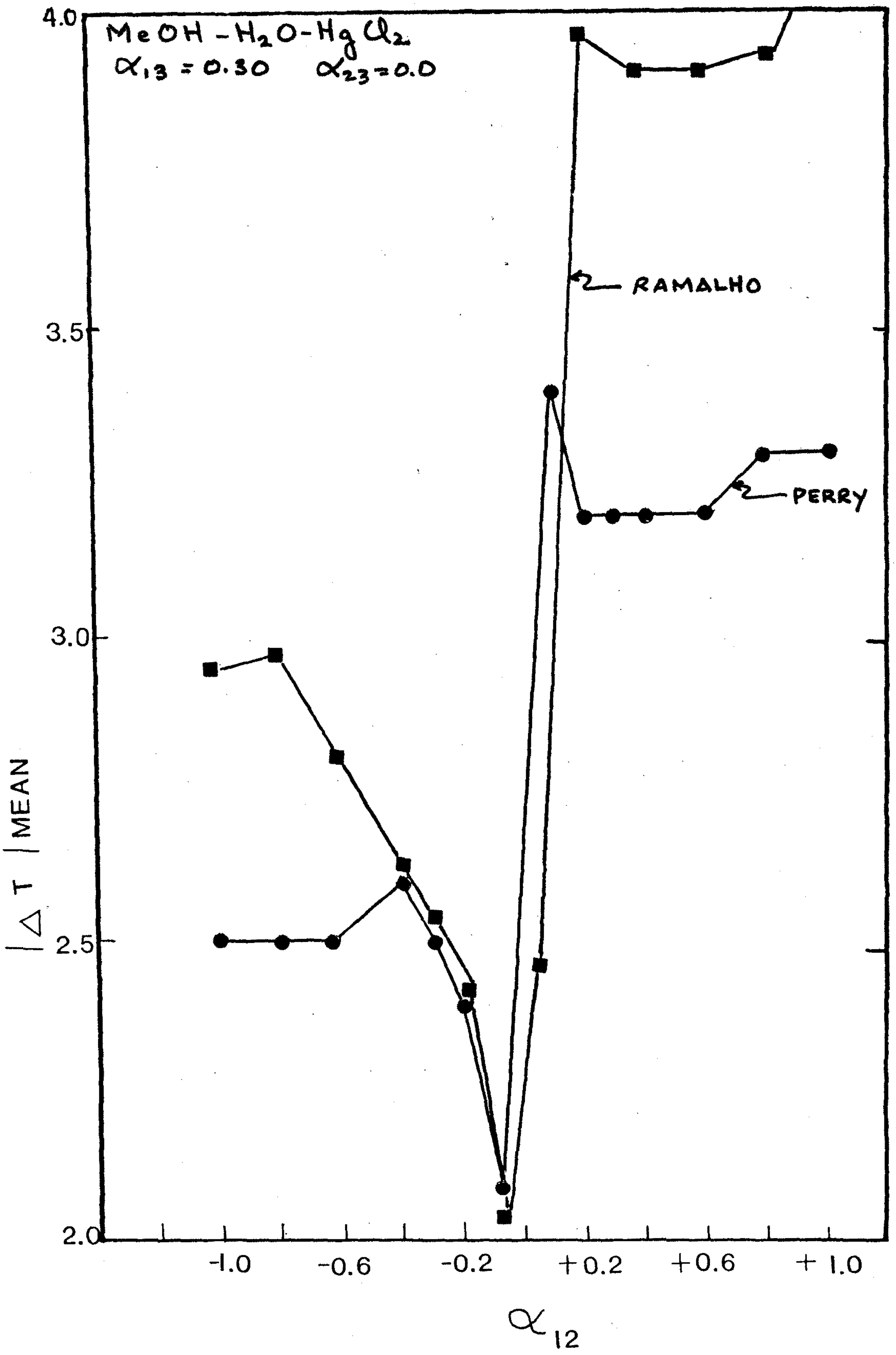

MeOH - H2O - HgCl2
α13 = 0.30 α23 = 0.0
RAMALHO
PERRY
4.0
3.5
3.0
2.5
2.0
|ΔT|MEAN
-1.0
-0.6
-0.2
+0.2
+0.6
+1.0
α12

FIGURE 12

FIGURE 13

METHANOL-WATER-MERCURIC CHLORIDE

$\alpha_{12} = -1.0$

● EXPERIMENTAL
+ CALCULATED
— SALT FREE

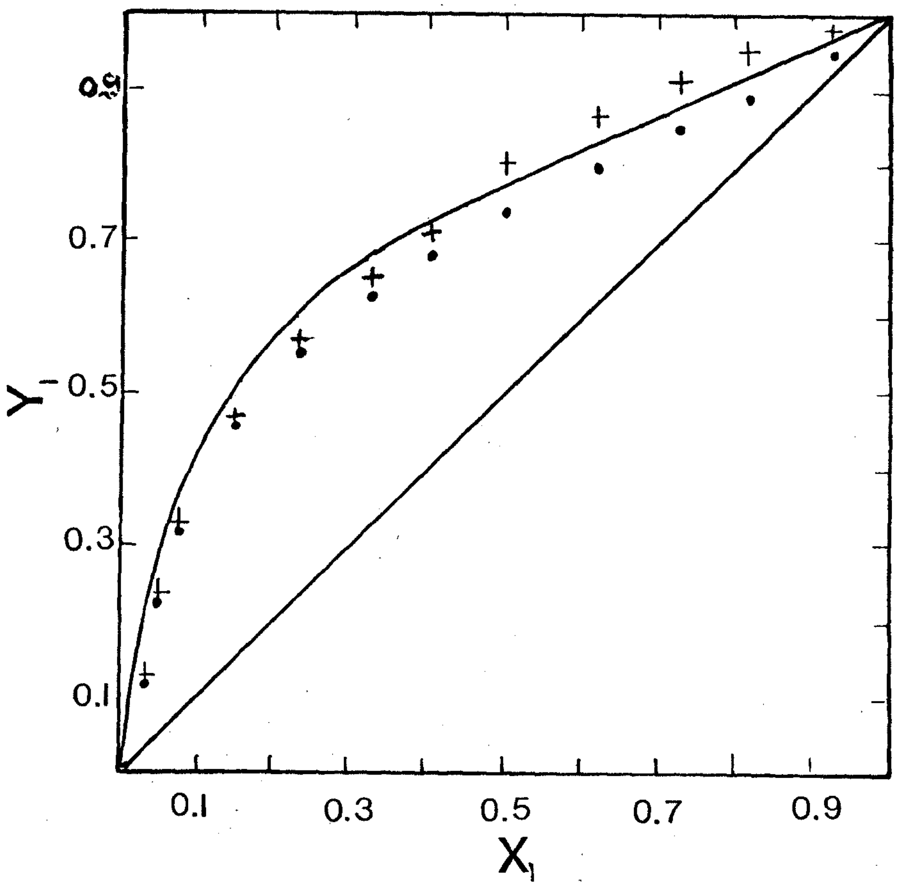
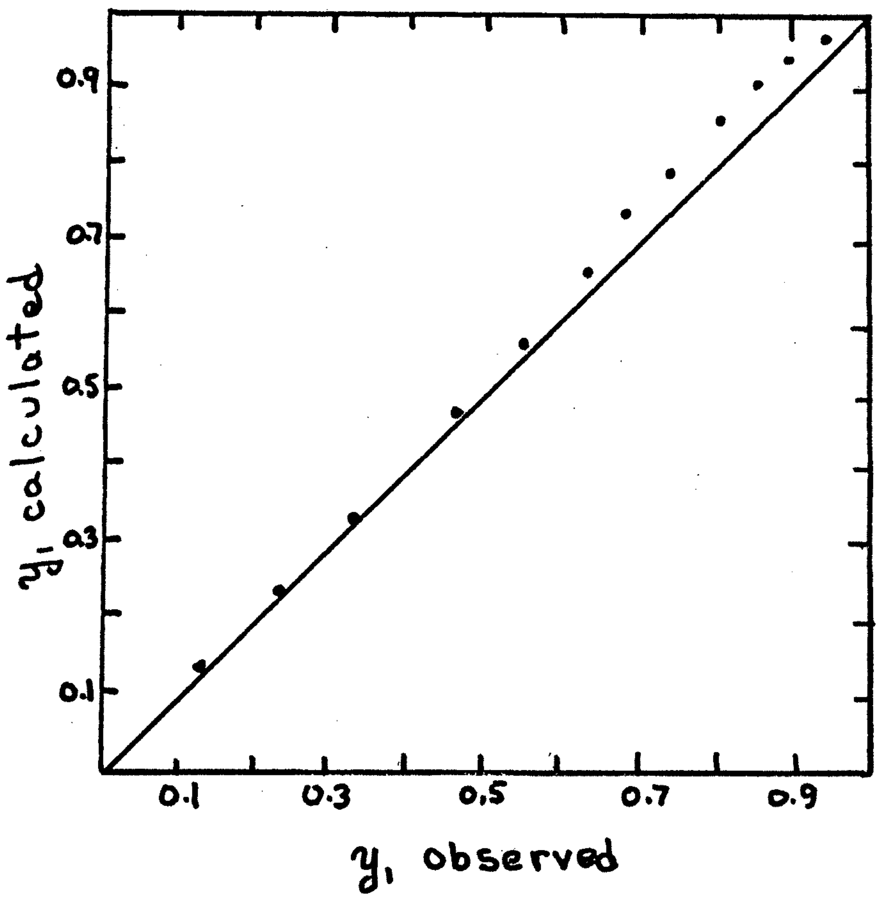


Fig 14

METHANOL-WATER-$HgCl_2$

$\alpha_{12} = -1.00$



D) Ethanol-Water-Mercuric Chloride.

The same procedure used for the last system was repeated for the ethanol-water-mercuric chloride. Again the water-mercuric chloride binary was assumed to behave ideally. The results are summarized in Table 10.

Figure 15 shows the behavior of $|\Delta y_1|_{mean}$ vs. α_{12} for the binary data of Ramalho and Perry. Figure 16 shows the behavior of $|\Delta T|_{mean}$ vs. α_{12} for the two sets of data. Figure 17 shows the plot of y_1 vs. x_1 for $\alpha_{12} = -0.30$ using the binary data of Ramalho. This plot shows that effect has been incorrectly predicted as salting-out. A reasonable explanation for the failure of the method in this system is offered in the discussion section. Figure 18 shows a plot of $y_{1\ cal}$ vs. $y_{1\ obs}$ for $\alpha_{12} = -0.30$.

ETHANOL-WATER-MERCURIC CHLORIDE

$\alpha_{13} = 0.30 \quad \alpha_{23} = 0.0$

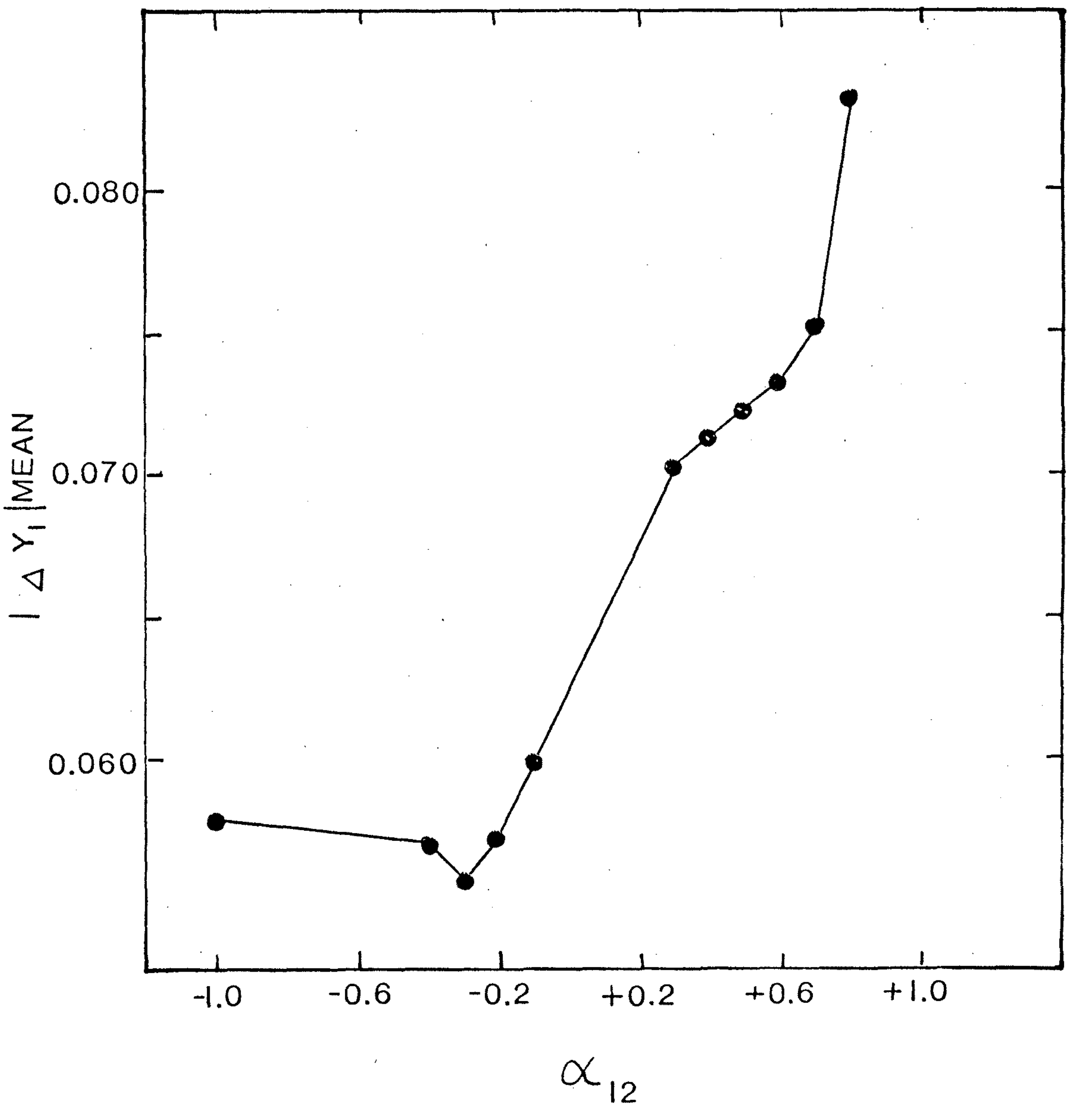


FIGURE 15

ETHANOL-WATER-MERCURIC CHLORIDE

$\alpha_{13} = 0.30 \qquad \alpha_{23} = 0.0$

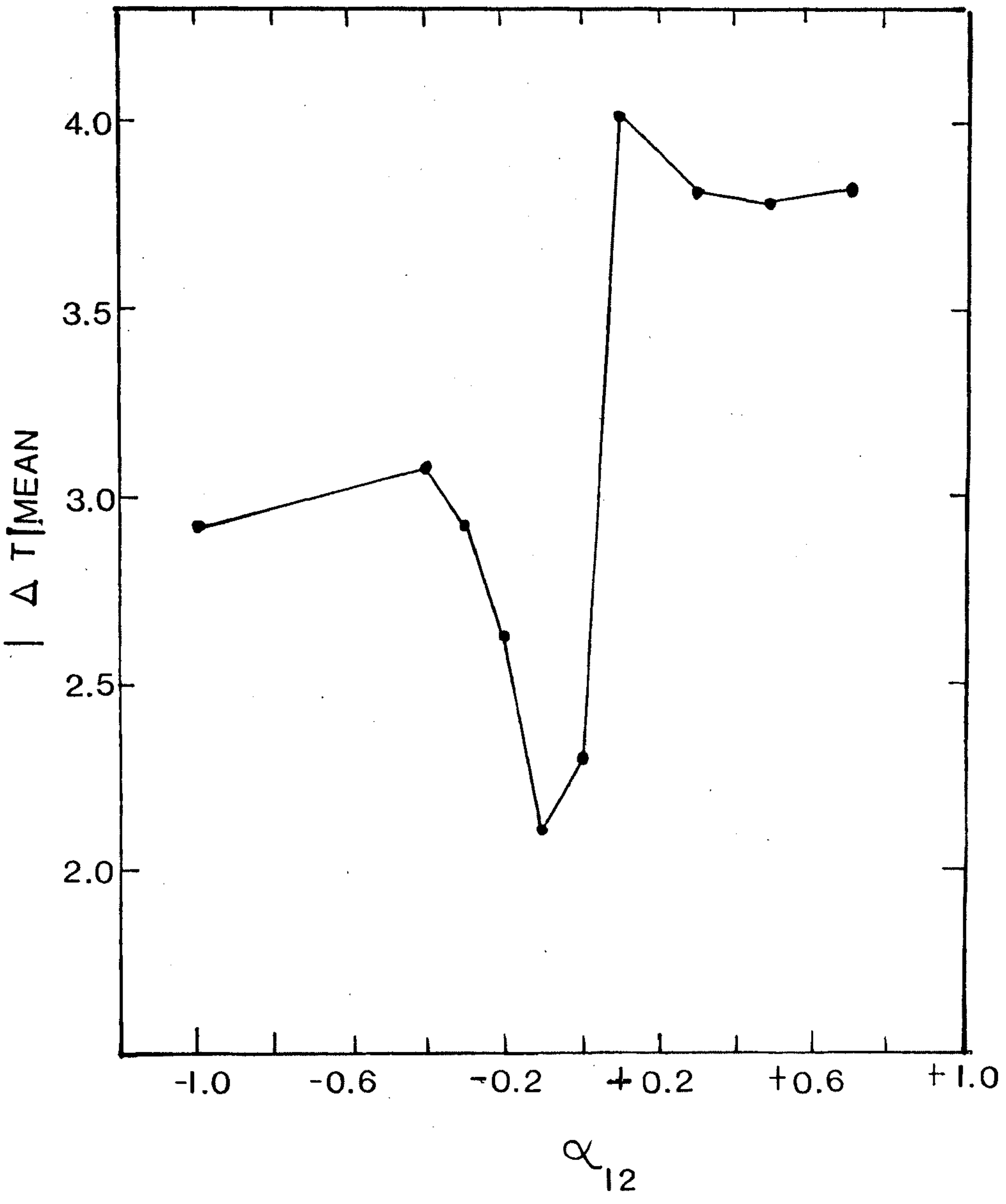


FIGURE 16

FIGURE 17

ETHANOL-WATER-MERCURIC CHLORIDE

$\alpha_{12} = -0.30$

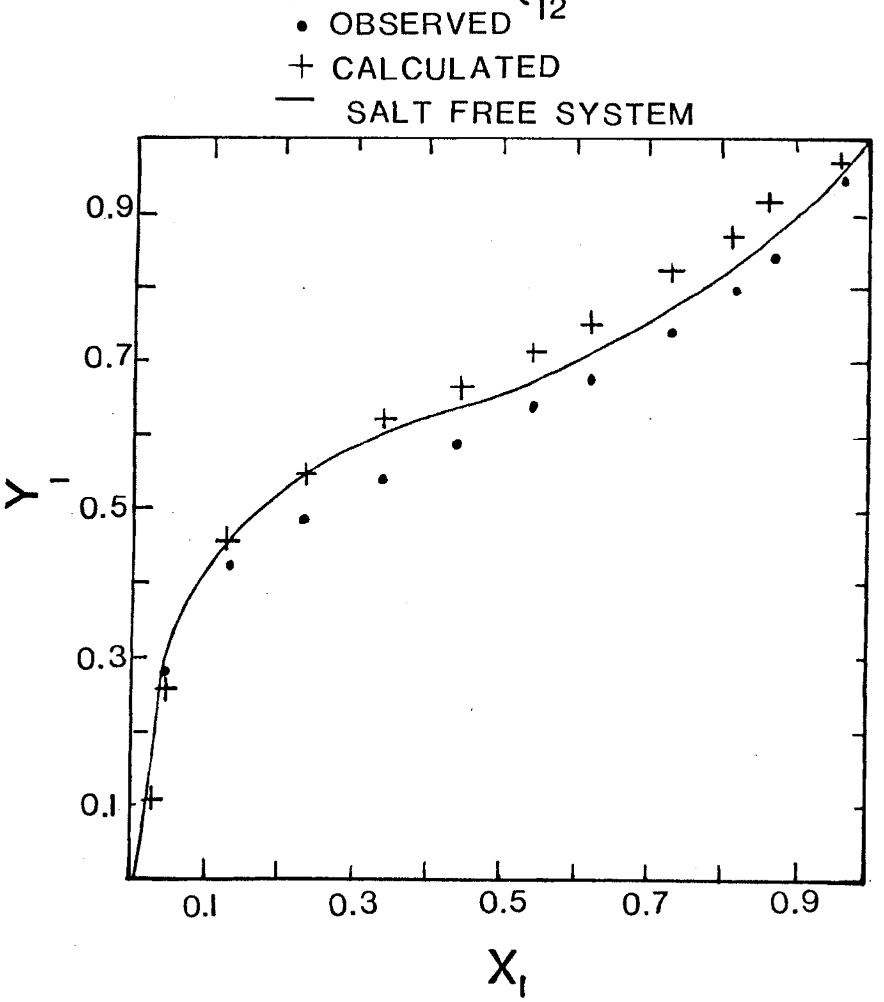


Fig 18

ETHANOL-WATER-$HgCl_2$

$\alpha_{12} = -0.30$

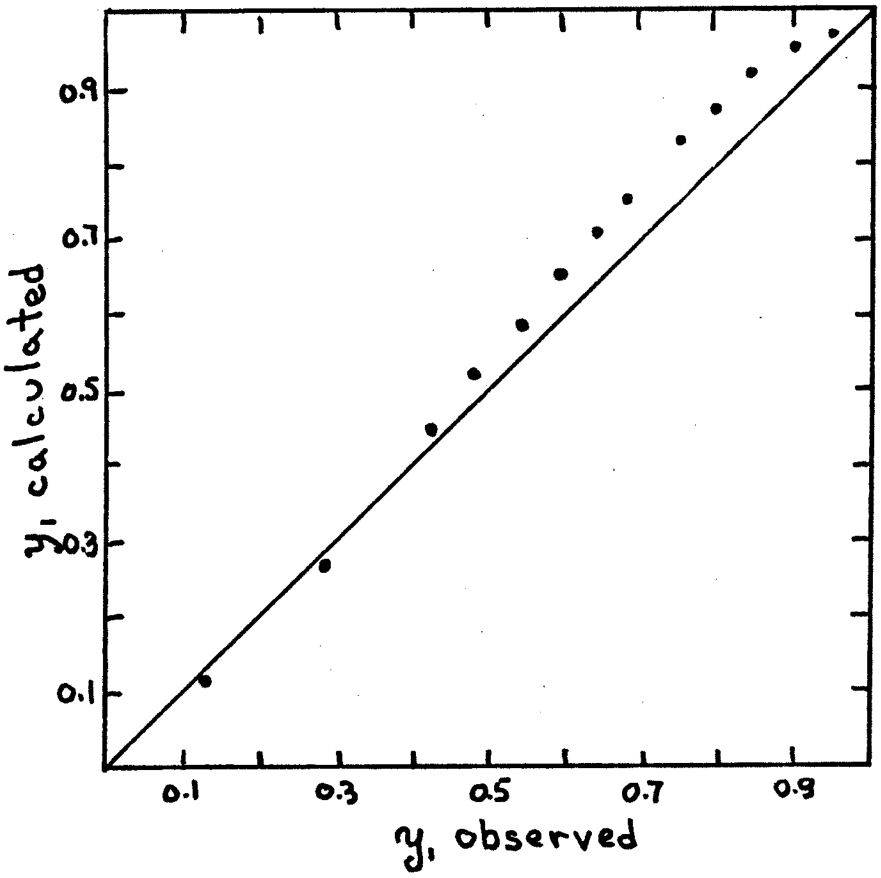


Table 10

Results for Ethanol-Water-Mercuric Chloride
Assuming Ideality of the Water-Mercuric
Chloride Binary* ($\alpha_{13} = 0.30$).

α_{12}	$\lvert\Delta y_1\rvert_{mean}$	Max.Error in y_1	Max.Error in γ_1	Max.Error in γ_2	Max.Error in Temp.
-1.00	.058	.100	17.1	73.3	3.9
-0.40	.057	.102	18.8	74.7	4.1
-0.30	.055	.097	16.6	72.9	4.0
-0.20	.057	.092	17.9	70.3	3.4
-0.10	.060	.083	19.3	65.5	2.8
0.00	.071	.103	35.9	70.2	4.0
0.30	.070	.123	33.6	81.9	4.9
0.40	.071	.125	34.1	81.5	4.9
0.50	.072	.126	34.9	81.3	4.9
0.60	.073	.127	36.2	81.2	4.9
0.70	.075	.129	37.7	81.1	4.8
0.80	.083	.138	42.1	79.9	4.9

* Data of Perry (31) used for the 1-2 binary.

E) The Use of Ionic Quantities in the System Methanol-Water-Lithium Chloride at 60° C.

Due to the difficulties encountered in correlating the isobaric systems by the use of analytical mole fractions, the ionic mole fractions were defined and used in correlating those systems. In order to determine if the use of ionic mole fractions would generate good ternary results for isothermal systems as well, the system methanol-water-lithium chloride was reexamined.

For this analysis, the extended data of Broul et al. (40 data points) was used (2). Values of α_{12} in the range from -2.0 to +1.0 were examined while the values of α_{13} and α_{23} were set at 0.30. Table 11 compares the results obtained for various values of α_{12} to those of Broul and Hala. The best results were obtained for $\alpha_{12} = -1.00$. At this value of α_{12}, the results are considerably better than those obtained by the Broul correlation and slightly better than those of the Hala correlation. Figure 19 shows a combined plot of $|\Delta y_1|_{mean}$ and $|\Delta P|_{mean}$ (the average absolute error in the calculation of pressure) against α_{12}.

TABLE 11

COMPARISON OF RESULTS OBTAINED FOR THE SYSTEM METHANOL-WATER-LITHIUM CHLORIDE TO THE RESULTS OBTAINED BY BROUL AND HALA.

		NRTL		Correlation of	
	$\alpha_{12}=-0.10$	$\alpha_{12}=-0.40$	$\alpha_{12}=-1.00$	Broul	Hala
y_1 obs.	y_1 calc.	y_1 calc.	y_1 calc.	y_1 calc.	y_1 calc.
0.093	0.060	0.066	0.079	0.083	0.083
0.114	0.079	0.087	0.104	0.107	0.107
0.042	0.063	0.065	0.070	0.067	-
0.103	0.098	0.102	0.110	0.104	0.105
0.166	0.130	0.141	0.163	0.161	0.162
0.155	0.148	0.153	0.164	0.157	0.158
0.245	0.189	0.204	0.232	0.263	0.229
0.156	0.165	0.166	0.168	0.170	-
0.243	0.216	0.224	0.239	0.229	0.230
0.335	0.288	0.306	0.339	0.332	0.334
0.414	0.361	0.379	0.412	0.407	0.408
0.340	0.336	0.345	0.362	0.351	-
0.340	0.345	0.347	0.351	0.353	-
0.499	0.447	0.464	0.496	0.492	0.493
0.432	0.423	0.432	0.448	0.431	0.441
0.725	0.612	0.631	0.667	0.748	0.742
0.499	0.490	0.497	0.512	0.506	-
0.588	0.546	0.560	0.587	0.589	0.597
0.490	0.489	0.490	0.494	0.495	-
0.571	0.559	0.566	0.579	0.575	0.575
0.801	0.746	0.758	0.778	0.847	-
0.673	0.645	0.656	0.676	0.687	0.686
0.616	0.604	0.611	0.622	0.620	0.620
0.646	0.638	0.643	0.653	0.653	0.653
0.729	0.719	0.726	0.738	0.754	-
0.709	0.697	0.701	0.710	0.715	0.714
0.849	0.833	0.837	0.846	0.904	-
0.776	0.781	0.784	0.791	0.812	0.809
0.761	0.766	0.768	0.773	0.785	0.783
0.752	0.761	0.762	0.764	0.766	-
0.877	0.884	0.884	0.885	0.933	-
0.808	0.819	0.820	0.822	0.843	-
0.810	0.823	0.823	0.825	0.843	-
0.826	0.838	0.838	0.839	0.857	0.855
0.850	0.862	0.861	0.861	0.882	0.878
0.900	0.914	0.912	0.910	0.943	-
0.876	0.890	0.889	0.887	0.915	-
0.846	0.856	0.856	0.856	0.861	0.860
0.895	0.909	0.907	0.904	0.928	-
0.942	0.953	0.951	0.948	0.967	0.965
$\lvert\Delta y\rvert_{mean}$	0.021	0.016	0.011	0.019	0.012

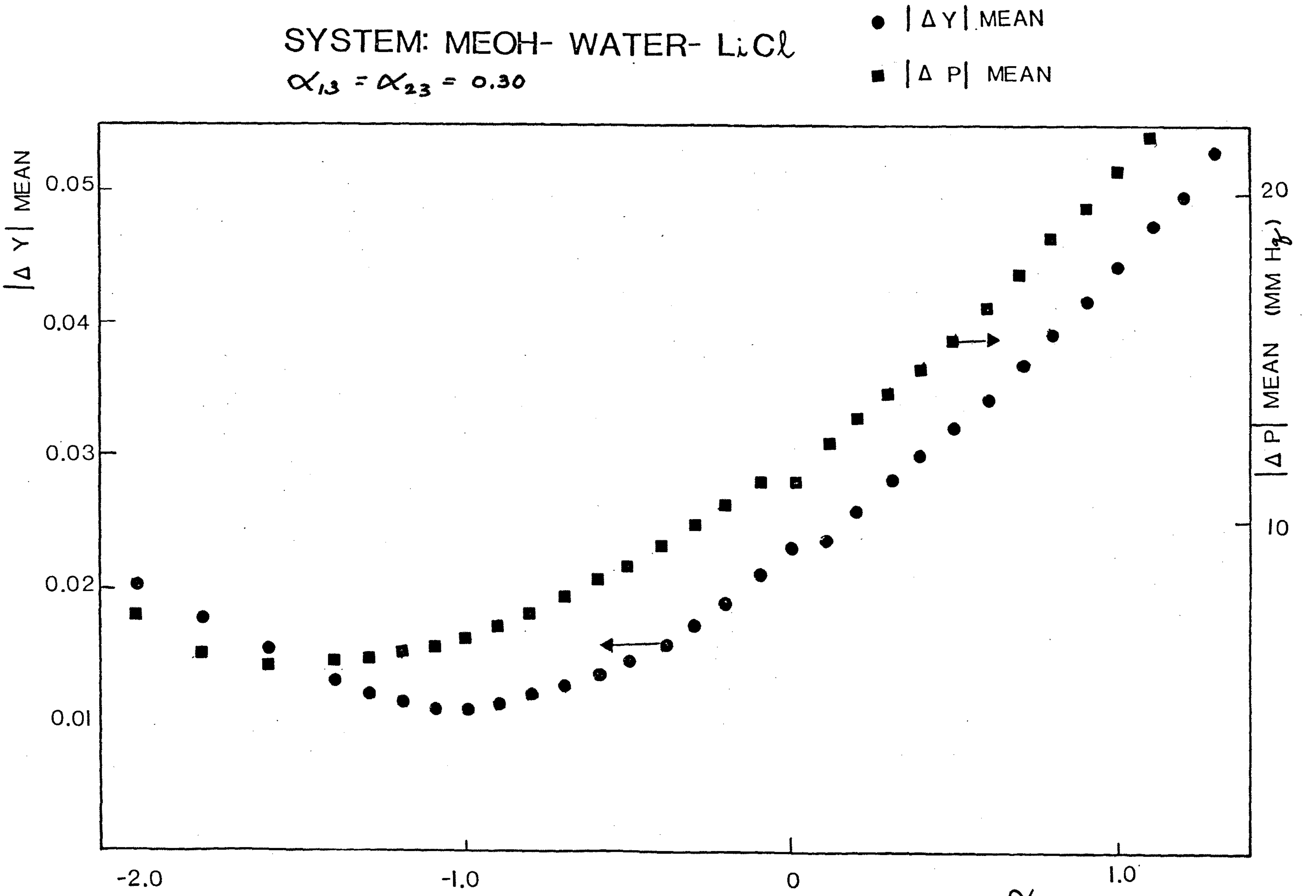

SYSTEM: MEOH- WATER- LiCl
$\alpha_{13} = \alpha_{23} = 0.30$
● |ΔY| MEAN
■ |ΔP| MEAN
|ΔY| MEAN
0.05
0.04
0.03
0.02
0.01
|ΔP| MEAN (MM Hg)
20
10
-2.0
-1.0
0
1.0
α_{12}

FIGURE 19

DISCUSSION.

The purpose of this work has been to develop a method of correlation for ternary systems containing a salt that could be used as a tool for the prediction of the vapor liquid equilibrium of such systems in the absence of ternary data. Previous methods of correlation have treated such systems as pseudo-binaries, thus being unsuitable for use as a predictive tool.

The Wilson equation was initially chosen because of its ability to make good ternary predictions from binary data alone. The parameters of this equation have a degree of built-in temperature dependency which makes the equation particularly suitable for isobaric systems.

The isothermal system methanol water-lithium chloride was chosen for the initial trials. This system being isothermal eliminated the consideration of the temperature dependency of the parameters. The binary data was recent and of good quality.

Since the activity coefficient of the salt cannot be correlated by the Wilson equation, only the activity coefficient of the solvent was used to derive the parameters for the solvent-salt pairs. Thus, only the Wilson equation applying to γ_1 was used for these binaries.

To investigate the behavior of the calculated activity coefficients with the parameters Λ_{12} and Λ_{21}, a parametric technique was used. One parameter, Λ_{21}, was expressed as a function of the other parameter and the activity coefficient. This method generates a family of curves for the activity coefficients vs. Λ_{12}. When each observed activity coefficient is compared to the value on the curve, a locus of all such points is obtained for each region where a solution to the Wilson equation for the particular system can be obtained.

According to Silverman and Marina, three sets of positive roots exist for the Wilson equation for systems that exhibit negative deviations from Raoult's Law; that is, systems where the activity coefficients are less than unity ([illegible]). The parametric method failed to show the existence of a set of positive roots for either binary system. By inspection of equations (I-33) and (I-33b) that define the parameters Λ_{12} and Λ_{21} it can be seen that negative values for these parameters are physically impossible. Yet, the parametric method yielded roots for which the value of the parameter Λ_{21} is negative.

The two binary systems were then examined by means of a non-linear regression subroutine. The initial trials resulted in a breakdown of the regression subroutine. This failure occurred because of attempts to assign negative trial values to the parameter Λ_{12} which is contained within a logarithmic term. To prevent this type of failure, a restraint was placed on the trial values of Λ_{12} in the main program. This restraint permitted the program to print results prior to the breakdown but did not result in convergence. A change in the starting values of the parameters permitted the program to converge to reasonably low values of the sum of the squares function. However, for both binaries tried, the best results were obtained for negative values of Λ_{21}. It is interesting to note that the best regressed values were obtained when the starting values of the parameters were set in the neighborhood of the region obtained by the parametric method. However, as discussed above, negative values of the Wilson parameters are physically impossible. One trial resulted in a set of positive regressed parameters for the mathanol-lithium chloride binary. The fit of the data, however, was not as good as in the case with the negative value of Λ_{21}. When the same set of starting values was used for the system water-lithium chloride, the regressed value of Λ_{21} was negative.

Because of the difficulties encountered in the use of the Wilson equation, it was decided to discontinue efforts with this equation. The NRTL equation was examined next as it does not contain any logarithmic terms that would result in premature breakdown of the program. No restrictions exist as to the values of the parameters of the NRTL equation.

As initially conceived, the NRTL equation consisted of two variable parameters A and B and a parameter α_{12} that could be preset at various values in the range 0.2 to 0.47 depending on the characteristics of the binary system. Theoretically, the value of α_{12} should be greater than 0. and less than +1. Marina has shown, however, that when α_{12} is pre-set at a value of -1.0, a good binary fit is obtained and better ternary predictions from the binary parameter are attained than by using the values of α_{12} recommended by the rules of Renon and Prausnitz (31). This finding makes the NRTL equation empirical in nature and permits the variation of α_{12}.

Other authors have used variable values of α_{12} (7, [illegible]). Rousseau and co-workers used a variable value of α_{12} in correlating ternary systems containing a salt as pseudo-binaries.

As with the Wilson equation, different sets of parameters can result from the use of different sets of starting values. Marina has recommended the use of $A_{ST} = B_{ST} = 0.0$ as the starting values of the parameters of the NRTL equation when using the LSQ2 subrouting for their evaluation. This recommendation was followed.

The two binary solvent-salt binaries were correlated by using values of α_{13} and α_{23} in the range from -1.00 to 0.30. The results for the two binaries were similar. The value of $\alpha_{13}, \alpha_{23} = -1.00$ suggested by Marina resulted in the poorest fit of the binary data. The value of $\alpha_{13}, \alpha_{23} = 0.30$ resulted in a better fit. When the sum of the squares of the difference between the observed and calculated activity coefficients is plotted against α_{13} and α_{23} it was noted that the curves had sharp minima at values of α_{13} and α_{23} close to 0.0. These minima corresponded very closely to the values obtained when α_{13} and α_{23} were regressed rather than pre-set. These regressed values were used in correlating the ternary data at this stage.

The ternary data was correlated by using values of α_{12} in the range from -1.0 to 0.30. It was found that a value of

α_{12} in the neighborhood of - 0.40 yielded the best fit of the ternary data. The average absolute error in the vapor phase mole fraction for $\alpha_{12} = -0.40$ was 0.0076 which compares favorably with value of 0.012 reported by Hala for his correlation. The regressed value of $\alpha_{12} = -0.15$ yielded a somewhat poorer fit of the ternary data, the average absolute error in y_1 being equal to 0.021.

Hala has correlated this system by superimposing an expression for the coloumbic interactions on the Margules equations. A series of trials were made to determine if a better fit could be obtained if the expression for the coloumbic interaction is superimposed on the NRTL equation. Only two of the six trials yielded acceptable results. One of these trials, for the case $\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.0$ gave an exceptionally good fit. It can be shown that for the case where all the parameters equal zero, the NRTL equation reduces to the Margules two-suffix equation. Since this form of the Margules equation works best for symmetrical systems and the methanol-water system is nearly symmetrical, these results cannot be generalized to non-symmetrical systems.

From the brief testing of the superposition technique, it was concluded that the method offered no advantages over the original NRTL when the latter is interpreted as an empirical equation. The larger number of parameters required by the superimposition cannot be justified in cases where the binary solvent-salt data is not extensive. Two different types of programs were required for the input of data. The first type of program was one in which the parameter c was regressed while the second type used the regressed value of c for the first binary as input data for the second binary. This procedure is somewhat less convenient than the procedure for the original NRTL equation, where the parameters for both solvent-salt systems can be generated co-currently.

The study of this ternary system was temporarily discontinued to investigate how the NRTL equation can be used to correlate isobaric systems. The binary solvent-salt systems were correlated as before using only the expression for the activity coefficient of the solvent in the NRTL equation. Boiling point elevation data was used in correlating the binary solvent-salt systems and the Antoine constants for the solvent were used to describe the change of vapor pressure with temperature for the pure solvent.

A bubble-point subroutine was written for the ternary program. This subroutine consisted of an iterative method for the systematic search for the temperature that would solve the bubble-point equation. Due to the large errors in the calculated activity coefficients, the bubble-point subroutine failed to converge. It was observed that by redefining the mole fractions and activity coefficients by the assumption of full dissociation of the salt in the binaries and binary systems. This assumption was previously made by Hala. Although the validity of this assumption for water-salt binaries is generally accepted for most inorganic salts, its validity for non-aqueous solvent-salt mixtures cannot be readily proven.

The redefinition of the mole fractions and activity coefficients based on the assumption of complete dissociation of the salt resulted in convergence of the bubble-point subroutine. It was observed that the binary ionic activity coefficients derived from boiling-point elevation data did not deviate greatly from unity for such binary systems where the salt was not very soluble in the solvent. It was shown that by assuming such binaries to behave ideally, the quality of the ternary fit was either unchanged or improved. This assumption resembles the treatment given to the data by Rousseau and coworkers in correlating systems containing a salt (42).

A study was made of the effect of the parameter α_{12} on the quality of the fit. For this study the value of the other α were pre-set at either 0.00 or 0.30 depending on whether the particular binary could be assumed to behave ideally from inspection of the activity coefficients. Table 12 shows the optimum value of α_{12} for the negative and positive regions for all five systems investigated. It can be seen from these results that no single value of α_{12} can be chosen to give optimum results, but in general better results are obtained for values of α_{12} in the negative region. The results are extremely good for the system methanol-water-calcium chloride. For the systems methanol-water-potassium acetate, methanol-water-mercuric chloride and ethanol-water-mercuric chloride, the calculations are of lesser accuracy.

In the previous section mention was made of the large temperature errors observed for methanol-water-potassium acetate system. A modification was made on the computer program to provide an additional degree of temperature dependency

Table 12

OPTIMUM VALUES OF α_{12} IN THE POSITIVE AND NEGATIVE REGIONS BASED ON TERNARY VAPOR MOLE FRACTION CALCULATION

SYSTEM	NEGATIVE REGION		POSITIVE REGION	
	α_{12}	$\lvert\Delta y_1\rvert_{mean}$	α_{12}	$\lvert\Delta y_1\rvert_{mean}$
MeOH-water-$CaCl_2$	-0.1	0.024	1.0	0.019
MeOH-water-Pot.acet.	-0.2	0.038*	0.2	0.040*
MeOH-water-$HgCl_2$	-1.0	0.037	0.4	0.042
MeOH-water-LiCl	-1.1	0.010	none	
EtOH-water-$HgCl_2$	-0.3	0.056	none	

*= For α_{12} = 0.0, $\lvert\Delta y_1\rvert_{mean}$ = 0.036

to the NRTL parameters. It was hoped that this modification, which is described in the Appendix, would improve the temperature fit for this system. Although a slight improvement was observed in the y_1 fit by the use of temperature dependent parameters, no appreciable improvement was observed in the temperature fit.

Meranda and Furter (24) reported great difficulties in obtaining the data for this system due to the high solubility of the salt. These difficulties may have resulted in experimental errors. However, it is also very likely that the assumption of full dissociation of the salt is not entirely valid for this system. Nevertheless, it must be remembered that neglecting this assumption prevented convergence of the bubble-point subroutine.

For the systems methanol-water-mercuric chloride and ethanol-water-mercuric chloride erroneous predictions as to the type of salt effect were obtained. Both systems exhibit a salting-in effect while the method predicts a slight salting-out effect for the ethanol-water-$HgCl_2$ system and no appreciable effect for the methanol-water-$HgCl_2$ system. Uncertainties exist about the accuracy of the data used for the two $HgCl_2$ systems. The maximum boiling point elevation for the EtOH-$HgCl_2$ is only 0.755°C and for the MeOH-$HgCl_2$ is 1.27°C with most of the data points falling within 0.2°C. The data were obtained in 1896 and 1890 respectively. One additional point for each system, consisting of the alcohol saturated with $HgCl_2$, was obtained from the Johnson and Furter data. The concentration of mercuric chloride in the ternaries had to be calculated from the Johnson and Furter solubility equation as the numerical data was not given in their tabulations. In addition, Jaques and Furter (14) indicate that the ethanol-water-mercuric chloride data failed to meet their thermodynamic consistency test. Therefore, the data for these two systems have been used with some degree of reservation about their validity.

Aside from these reservations, however, the erroneous predictions of the type of salt-effect obtained for the mercuric chloride systems may be explained by the possible inadequacy of the full dissociation assumption. Data on the true degree of dissociation of this salt in the pure solvents and in the mixture are not currently available.

To determine the effect that the particular set of solvent-solvent date has on the ternary fit, a second set of isobaric methanol-water data was examined. The systems methanol-water-$CaCl_2$ and methanol-water-potassium acetate were used for this particular study. The data of Ramalho (33) - considered to be of better quality than the initial set obtained from Perry (31) - resulted in improvements in the ternary y_1 fit for the three systems considered. The minimum absolute mean error in y_1 was reduced from 0.022 to 0.019 for the $CaCl_2$ system, from 0.040 to 0.036 for the potassium acetate system, and from 0.040 to 0.037 for the mercuric chloride system. The data of Ramalho, however, did not appreciably improve the ternary temperature fit for the methanol-water-potassium acetate system.

To test the effect of the redefinition of mole fractions and activity coefficients on the fit of the isothermal system methanol-water-lithium chloride, the system was re-examined by using the extended data of Broul. The ternary fit was obtained for the range $-2.0 < \alpha_{12} < +2.0$. It was seen that the optimum results were obtained in the neighborhood of $\alpha_{12} = -1.00$. The ionic quantities defined for the isobaric systems seemed to hold for this system as well. As seen in the previous section, the results compared very favorably with those of Hala and Broul.

CONCLUSIONS:

A method has been developed for the correlation of vapor-liquid equilibrium data for solvent mixtures containing a dissolved salt. The method could be used for predictive purposes once sufficient data becomes available to determine the optimum value of α for the solvent-solvent binary. Further refinements in the technique such as a more rigorous treatment of the degree of salt dissociation could lead to improvements in the ternary data fit.

APPENDIX A

Data Sources

I. Ternary Systems

1. Methanol-water-lithium chloride @ 60°C	(2)
2. Methanol-water-calcium chloride @ 752 mm Hg.	(17)
3. Methanol-water-potassium acetate @ 764 mm Hg.	(25)
4. Methanol-water-mercuric chloride @ 758 mm Hg.	(17)
5. Ethanol-water-mercuric chloride @ 750 mm Hg.	(17)

II. Binary Systems

1. Methanol-water @ 60°C	(2)
2. Methanol-water @ 760 mm Hg.	(31), (33)
3. Ethanol-water @ 760 mm Hg.	(11)
4. Water-lithium chloride @ 60°C	(2)
5. Water-calcium chloride @ 760 mm Hg.	(45)
6. Water-potassium acetate @ 760 mm Hg.	(45)
7. Water-mercuric chloride @ 760 mm Hg.	(45)
8. Methanol-lithium chloride @ 60°C	(2)
9. Methanol-calcium chloride @ 760 mm Hg.	(45)
10. Methanol-potassium acetate @ 760 mm Hg.	(45)
11. Methanol-mercuric chloride @ 760 mm Hg.	(45)
12. Ethanol-mercuric chloride @ 760 mm Hg.	(45)

III. Antoine Constants	(11)
IV. Parameters for the Solubility Equation (Used for the mercuric chloride systems.)	(17)

Appendix B

Derivation of the Parametric Method for the Wilson Equation.

The Wilson equation relates the activity coefficients to the liquid phase composition as follows:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \qquad (1)$$

This can be rewritten as follows:

$$\ln \left[\gamma_1 (x_1 + \Lambda_{12} x_2) \right] = x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right] \qquad (2)$$

Let $T = (x_1 + \Lambda_{12} x_2)$, then

$$\ln(\gamma_1 T) = x_2 \left[\frac{\Lambda_{12}}{T} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \qquad (3)$$

$$\frac{\ln(\gamma_1 T)}{x_2} = \frac{\Lambda_{12}}{T} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \qquad (4)$$

Solving equation (4) for Λ_{21},

$$\frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2} = \frac{\Lambda_{12}}{T} - \frac{\ln\gamma_1 T}{x_2} \qquad (5)$$

$$\Lambda_{21} = (\Lambda_{21}x_1 + x_2)\left[\frac{\Lambda_{12}}{T} - \frac{\ln\gamma_1 T}{x_2}\right] \qquad (6)$$

Let $Q = \left[\frac{\Lambda_{12}}{T} - \frac{\ln\gamma_1 T}{x_2}\right]$, then

$$\Lambda_{21} = \Lambda_{21}x_1 Q + x_2 Q \qquad (7)$$

$$\Lambda_{21} = \frac{x_2 Q}{1 - x_1 Q} = \frac{x_2\left[\frac{\Lambda_{12}}{T} - \frac{\ln\gamma_1 T}{x_2}\right]}{1 - x_1\left[\frac{\Lambda_{12}}{T} - \frac{\ln\gamma_1 T}{x_2}\right]} \qquad (8)$$

Let the Wilson equation for a subsequent point be expressed as follows:

$$\ln\gamma_1^2 = -\ln(x_1^2 + \Lambda_{12}x_2^2) + x_2^2\left[\frac{\Lambda_{12}}{x_1^2 + \Lambda_{12}x_2^2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1^2 + x_2^2}\right] \qquad (9)$$

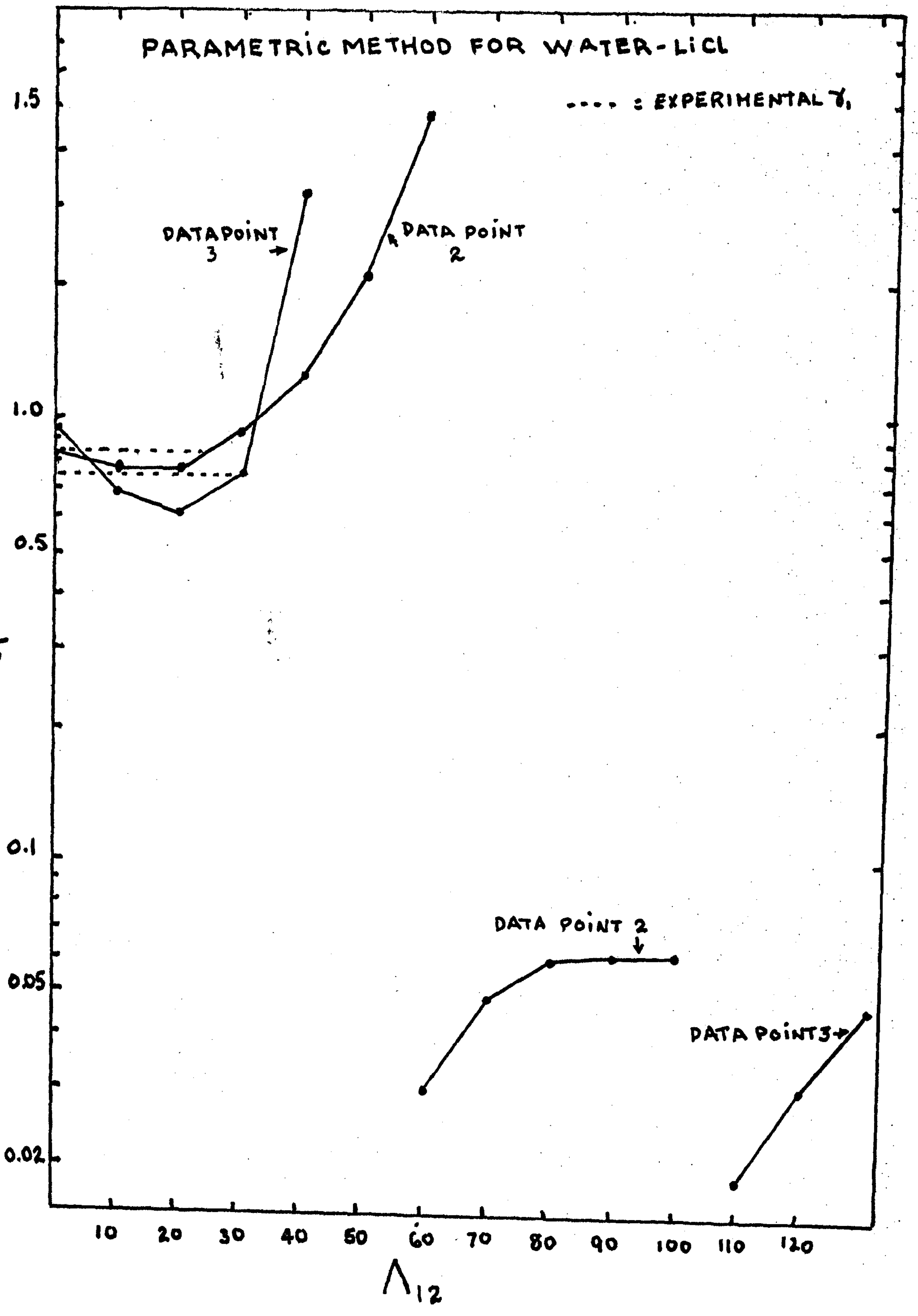
Substituting equation (8) into (9)

$$\ln \gamma_1^2 = -\ln(x_1^2 + \Lambda_{12} x_2^2) + x_2^2 \Bigg[\frac{\Lambda_{12}}{x_1^2 + \Lambda_{12} x_2^2} - \frac{x_2 \left(\frac{\Lambda_{12}}{(x_1 + \Lambda_{12} x_2)} - \frac{\ln(\gamma_1 (x_1 + \Lambda_{12} x_2))}{x_2} \right)}{x_2^2 + (x_1^2 x_2 - x_2^2 x_1) [\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\ln(\gamma_1 (x_1 + \Lambda_{12} x_2))}{x_2}} \Bigg] \quad (10$$

In equation (10) the mole fractions and activity coefficient without a superscript (x_1, x_2 and γ_1) refer to the first data point, while the superscript 2 refers to those quantities for the second data point (x_2^2, x_1^2, γ_1^2). Equation (10) can be used to generate a family of curves that relates the calculated activity coefficient to the parameter Λ_{12}. By comparing the calculated activity coefficients to the observed values, a range is found for the parameter Λ_{12} where a solution of the Wilson equation exists. An example of such a family of curves is given by Figure A-1. A discontinuity is observed in both curves presented in this figure. This discontinuity arises from the calculation of negative values for the parameter Λ_{21}: As negative values of the Wilson parameters are physically impossible, this discontinuity hints at the failure of the Wilson equation to represent the solvent-salt binaries.

It can be seen that if values of Λ_{21} in the negative region are permitted, the term $(\Lambda_{21}x_1 + x_2)$ in equation (1) can attain the value of zero giving rise to the discontinuity

FIG A-1


PARAMETRIC METHOD FOR WATER-LiCl
---- : EXPERIMENTAL γ_1
DATAPOINT 3
DATA POINT 2
DATA POINT 2
DATA POINT3
1.5
1.0
0.5
0.1
0.05
0.02
γ_1
10
20
30
40
50
60
70
80
90
100
110
120
Λ_{12}

APPENDIX C

CONSTANTS FOR ANTOINE'S VAPOR PRESSURE EQUATION.

		A	B	C	Reference
1.	Water	7.96681	1668.21	228.00	Broul et al. (1969)
2.	Methanol	8.07246	1574.99	238.86	Broul et al. (1969)
3.	Ethanol	8.16290	1623.22	228.98	Hala (1968)

Appendix D

Definition of Temperature Dependent Parameters.

The parameters of NRTL equation are:

$$A = \frac{(g_{21} - g_{11})}{RT}$$

$$B = \frac{(g_{12} - g_{22})}{RT}$$

The terms contained within the parenthesis are generally treated as constants; however, for large temperature variations these terms should be expressed as functions of temperature. In this study a linear temperature dependence was chosen. These parameters are defined as follows:

$$A' = \frac{a + bT}{RT}$$

$$B' = \frac{c + dT}{RT}$$

APPENDIX E

The LSQ2 Subroutine

This subroutine designed by Gardner (7) and used by Marina (22) in correlating VLE data minimizes a function of several independent variables. In this study the minimized function is the sum of the squares of the differences between the calculated and observed values of the activity coefficients. The independent variables are the parameters of the equation for the activity coefficients.

The LSQ2 subroutine is called by the Main Program. The LSQ2 subroutine then calls the FN subroutine which contains the equation for the activity coefficients and the sum of the squares function. From the value of the minimized function LSQ2 generates a new set of parameters. This cycle is repeated until the sum of the squares falls below a specified limit or until a predetermined number of iterations have been performed. The following arguments must be specified by the calling program:

XT (1), XT (2),...., a vector containing the values of the independent variables (parameters of the NRTL equation, for instance) starting values must be specified in the calling program.

X, a strong matrix containing the values of XT.

DX, increment applicable to each independent variable. May be expressed as a vector if different increments are desired for each variable.

Y, a vector of M1 components containing the values of the dependent variable, the sum of the squares in this study. One exit from LSQ2, Y (1) is the values of the sum of squares for the optimum values of the parameters.

M, the number of independent variables (parameters)

M1= M+1

M3= M+3

L, the maximum number of iterations

E, the allowable error

APPENDIX F

Description of Main Programs

1) PROGRAM NRTL

This program calculates the optimum values of the parameters A and B of the NRTL equation for a solvent-salt system with a preset value of α. The program uses the assumption of full dissociation of the salt.

2) PROGRAM SOLSOL

This program calculates the optimum values of the parameters A and B of the NRTL equation for a solvent-solvent system with a preset value of α.

3) PROGRAM MNFT

This program calculates the ternary results from binary parameters of the NRTL equation for an isobaric solvent-solvent-salt system. The program uses the assumption of full dissociation of the salt.

4) PROGRAM ISOTH

This program calculates the ternary results from binary parameters of the NRTL equation for an isothermal solvent-solvent-salt system with the assumption of full dissociation.

```
      PROGRAM [illegible]
      INTEGER [illegible]
      INTEGER F
      INTEGER H
      COMMON X1(25),X2(25),N,ERROR(25),G(25),GAMMA(25),ALFA,TK(25)
      DIMENSION PT(25),X(3,6),Y(4),XT(3),XAN1(25),XAN2(25),TEMP(25),P0(2
     15),DX(3)
  100 FORMAT (G10.5,2G10.3)
  101 FORMAT (I2)
  120 FORMAT (3G10.5)
  163 FORMAT (//,T4,'X1',T24,'GAMMAOBS',T37,'GAMMACAL',T47,'ERROR')
  164 FORMAT ('ALFA12=',F10.6)
  165 FORMAT ('A12ST=',G12.5,'A21ST=',G12.5,'A12=',G12.5,'A21=',G12.5,
     1'SUM OF SQUARES=',G12.5)
  166 FORMAT (9X,F8.4,2F11.4,F8.2)
  168 FORMAT (//'ABS.MEAN ERROR IN PRESS.=',F10.5)
  7   FORMAT (2G10.5)
      READ 101,N
      READ 120,AA,AB,AC
      READ 100,(XAN1(I),PT(I),TEMP(I),I=1,N)
      DO 10 I=1,N
      XAN2(I)=1.-XAN1(I)
      X1(I)=XAN1(I)/(XAN1(I)+3.*XAN2(I))
      X2(I)=1.00-X1(I)
      TK(I)=TEMP(I)+273.2
      P0(I)=10.0**(AA-AB/(TEMP(I)+AC))
      GAMMA(I)=PT(I)/(X1(I)*P0(I))
      PRINT 166,X1(I),GAMMA(I),TK(I),TEMP(I)
   10 CONTINUE
      DO 20 H=1,[illegible]
      DO 20 F=1,[illegible]
      X(H,F)=0.0
   20 CONTINUE
      XT(1)=0.000
      XT(2)=0.0000
      A=XT(1)
      B=XT(2)
      M=2
      M1=M+1
      M3=M+3
      DX(1)=10.00
      DX(2)=10.00
      L=1000
      E=0.000[illegible]
      CALL LSQ (XT,X,DX,Y,M,M1,M3,L,E)
      PRINT 164,ALFA
      PRINT 165,A,B,XT(1),XT(2),Y(1)
      PRINT 16[illegible],(X1(J),GAMMA(J),G(J),ERROR(J),J=1,N)
      STOP
      END
```

```
          SUBROUTINE FN(YY,XT)
          COMMON X1(25),X2(25),N,ERROR(25),G(25),GAMMA(25),ALFA,TK(25)
          DIMENSION XT(3)
          ALFA=0.30
          YS=0.0
          DO 30 I=1,N
          U1=XT(1)/(1.9872*TK(I))
          U2=XT(2)/(1.9872*TK(I))
          R=(X2(I)+X1(I)*EXP(-ALFA*U1))**2
          P=EXP(-ALFA*U1)
          T=(X1(I)+X2(I)*EXP(-ALFA*U2))**2
          Q=EXP(-2.*ALFA*U2)
          S=((X2(I))**2)*(U2*Q/T+U1*P/R)
          G(I)=EXP(S)
          IF (G(I)-(10.**19))31,32,32
    31    Y=(G(I)-GAMMA(I))**2
          ERROR(I)=(G(I)-GAMMA(I))*100./GAMMA(I)
          YS=YS+Y
     30    CONTINUE
          YY=YS
          GO TO 33
    32    YY=YY*2.
    33    CONTINUE
          RETURN
          END
```

```
      PROGRAM SOLSOL
      INTEGER SYST
      INTEGER F
      INTEGER H
      COMMON X1(25),X2(25),Y1(25),Y2(25),ERROR(25),ERROR2(25),GAMMA(25),
     1GAMMA2(25),G(25),G2(25),ALFA,TK(25),N
      DIMENSION PT(25),X(4,7),Y(5),XT(4),Y1CAL(25),DIFF(25),P01(25),
     1P02(25),TEMP(25)
100   FORMAT (2G10.5,2G10.3 )
101   FORMAT (I2)
164   FORMAT (F9.4)
165   FORMAT (5G12.5)
166   FORMAT (9X,2F8.4,4F11.4,2F8.2)
168   FORMAT (///F10.5)
130   FORMAT (3G10.5)
      READ 101,N
      READ 130,AA1,AB1,AC1
      READ 130,AA2,AB2,AC2
      DO 10 I=1,N
      READ 100,X1(I),Y1(I),PT(I),TEMP(I)
      X2(I)=1.000-X1(I)
      Y2(I)=1.000-Y1(I)
      TK(I)=TEMP(I)+273.1
      P01(I)=10.0**(AA1-AB1/(TEMP(I)+AC1))
      P02(I)=10.0**(AA2-AB2/(TEMP(I)+AC2))
      GAMMA(I)=PT(I)*Y1(I)/(P01(I)*X1(I))
      GAMMA2(I)=PT(I)*Y2(I)/(P02(I)*X2(I))
10    CONTINUE
      DO 20 H=1,4
      DO 20 F=1,7
      X(H,F)=0.0
20     CONTINUE
      XT(1)=0.000
      XT(2)=0.000
      XT(3)=0.00
      XT(4)=0.00
      M=4
      M1=M+1
      M3=M+3
      DX=10.0
      L=1000
      E=0.00001
      CALL LSQ2 (XT,X,DX,Y,M,M1,M3,L,E)
      PRINT 164,ALFA
      PRINT 165,XT(1),XT(2),XT(3),XT(4),Y(1)
      DO 15 J=1,N
      PRINT 166,X1(J),Y1(J),GAMMA(J),G(J),GAMMA2(J),G2(J),ERROR(J),
     1ERROR2(J)
15    CONTINUE
      YSUM=0.000
```

```
        DO 38 I=1,N
        Y1CAL(I)=(G(I)*X1(I)*PC1(I))/PT(I)
        DIFF(I)=Y1CAL(I)-Y1(I)
        YSUM=YSUM+ABS(DIFF(I))
 38     CONTINUE
        YMEAN =YSUM/N
 120    FORMAT (4F12.5)
        PRINT 120,(X1(I),Y1(I),Y1CAL(I),DIFF(I),I=1,N)
         PRINT 168,YMEAN
        STOP
        END
```

```
      SUBROUTINE FN(YY,XT)
      COMMON X1(25),X2(25),Y1(25),Y2(25),ERROR(25),ERROR2(25),GAMMA(25),
     1GAMMA2(25),G(25),G2(25),ALFA,TK(25),N
      DIMENSION XT(4)
      ALFA=-.10
       YS=0.0
      DO 30 I=1,N
      U1=(XT(1)+XT(2)*TK(I))/(1.9872*TK(I))
      U2=(XT(3)+XT(4)*TK(I))/(1.9872*TK(I))
      T=(X1(I)+X2(I)*EXP(-ALFA*U2))**2
      P=EXP(-ALFA*U1)
      R=(X2(I)+X1(I)*EXP(-ALFA*U1))**2
      Q=EXP(-2*ALFA*U2)
      S=((X2(I))**2)*(U2*Q/T+U1*P/R)
      G(I)=EXP(S)
      T2=(X2(I)+X1(I)*EXP(-ALFA*U1))**2
      P2=EXP(-ALFA*U2)
      R2=(X1(I)+X2(I)*EXP(-ALFA*U2))**2
      Q2=EXP(-2*ALFA*U1)
       S2=((X1(I))**2)*(U1*Q2/T2+U2*P2/R2)
      G2(I)=EXP(S2)
      ERROR(I)=(G(I)-GAMMA(I))*100./GAMMA(I)
      ERROR2(I)=((G2(I)-GAMMA2(I))*100./GAMMA2(I))
      FY1=(G(I)-GAMMA(I))**2
      FY2=(G2(I)-GAMMA2(I))**2
      Y=FY1+FY2
      YS=YS+Y
   30  CONTINUE
      YY=YS
      RETURN
      END
```

```
      SUBROUTINE LS02(XT,X,DX,Y,M,M1,M2,L,E)
      DIMENSION XT(3),X(3,6),Y(4),JJ(4),A(4,4)
   10 L1C = 0
      IF(L.LE.0) GO TO 50
      IHC = M1+1
      EN = M
      EN = EN*1.5
      L1 = L
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
  100 X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX
      DO 104 I=1,M
  104 X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
  106 CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
  108 L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
   50 YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH) GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
 1091 IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
  109 IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
```

```
 1101 IF(Y(J).GT.Y3) GO TO 110                                          LS
      Y3 = Y(J)                                                         LS
      I3 = J                                                            LS
  110 CONTINUE                                                          LS
      L2C = L2C+1                                                       LS
      IF(L2C.LT.L2) GO TO 111                                           LS
      L2C = 0                                                           LS
      JJ(1) = IL                                                        LS
      JJ(2) = I2                                                        LS
      JJ(3) = I3                                                        LS
      DO 60 K1=1,K3                                                     LS
      J1 = JJ(K1)                                                       LS
      DO 60 K2=K1,K3                                                    LS
      J2 = JJ(K2)                                                       LS
      S = 0.0                                                           LS
      DO 55 I=1,M                                                       LS
   55 S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))                         LS
   60 A(K1,K2) = S                                                      LS
      D = A(1,1)*A(2,2)-A(1,2)**2                                       LS
      GO TO(62,61),K4                                                   LS
   61 D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)                                  LS
      D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)              LS
   62 IF(D .EQ. 0.0)GO TO 65
      IF(D .LE. 0.)D = ABS(D)
      D = (D/4.0)**G
      IF(D.LT.E) GO TO 65                                               LS
      FLG = 1.0                                                         LS
      GO TO 111                                                         LS
   65 IF(FLG.LT.0.0) GO TO 400                                          LS
      FLG = -1.0                                                        LS
  111 DO 115 I=1,M                                                      LS
      XT(I) = 0.0                                                       LS
      DO 112 J=1,M1                                                     LS
      IF(J.NE.IH) XT(I) = XT(I)+X(I,J)                                  LS
  112 CONTINUE                                                          LS
  115 XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)                    LS
  121 CALL FN(YT,XT)                                                    LS
      IF(YT,GE,Y2) GO TO 167                                            LS
      IHC = M1+1                                                        LS
      IF(YT,GE,YL) GO TO 140                                            LS
      YTT = YT                                                          LS
      DO 135 I=1,M                                                      LS
  135 XT(I) = 1.5*XT(I)-0.5*X(I,IH)                                     LS
      CALL FN(YT,XT)                                                    LS
      IF(YT.LE.YL ) GO TO 140                                           LS
      DO 138 I=1,M                                                      LS
  138 X(I,IH) = (2.0*XT(I)+X(I,IH))/3.                                  LS
      Y(IH) = YTT                                                       LS
      GO TO 103                                                         LS
  140 DO 142 I=1,M                                                      LS
```

```
 142  X(I,IH) = XT(I)                                          LSQ2
      Y(IH) = YT                                               LSQ2
      GO TO 108                                                LSQ2
 167  IHC = IHC-1                                              LSQ2
      IF(IHC.EQ.0) GO TO 300                                   LSQ2
      IF(YT.GE.YH) GO TO 173                                   LSQ2
      DO 168 I=1,M                                             LSQ2
      XS = XT(I)                                               LSQ2
      XT(I) = X(I,IH)                                          LSQ2
 168  X(I,IH) = XS                                             LSQ2
 173  DO 174 I=1,M                                             LSQ2
 174  XT(I)   = 0.75*X(I,IH)+0.25*XT(I)                        LSQ2
      CALL FN(YT,XT)                                           LSQ2
      IF(YT.GT.YH) GO TO 180                                   LSQ2
      Y(IH) = YT                                               LSQ2
      DO 175 I=1,M                                             LSQ2
 175  X(I,IH) = XT(I)                                          LSQ2
      GO TO 108                                                LSQ2
 180  DO 185 J=1,M1                                            LSQ2
      IF(J.EQ.IL) GO TO 185                                    LSQ2
      DO 182 I=1,M                                             LSQ2
      XT(I) = (X(I,J)+X(I,IL))/2.0                             LSQ2
 182  X(I,J) = XT(I)                                           LSQ2
      CALL FN(Y(J),XT)                                         LSQ2
 185  CONTINUE                                                 LSQ2
      GO TO 108                                                LSQ2
 300  IHC = 2*M1                                               LSQ2
      IF(M.GE.3) GO TO 350                                     LSQ2
      S = 0.0                                                  LSQ2
      DO 302 I=1,M                                             LSQ2
      X(I,M+2) = X(I,IH)-X(I,IL)                               LSQ2
      X(I,M+3) = X(I,IH)-X(I,I3)                               LSQ2
 302  S = S+X(I,M+2)**2                                        LSQ2
 303  S = SQRT(S)                                              LSQ2
      IF (S.EQ.0.0) S=1.0 E-5
 304  U = -X(2,M+2)/S                                          LSQ2
      X(2,M+2) = X(1,M+2)/S                                    LSQ2
      X(1,M+2) = U                                             LSQ2
      S = X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)                  LSQ2
      DO 305 I=1,M                                             LSQ2
 305  X(I,M+2) = X(I,M+2)*S                                    LSQ2
 306  DO 307 I=1,M                                             LSQ2
 307  XT(I) = X(I,IH)+X(I,M+2)                                 LSQ2
      CALL FN(YT,XT)                                           LSQ2
      DO 309 I=1,M                                             LSQ2
 309  XT(I) = X(I,IH)-X(I,M+2)                                 LSQ2
      CALL FN(YTT,XT)                                          LSQ2
      IF(YTT.LE.YT) GO TO 320                                  LSQ2
      DO 311 I=1,M                                             LSQ2
 311  XT(I) = X(I,IH)+X(I,M+2)                                 LSQ2
```

```
       YTT = YT                                                       LSQ2
320    Y(IH) = YTT                                                    LSQ2
       DO 321 I=1,M                                                   LSQ2
321    X(I,IH) = XT(I)                                                LSQ2
       GO TO 105                                                      LSQ2
350    DO 352 I=1,M                                                   LSQ2
       XT(I) = X(I,IH) - X(I,IL)                                      LSQ2
       X(I,M+2) = X(I,IH) - X(I,I2)                                   LSQ2
352    X(I,M+3) = X(I,IH) - X(I,I3)                                   LSQ2
       S = 0.0                                                        LSQ2
       S1 = 0.0                                                       LSQ2
       DO 355 I=1,M                                                   LSQ2
       S = S+XT(I)**2                                                 LSQ2
355    S1 = S1+X(I,M+3)**2                                            LSQ2
       S  = SQRT(S )                                                  LSQ2
       S1 = SQRT(S1)                                                  LSQ2
       S2 = 0.0                                                       LSQ2
       DO 357 I=1,M                                                   LSQ2
       XT(I) = XT(I)/S                                                LSQ2
       S2 = S2+XT(I)*X(I,M+2)                                         LSQ2
357    X(I,M+3) = X(I,M+3)/S1                                         LSQ2
       DO 360 I=1,M                                                   LSQ2
360    X(I,M+2) = X(I,M+2)-XT(I)*S2                                   LSQ2
       S1 = 0.0                                                       LSQ2
       DO 362 I=1,M                                                   LSQ2
362    S1 = S1+X(I,M+2)**2                                            LSQ2
       S1 = SQRT(S1)                                                  LSQ2
       DO 365 I=1,M                                                   LSQ2
365    X(I,M+2) = X(I,M+2)/S1                                         LSQ2
       S1 = 0.0                                                       LSQ2
       S2 = 0.0                                                       LSQ2
       DO 367 I=1,M                                                   LSQ2
       S1 = S1+XT(I)*X(I,M+3)                                         LSQ2
367    S2 = S2+X(I,M+2)*X(I,M+3)                                      LSQ2
       DO 370 I=1,M                                                   LSQ2
370    X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))                   LSQ2
       GO TO 306                                                      LSQ2
400    S = Y(1)                                                       LSQ2
       Y(1) = Y(IL)                                                   LSQ2
       Y(IL) = S                                                      LSQ2
       DO 402 I=1,M                                                   LSQ2
       XT(I) = X(I,IL)                                                LSQ2
       X(I,IL) = X(I,1)                                               LSQ2
402    X(I,1) = XT(I)                                                 LSQ2
       RETURN                                                         LSQ2
       END                                                            LSQ2
```

```
      PROGRAM CNSFT
      INTEGER SYST
      COMMON N,GEE(3,3),ALFA(3,3),A1,A2,B1,B2,C1,C2,T(100),TEMP(50),TB(5
     10),X(3,50),Y(3,50),GAMMA(3,50),GAMT(3,50),G(3,3),DAT(50),PT(50),
     1ERROR(3,50)
      DIMENSION Y1CAL(50),YERR(50),XAN(3,50)
1     FORMAT (3G8.5)
2     FORMAT (5G10.4)
3     FORMAT (3G10.5)
4     FORMAT (11F10.5)
5     FORMAT (9X,'A12=',F9.1,'A21=',F9.1,'A13=',F9.1,'A31=',F9.1,
     1'A23=',F9.1,'A32=',F9.1)
6     FORMAT (9X,'ALFA12=',F9.4,'ALFA13=',F9.4,'ALFA23=',F9.4)
9     FORMAT (4F12.5)
90    FORMAT (T8,'X1',T20,'Y1OBS',T32,'Y1CAL',T44,'DIFF')
11    FORMAT (/'MEAN DIFF IN Y1=',F9.5)
13    FORMAT (T4,'X1',T15,'X2',T27,'Y1',T32,'GAMMA1OBS',T42,'GAMMA1CAL',
     1T53,'ERROR1',T63,'GAMMA2OBS',T73,'GAMMA2CAL',T84,'ERROR2',T94,
     1'TEMPOB',T104,'TEMPCAL')
14    FORMAT (I2)
15    FORMAT (2G8.2)
16    FORMAT (G3.1)
      READ 14,N
      READ 16,VV
      NCOMP=3
      NC=NCOMP-1
      DO 25 L=1,N
      READ 2,XAN(1,L),XAN(2,L),Y(1,L),PT(L),TEMP(L)
25    CONTINUE
      READ 15,T(1),T(2)
      READ 3,A1,B1,C1
      READ 3,A2,B2,C2
      DO 40 L=1,N
      XAN(3,L)=1.-(XAN(1,L)+XAN(2,L))
      Z=XAN(1,L)+XAN(2,L)+VV*XAN(3,L)
      X(2,L)=XAN(2,L)/Z
      X(1,L)=XAN(1,L)/Z
      X(3,L)=1.-(X(1,L)+X(2,L))
      Y(2,L)=1.-Y(1,L)
40    Y(3,L)=0.0000
      NN=1
      DO 400 NN=1,9
      DO 10 I=1,NCOMP
10    READ 1,(GEE(I,J),J=1,NCOMP)
      DO 20 I=1,NCOMP
20    READ 1, (ALFA(I,J),J=1,NCOMP)
      PRINT 5,GEE(1,2),GEE(2,1),GEE(1,3),GEE(3,1),GEE(2,3),GEE(3,2)
      PRINT 6, ALFA(1,2),ALFA(1,3),ALFA(2,3)
      PRINT 13
      CALL BPPT (T,TP)
```

```
          DO 500 L=1,N
  500     PRINT 4, X(1,L),X(2,L),Y(1,L),GAMMA(1,L),GAMT(1,L),ERROR(1,L),
         1GAMMA(2,L),GAMT(2,L),ERROR(2,L),TEMP(L),TB(L)
          YTOT=0.000
          PRINT 90
          DO 998 L=1,N
          Y1CAL(L)=RAT(L)/(1+RAT(L))
          YERR(L)=ABS(Y1CAL(L)-Y(1,L))
          PRINT 9,X(1,L),Y(1,L),Y1CAL(L),YERR(L)
          YTOT=YTOT+YERR(L)
  998     CONTINUE
          YMEAN=YTOT/N
          PRINT 11,YMEAN
  400     CONTINUE
          STOP
          END
```

```
      SUBROUTINE BBPT (T,TT)
      COMMON M,GEE(3,3),ALFA(3,3),A1,A2,B1,B2,C1,C2,T(100),TEMP(50),IB(5
     10),X(3,50),Y(3,50),GAMMA(3,50),GAMT(3,50),G(3,3),RAT(50),PT(50),
     1ERROR(3,50)
      DIMENSION P01(100),P02(100),Q(100),F(100),TAOU(3,3),CC(3),A(3),
     1BB(3),GLC(3),W(3),C(3),D(3),AA(3),OP01(50),OP02(50)
      NCOMP=3
      NC=NCOMP-1
      DO 400 L=1,N
      OP01(L)=10.0**(A1-B1/(TEMP(L)+C1))
      OP02(L)=10.0**(A2-B2/(TEMP(L)+C2))
      GAMMA(1,L)=(Y(1,L)*PT(L))/(X(1,L)*OP01(L))
      GAMMA (2,L)=(Y(2,L)*PT(L))/(X(2,L)*OP02(L))
      DO 1000 M=1,100
      T(1)=0.00
      T(2)=200.0
      IF (M.LE.2) GO TO 350
      IF ((Q(1)*Q(M-1)).LE.0.0) T(M)=(T(1)+T(M-1))/2.
      IF ((Q(1)*Q(M-1)).GT.0.0) T(M)=( T(M-1)+TTT)/2.
  350 P01(M)=10.0**(A1-B1/(T(M)+C1))
      P02(M)=10.0**(A2-B2/(T(M)+C2))
      PPP1=P01(M)
      PPP2=P02(M)
      DO 45 I=1,NCOMP
      DO 50 J=1,NCOMP
      TAOU(I,J)=GEE(I,J)/(1.9872*(T(M)+273.2))
   50 G(I,J)=EXP(-ALFA(I,J)*TAOU(I,J))
   45 CONTINUE
      DO 302 I=1,NC
      CC(I)=0.
      A(I)=0.
      W(I)=0.
      DO 301 J=1,NCOMP
      C(J)=0.
      D(J)=0.
      DO 300 K=1,NCOMP
      IF(J.GE.2) GO TO 299
      A(I)=A(I)+TAOU(K,I)*G(K,I)*X(K,L)
      W(I)=W(I)+G(K,I)*X(K,L)
  299 C(J)=C(J)+X(K,L)*TAOU(K,J)*G(K,J)
       D(J)=D(J)+G(K,J)*X(K,L)
  300 CONTINUE
      AA(I)=A(I)/W(I)
      BB(J)=C(J)/D(J)
      CC(I)=CC(I)+((X(J,L)*G(I,J))/D(J))*(TAOU(I,J)-BB(J))
  301 CONTINUE
      GLC(I)=AA(I)+CC(I)
       GAMT(I,L)=EXP(GLC(I))
      ERROR(I,L)=(GAMT(I,L)-GAMMA(I,L))*100./GAMMA(I,L)
  302 CONTINUE
```

```
         F(M)=GAMT(1,L)*X(1,L)*P01(M)+GAMT(2,L)*X(2,L)*P02(M)
         Q(M)=F(M)-PT(L)
 37      FORMAT (2F10.4,I2)
         IF (Q(M).GT.0.0) TIT=T(M)
         IF (ABS(Q(M)).LE.1.0) TB(L)=T(M)
         IF (ABS(Q(M)).LE.1.0) GO TO 103
 51      FORMAT ('M=100')
         IF (M.EQ.100) PRINT 51
 1000    CONTINUE
 103     CONTINUE
 55      FORMAT (6F10.4)
         RAT(L)=GAMT(1,L)*X(1,L)*PPP1/(GAMT(2,L)*X(2,L)*PPP2)
 400     CONTINUE
         RETURN
         END
```

```
      PROGRAM ISOTH
      INTEGER SYST
      DIMENSION X(3,40).Y(3,40),ALFA(3,3),GAMMA(3,40).GAMT(3,40),P0(2),
     1PT(40),A(2),W(2),G(3,40),D(3),TAOU(3,3),C(3),AA(2),BB(3),CC(2),
     1GLC(2),ERROR(3,40),XAN(3,40),Z(40).XPM(2,40),LGAMT(2,40).
     1Y1CAL(40),YERR(40),P1CAL(40),PERR(40)
      N=40
      NCOMP=3
      NC=NCOMP-1
 1    FORMAT (3G8.5)
 2    FORMAT (4G10.5)
 3    FORMAT (2G10.5,I2)
 4    FORMAT (9F10.5)
 5    FORMAT (9X,6F8.2)
 6    FORMAT (9X,3F8.2)
 7    FORMAT (1F12.5)
 8    FORMAT (/)
      DO 25 L=1,N
 25   READ 2,XAN(1,L),XAN(2,L),Y(1,L),PT(L)
      READ 3, P0(1),P0(2),SYST
      DO 40 L=1,N
      XAN(3,L)=1.-(XAN(1,L)+XAN(2,L))
      Y(2,L)=1.-Y(1,L)
      Z(L)=XAN(1,L)+XAN(2,L)+2.*XAN(3,L)
      X(1,L)=XAN(1,L)/Z(L)
      X(2,L)=XAN(2,L)/Z(L)
      X(3,L)=1.-(X(1,L)+X(2,L))
 40   Y(3,L)=0.0000
      DO 35 I=1,NC
      DO 30 L=1,N
 30   GAMMA(I,L)=(Y(I,L)*PT(L))/(X(I,L)*P0(I))
 35   CONTINUE
      DO 403 NN=1,3
      DO 10 I=1,NCOMP
 10   READ 1,(TAOU(I,J).J=1,NCOMP)
      DO 20 I=1,NCOMP
 20   READ 1, (ALFA(I,J),J=1,NCOMP)
      PRINT 5, TAOU(1,2),TAOL(2,1),TAOU(1,3),TAOU(3,1),TAOU(2,3),
     1TAOU(3,2)
      PRINT 6, ALFA(1,2),ALFA(1,3),ALFA(2,3)
      DO 50 I=1,NCOMP
      DO 50 J=1,NCOMP
 50   G(I,J)=EXP(-ALFA(I,J)*TAOU(I,J))
      DO 400 L=1,N
      DO 302 I=1,NC
      CC(I)=0.
      A(I)=0.
      B(I)=0.
      DO 301 J=1,NCOMP
      C(J)=0.
```

```
      D(J)=0.
      DO 300 K=1,NCOMP
      IF (J-2) 298,299,299
298   CONTINUE
      A(I)=A(I)+TAOU(K,I)*G(K,I)*X(K,L)
      W(I)=W(I)+G(K,I)*X(K,L)
299   C(J)=C(J)+X(K,L)*TAOU(K,J)*G(K,J)
       D(J)=D(J)+G(K,J)*X(K,L)
300   CONTINUE
      AA(I)=A(I)/W(I)
      BB(J)=C(J)/D(J)
      CC(I)=CC(I)+((X(J,L)*G(I,J))/D(J))*(TAOU(I,J)-BB(J))*
301   CONTINUE
      GLC(I)=AA(I)+CC(I)
      LGAMT(I,L)=GLC(I)
       GAMT(I,L)=EXP(GLC(I))
      ERROR(I,L)=(GAMT(I,L)-GAMMA(I,L))*100./GAMMA(I,L)
302   CONTINUE
400   CONTINUE
      DO 600 L=1,N
      PRINT 4, X(1,L),X(2,L),Y(1,L),GAMMA(1,L),GAMT(1,L),ERROR(1,L),
     1GAMMA(2,L),GAMT(2,L),ERROR(2,L)
600   CONTINUE
      PTOT=0.0
      YTOT=0.0
      PRINT 8
      DO 500 L=1,N
      RAT=(GAMT(1,L)*X(1,L)*P0(1))/(GAMT(2,L)*X(2,L)*P0(2))
      Y1CAL(L)=RAT/(1.+RAT)
      YERR(L)=ABS(Y1CAL(L)-Y(1,L))
      YTOT=YTOT+YERR(L)
      PTCAL(L)=GAMT(1,L)*P0(1)*X(1,L)/Y1CAL(L)
      PERR(L)=ABS(PTCAL(L)-PT(L))
      PTOT=PTOT+PERR(L)
500   PRINT 7,X(1,L),Y(1,L),Y1CAL(L),YERR(L)
      YMEAN=YTOT/N
      PMEAN=PTOT/N
      PRINT 93,YMEAN
      PRINT 94,PMEAN
93    FORMAT (//'YMEAN=',G12.5)
94    FORMAT (//'PMEAN=',G12.5)
403   CONTINUE
      STOP
      END
```

NOMENCLATURE

α = relative volatility in the absence of salt

α_s = relative volatility in the presence of salt

a_i = activity of component i

a_{12}, a_{21} = empirical constants in Wohl equation

A = empirical constant in several equations

B = empirical constant in several equations

C = empirical constant in several equations

C_s = salt concentration (moles of salt/moles of component i)

f_i = fugacity of component i in solution

f_i^0 = fugacity of pure component i

g_{ii}, g_{ij} = parameters of NRTL equation

$\bar{G}_i$ = partial Gibbs free energy

G^E = excess Gibbs free energy

G^M = Gibbs free energy of mixing

G_*^M = Gibbs free energy of mixing for an ideal solution

G_{ij} = function of NRTL equation

k_1, k_2 = empirical parameters

k_3 = salt effect parameter

M = salt concentration (g moles/kg of solvent)

n_i = number of moles of component i

N_i = generalized mole fraction of component i in any phase

P_T = total pressure

P_i^0 = saturated vapor pressure of pure component i

$\bar{P}_i$ = partial pressure of component i

P_1' = depressed vapor pressure

q_1, q_2 = effective molal volumes in Wohl equation

R = ideal gas constant

T = temperature, ^{0}K

v_i = molar volume of component i

V = total volume

x_i = analytical mole fraction of component i in liquid phase

x_i' = ionic mole fraction of component i in liquid phase

y_i = mole fraction of component i in the vapor phase

z_1, z_2 = effective volume fractions in Whol equation

α_{ij} = parameter of the NRTL equation

β_{ij} = generalized relative volatility

γ_i = activity coefficient of solvent i

γ_i' = ionic activity coefficient of solvent i

$\gamma_{i\pm}$ = mean rational activity coefficient of solvent i

Δ = difference between observed and calculated values

$\lambda_{ii}, \lambda_{ij}$ = parameters of Wilson equation

$\Lambda_{ii}, \Lambda_{ji}$ = parameters of Wilson equation

μ_i = chemical potential of component i

μ^E = excess chemical potential

ν = number of particles resulting from the dissociation of one mole of salt

References Cited:

1) Baker, et al., A.I.Ch.E. meeting, Detroit, 1973.

2) Broul, M.; Hlavaty, K. and J. Linek, Colln. Czech. Chem. Comm. (English), 34, 3428 (1969).

3) Chen, D.H. and R. Thompson, J. of Chem. and Eng. Data, 15, 4, 471 (1970).

4) Cook, R.A. and W.F. Furter, The Can. J. of Chem. Eng., 46, 119 (1968).

5) Furter, W.F., Extractive and Azeotropic Distillation, Advances in Chemistry Series, 115, 35 (1972).

6) Furter, W.R. and R.A. Cook, Int'l J. of Heat and Mass Transfer, 10, 1, 23 (1967).

7) Gardner, R.S., "A Subroutine to Minimize a Function of Several Variables" Inside Publication, 2698, U.S. Naval Ordinance Test Station, China Lake, California (1967).

8) Guffey, C.G. and A.H. Wehe, A.I.Ch.E.J., 18, 5, 913 (1972).

9) Hala, E., I. Chem. E. Symposium Series, No. 32, 5 (1969).

10) Hala, E.; Pick, J.; Fried, V. and O. Vilim, Vapour-Liquid Equilibrium, 2nd English Ed., Pergammon Press, Oxford (1967).

11) Hala, et al., Vapor-Liquid Equilibrium at Normal Pressures, Pergammon Press, New York (1968).

12) Hougen, O.A.; Watson K.M. and R.A. Ragatz, Chemical Process Principles Part II, John Wiley and Sons, Inc., New York (1959).

13) Jaques, D. and W.F. Furter, The Can. J. of Chem. Eng., 50, 502 (1972).

14) Jaques, D. and W.F. Furter, A.I.Ch.E.J., 18, 2. 343 (1972).

15) Jaques, D. and W.F. Furter, Extractive and Azeotropic Distillation, Advances in Chemistry Series, 115, 159 (1972).

16) Johnson, A.I. and W.F. Furter, Can. J. of Tech., 34, 413 (1957).

17) Johnson, A.I. and W.F. Furter, The Can. J. of Chem. Eng., 38, 78 (1960).

18) Johnson, A.I.; Ward, D.M. and W.F. Furter, Can. J. of Tech., 34, 514 (1957).

19) Kato, M.; Sato, T. and M. Hirata, J. of Chem. Eng. of Japan, 4, 4, 308 (1971).

20) Lindberg, G.W. and D. Tassios, J. of Chem. and Eng. Data, 16, 1, 52 (1971).

21) Long, F.A. and W.F. McDevit, Chem. Rev., 51, 119 (1952).

22) Marina, J.M., Ph.D. Dissertation, Newark College of Engineering (1971).

23) Marina, J.M. and D. Tassios, A.I.Ch.E. National Meetings, Houston (February 1971).

24) Meranda, D. and W.F. Furter, The Can. J. of Chem. Eng., 44, 10, 298 (1966).

25) Meranda, D., and W.F. Furter, A.I.Ch.E.J., 17, 1, 38 (1971).

26) Meranda, D. and W.F. Furter, A.I.Ch.E.J., 18, 1, 111 (1972).

27) Nagata, Isamu, J. of Chem. Eng. of Japan, 6, 1, 18 (1972).

28) Newstead, W.T. and W.F. Furter, A.I.Ch.E.J., 17, 5, 1246 (1971).

29) Ohe, S.; Yokoyama, K. and S. Nakamura, J. of Chem. and Engineering Data, 16, 1, 70 (1971).

30) Orye, R.V. and J.M. Prausnitz, Industrial and Engineering Chemistry, 57, 5 (1965).

31) Perry, J.H., Chemical Engineer's Handbook, 4th ed., McGraw-Hill (1963).

32) Prausnitz, J.M. and J.G. Targovnik, Chem. and Eng. Data Series-Industrial and Eng. Chem., 3, 2, 234 (1958).

33) Ramalho et al., I.E.C., 53, 895 (1961).

34) Renon, H. and J.M. Prausnitz, A.I.Ch.E.J., 14, 135 (1968).

35) Renon, H. and J.M. Prausnitz, I.E.C., 8, 413 (1969).

36) Rieder, M. and A.R. Thompson, Ind. Eng. Chem., 42, 2, 379 (1950).

37) Rius Miro, A.; Otero DeLa Gandara, J.L. and J.R. Alvarez Gonzalez, Anales Real Soc. Espan. Fis. y Quim., 53-B, 171 (1957).

38) Rius Miro, A.; Otero DeLa Gandara, J.L. and J.R. Alvarez Gonzalez, Anales Real Soc. Espan. Fis. y Quim., 53-B, 185 (1957).

39) RiusMiro, A. and A. Gonzalez, Anales Real Soc. Espan. Fis. y Quim., 54-B, 797 (1958).

40) Rius Miro, A.; Gonzalez, A. and A. Uriarte, Anales Real Soc. Espan. Fis. y Quim., 56-B, (1960).

41) Rius Miro, A.; Gonzalez A. and E. Artacho, Anales Real Soc. Espan. Fis. y Quim., 57-B, 219 (1961).

42) Rousseau, R.Q.; Ashercraft. D.L. and E.M. Schoenborn. A.I.Ch.E.J., 18, 4, 825 (1972).

43) Sada, E. and T. Morisue, J. of Chem. Eng. of Japan, 6, 5, 385 (1973).

44) Silverman, and D. Tassios, I.E.C., Process Design & Development, paper submitted for publication.

45) Timmermans, J., Physico-Chemical Constants of Binary Systems, Vol. 3, Interscience Publishers Inc., New York (1960).

46) Tsiparis, I.N., Data of Salt Effect in Vapour-Liquid Equilibrium, (in Russian), Edition of Lithuanian Agr. Acad., Kaunas, Lithuania, USSR (1966).

47) Tsiparis, I.N. and N.Yu., Smorigaite, Zhumal Obscher Khimir, 34, 12, 3867 (1964) (English).

48) Wilson, G.M., J. Am. Chem. Soc., 86, 127 (1964).

49) Yoshida, F.; Yasunishi, A. and Y. Hamada, Kogaku, 2, 2, 162 (1964).