

EXCESS THERMODYNAMIC FUNCTIONS OF BINARY MIXTURE: SYSTEMS FLUOROBENZINE+TOLUENE

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ABSTRACT. The excess enthalpy and the excess volume of mixing for the binary system Toluene+Fluorobenzene at 25°C. have been experimentally determined with the microcalorimeter and the pycnometer respectively. The results have been examined in the light of Bulescu's method and our modified approach reported earlier (Anantaraman *et. al.* 1961, 1962, 1963). An interesting feature of the present system is that the values of h^E and v^E are of opposite sign.

INTRODUCTION

In continuation of our study on the accurate measurements of the thermodynamic excess functions of binary liquid mixtures, one component of which is slightly dipolar, and their interpretations in the light of the recent theories on the weak dipolar orientation, (Anantaraman, *et. al.* 1961, 1962, 1963) we report here the results of the study on the fluorobenzene-toluene system. Values of the excess enthalpy and the excess volume of mixing at 25°C are given and the results are analysed by our modified theoretical approach.

EXPERIMENTAL

Experimental procedures adopted for the measurement of the excess enthalpy and the excess volume change were almost the same as described earlier except that the heating unit in the thermostat of the excess enthalpy measuring gadget was replaced by a freon gas operated cooling unit.

Purification of the Sample

Fluorobenzene was prepared in this laboratory from the decomposition of stable salt benzene diazonium fluoborate by the method of Balz and Schiemann (1943). The distillate was separated from any phenol that had settled out. It was washed with 10% sodium hydroxide solution until the washings were almost colourless and then once with water. It was dried by shaking with crushed calcium chloride and then distilled in an all glass assembly. The middle fraction collected was further dried and distilled over a 40 plate fractionating column.

The purification of toluene was done in the same way as stated earlier (Anantaraman, *et. al.* 1963). Comparison of the densities of toluene and fluoro-

benzene measured in our laboratory with those from other standard works has been made in Table I.

TABLE I
Densities of Pure Substances

Substance	Density, g/cm (This work at 25°C)	Density, g/cm (other determinations)	Ref.
Toluene	0.86271	0.86250	J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds (Elsevier Publishing Co., 1950)
Fluorobenzene	1.0191	1.01919	

RESULTS AND DISCUSSION

The excess heat and volume change of mixing were determined at 25°C to enable us to compare the experimental results directly with the theoretical predictions without taking recourse to any interpretations. In the present work certain drawbacks of earlier works in this respect have been avoided. The excess heat against the mole fraction shows a minimum of 55.0 J/mole occurring near x_A (mole-fraction of toluene) = 0.5

On the other hand, similar plot for excess volume shows a maximum of 0.035 C.C. near $x_A = 0.35$.

The excess heat can be best represented by the equation

$$\frac{h^E}{x_A x_B} = -220.4 - 7.75(x_A - x_B) + 28.5(x_A - x_B)^2 \text{ J/mole} \quad (I)$$

Although the plot of excess volume shows a pronounced asymmetric behaviour where the maximum has been shifted far towards the polar end of the scale, too much importance should not be given to the exact shape of this curve. This is due to the fact that excess volume is itself very small and consequently the error

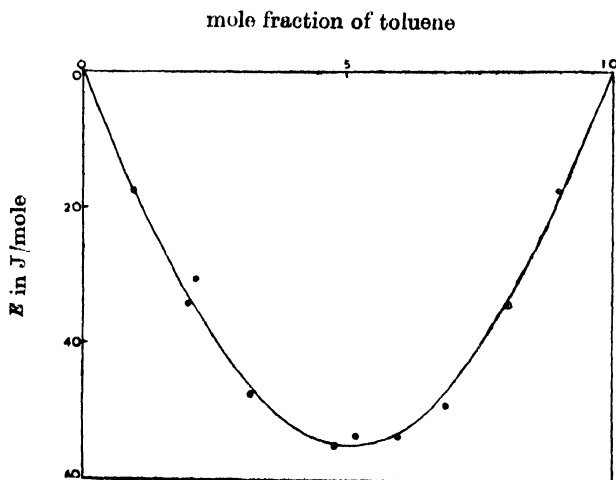


Fig. 1. Heats of mixing system: Toluene: Fluorobenzene—Temp. 25°C.

may be very large, particularly, at the both ends of the mole fraction scale. Due to this reason no empirical equation has been given for v^E . We satisfy ourselves with the value of v^E at $x_A = 0.5$. Table II and Table III give respectively the values of h^E and v^E measured at 25°C while figure 1 graphically represents the h^E data.

TABLE II
Heat of mixing

System : Toluene + Fluorobenzene
Temp. X_A =molefraction of toluene in the mixture, in J/mole
25°C

X_A	.0944	.1994	.2142	.3175	.4801	.5163	.5997	.6877
h^E	-17.6	-34.2	-30.0	-47.7	-55.1	-53.5	-53.5	-49.0
X_A					0.8038	0.9031		
h^E					-34.5	-17.6		

TABLE III
Volume change of mixing

System : Toluene + Fluorobenzene
Temp. 25°C
 x_A =mole fraction of toluene in the mixture ; in gm/mole.

x_A	0.0365	0.118	0.2748	0.3902	0.4887	0.6496	0.8619
v^E	+0.012	+0.011	+0.024	+0.027	+0.028	+0.020	+0.012
x_A	0.1819	0.3519	0.4696	0.5211			
v^E	+0.023	+0.031	+0.027	+0.030			

For a theoretical analysis we follow Anantaraman, Bhattacharyya and Palit, (1961) and treat the system as a mixture of polarizable dipolar and polarizable nonpolar molecules where each excess function consists of three terms such as

$$h^E = h_o^E + h_p^E(\text{pure dipolar}) + h_p^E(\text{polarizability}) \dots (2)$$

The first term of the R. H. S. of (2) is the contribution of central forces and the remaining two terms are due to orientational forces of dipolar origin. The contribution due to polarizability can be neglected and we are left with the first two terms only. If one assumes, for unlike molecules, the combination of "Lorentz —Berthelot" type, one gets the Balescu's (1955) expressions for the excess functions of pure dipolar origin. The corresponding expressions for the central forces should then be taken from equation (10.7.5) of Prigogine (1957). On the other hand, if there is a deviation from the above mentioned combination rule we shall use Anantaraman, Bhattacharyya and Palit's equations (24 and 25) for pure dipolar contributions and use corresponding expressions from central forces from Prigogine taking account of this deviation. Table IV gives the critical constants of pure substance.

TABLE IV
Critical constants of pure substance

Substance	t_c °C	p_c atmos.	v_c cm ³ /mole
Toluene	320.6 ⁹	41.6 ⁹	304.9
Fluoro benzene	286.5 ¹	44.62 ¹	268.9

We have preferred to calculate δ and ρ from critical constants of the pure components assuming that they obey the theorem of corresponding states. Only reliable value of t_c and p_c can be obtained for fluorobenzene and v_c of this component has been calculated from the empirical equation.

$$p_c = \frac{20.8T_c}{(\bar{V}_c - 8)} \quad \dots (3)$$

where p_c is in atmosphere, T_c is absolute temperature and \bar{V}_c indicates the critical molar volume. To maintain the uniformity and to reduce the errors same procedure has been adopted to obtain \bar{V}_c of toluene. Table V illustrates the close agreement of δ and ρ calculated from critical constants by two different methods, i. e.

$$1 + \delta = T_c^B / T_c^A \quad \dots (4)$$

$$= p_c^B V_c^B / p_c^A v_c^A \quad \dots (5)$$

and $(1 + \rho)^3 = v_c^B / v_c^A \quad \dots (6)$

$$= p_c^A \cdot T_c^B / p_c^B T_c^A \quad \dots (7)$$

where A is the reference component in terms of which ρ and δ have been expressed.

TABLE V
Values of δ and ρ calculated from two different equations

Reference Substance	$1 + \delta$			$1 + \rho$		
	from (4)	from (5)	mean	from (6)	from (7)	mean
Toluene	0.9426	0.9459	0.9443	0.9603	0.9596	0.9600
Fluorobenzene	1.0608	1.0572	1.0590	1.0413	1.0421	1.0417

The value of the dipolar perturbation Γ and all the configurational properties of the pure components at 25°C are taken from Anantaraman *et al.* (1963).

We first calculate the excess functions assuming that the "Lorentz-Brthelot" combination rule (i.e. $\theta = \delta^2/8$) is obeyed. For an equimolecular mixture with $\delta = 0.0577$ and $\rho = -0.040$, one obtains at 25°C.

$$h_o^E \text{ (Toluene as reference)} = 49.4 \text{ cal mole}^{-1},$$

$$h_o^E \text{ (Fluorobenzene as reference)} = 50.2 \text{ cal mole}^{-1}$$

$$\bar{h}_o^E \text{ (average)} = 49.8 \text{ cal mole}^{-1}; h_p^E = 68.8 \text{ cal mole}^{-1}$$

$$h^E = +118 \text{ cal mole}^{-1}$$

$$\begin{aligned}
 v_0^E \text{ (Toluene as reference)} &= 0.253 \text{ cm}^3 \text{ mole}^{-1} \\
 v_0^E \text{ (fluorobenzene as reference)} &= 0.251 \text{ cm}^3 \text{ mole}^{-1} \\
 \bar{v}_0^E \text{ (average)} &= 0.252 \text{ cm}^3 \text{ mole}^{-1} \\
 v_p^E &= 0.187 \text{ cm}^3 \text{ mole}^{-1}; \quad v^E = 0.439 \text{ cm}^3 \text{ mole}^{-1}
 \end{aligned}$$

While the experimental values for an equimolar mixture at 25°C are :

$$h^E = -13.1 \text{ cal mole}^{-1}; \quad v^E = 0.03 \text{ cm}^3 \text{ mole}^{-1}.$$

The calculated results are thus not in agreement with experimental data ; even the sign of h^E has not been correctly predicted.

Next we assume deviation from "Lorentz-Berthelot" approximation and proceed with the Anantaraman *et al's* treatment. We adjust θ to fit h^E the excess function believed to be most accurately obtained experimentally. The excess volume v^E is then predicted using the value of θ obtained in this way. One could, in principle, retain both ϵ_{AB} (i.e θ) for r_{AB}^0 in the expressions of excess functions and then adjust them to obtain the best possible fit. But such a procedure would hardly be worth while here as the data available for this system would not be sufficient to compare these parameters for consistency.

Proceeding as mentioned we obtained $\theta = +0.0207$ when toluene is taken as the reference substance, the value of δ and ρ remaining unchanged as before. For an equimolar mixture at 25°C the calculated excess functions are :

$$\begin{aligned}
 h_0^E \text{ (toluene as reference)} &= -85.8 \text{ cal mole}^{-1} \\
 h_0^E \text{ (fluorobenzene as reference)} &= -84.0 \text{ cal mole}^{-1} \\
 \bar{h}_0^E \text{ (average)} &= -84.9 \text{ cal mole}^{-1} \\
 h_p^E &= 71.8 \text{ cal mole}^{-1} \\
 h^E &= -13.1 \text{ cal mole}^{-1}
 \end{aligned}$$

and

$$\begin{aligned}
 v_0^E \text{ (toluene as reference)} &= -0.107 \text{ cm}^3 \text{ mole}^{-1} \\
 v_0^E \text{ (fluorobenzene as reference)} &= -0.104 \text{ cm}^3 \text{ mole}^{-1} \\
 \bar{v}_0^E \text{ (average)} &= 0.106 \text{ cm}^3 \text{ mole}^{-1} \\
 v_p^E &= 0.198 \text{ cm}^3 \text{ mole}^{-1} \\
 v^E &= 0.094 \text{ cm}^3 \text{ mole}^{-1}
 \end{aligned}$$

We find that the predicted v^E is very close to the experimental result and the agreement is more or less satisfactory. As the absolute value of v^E is itself very small and as the theoretical value of v^E is obtained from the difference of two large quantities, a small error in any of the parameters used for theoretical calculation will cause here a large discrepancy between the experimental and the predicted result. The main source of error lies, of course, in the estimation of ρ and δ , which may contain an uncertainty from 5 to 10%. Beside this, we have neglected the contribution from another important source, viz., the contributions of globular origin. The latter effect has been supposed to be appreciable for many similar systems*. It is possible, in principle, to estimate this effect from the simul-

*S. N. Bhattacharyya (unpublished results to be communicated shortly).

taneous measurement of all three major excess functions i.e., g^E , h^E and v^E . Work is in progress in this laboratory to obtain g^E of this system and to ascertain from it such effects. It might be mentioned in this connection that the excess functions of this system are very peculiar and interesting in the sense that they have opposite signs i.e., $h^E < 0$ and $v^E > 0$. Two other systems studied by Anantaraman *et al* (1961, 1963) might be recalled here for comparison. One is the "carbontetrachloride+chlorobenzene" system where $h^E > 0$ and $v^E < 0$ whereas in another, "chlorobenzene+toluene" both h^E and v^E have negative values. Most of the other system of this types have $h^E > 0$ and $v^E > 0$. The fair success of the present approach to such an unusual set of excess functions again shows its validity and demonstrates clearly the complex nature of their origin.

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REFERENCES

- Anantaraman, A. V. Bhattacharyya S. N. and Palit, S. R. 1961, *Trans. Faraday Soc.*, **57**, 40.
- Anantaraman, A. V. Bhattacharyya S. N. and Palit, S. R. 1963, *Trans. Faraday Soc.*, **59**, 1101.
- Anantaraman, A. V. Bhattacharyya S. N. and Palit, S. R. 1963, *Ind. Jour. Chem.*, **1**, 459.
- Balescu R., 1955, *Acad. Roy. Belg., Cl. Sc.*, **41**, 1242.
- Bhattacharyya S. N. Anantaraman A. V. and Palit, S. R. 1962, *Physica*, **28**, 633.
- Flood D. T. in "Organic Syntheses" Blat-(A. II. Editor), 1943, Collective Vol. 2, (John Wiley & Sons Inc., New York), pp. 295.
- Prigogine, I. 1957, "Molecular theory of Solutions" (North-Holland Publishing Company, Amsterdam,) Chapter XIV.
- Prigogine, I. *ibid*, pp. 215.
- Prigogine, I. *ibid*, pp. 196.
- Timmermans, J. 1950, "Physico-chemical constants of pure organic compounds" (Elsevier Publishing Co.) p. 152, 281.