

AROMATIC FLUOROCARBON MIXTURES

II.* CARBON TETRACHLORIDE+HEXAFLUOROBENZENE

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Abstract

The molar excess enthalpies and molar excess volumes of carbon tetrachloride+hexafluorobenzene have been measured at 298·15 K and 308·15 K. The values for the equimolar mixture at 298·15 K are 490 J mol⁻¹ and 0·875 cm³ mol⁻¹ respectively. The results are compared with the values for other liquid mixtures containing a fluorocarbon as one component, and discussed in terms of solubility parameter theory.

Solutions in which one of the components is an aliphatic or alicyclic fluorocarbon have been extensively investigated.^{1,2} While some such solutions display positive deviations from ideality in qualitative agreement with theoretical expectations, many (e.g. those with aliphatic or alicyclic hydrocarbons) show anomalously large positive deviations leading in many cases to incomplete miscibility. Interpretations of this anomalous behaviour of fluorocarbon solutions have been discussed by Scott.¹

Following the discovery by Patrick and Prosser³ that benzene and hexafluorobenzene form a 1 : 1 intermolecular compound in the solid state, there have been several studies of aromatic hydrocarbon+aromatic fluorocarbon systems and concomitant alicyclic hydrocarbon+aromatic fluorocarbon and alicyclic hydrocarbon+alicyclic fluorocarbon systems. This work has recently been reviewed.⁴ Much of it has been discussed in terms of complex formation between the unlike molecules in the aromatic hydrocarbon+aromatic fluorocarbon systems.

As a continuation of the above studies we have measured the molar excess enthalpies (molar heats of mixing) and molar excess volumes (molar volumes of mixing) of carbon tetrachloride+hexafluorobenzene. It is believed that no complex formation takes place in this system and that it can consequently be discussed in terms of current theories of nonelectrolyte solutions.

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¹ Scott, R. L., *J. phys. Chem.*, 1958, **62**, 136.

² Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L., "Regular and Related Solutions," (Van Nostrand-Reinhold: New York 1970).

³ Patrick, C. R., and Prosser, G. S., *Nature*, 1960, **187**, 1021.

⁴ Fenby, D. V., *Rev. pure appl. Chem.*, 1972, **22**, 55.

Experimental

The calorimeter was similar to that of Larkin and McGlashan⁵ and has been discussed elsewhere.⁶ The molar excess volumes were measured using the dilatometer discussed previously.⁷

Carbon tetrachloride (BDH Analar) was dried over freshly activated molecular sieve (type 10X) and then fractionally distilled in a column of 15 theoretical plates at a reflux ratio of 20 in an atmosphere of dry nitrogen. The middle fraction was degassed by successive freezing, pumping, and melting cycles, and was further dried over P₂O₅.

Hexafluorobenzene (I.S.C. Chemicals) had a purity, as indicated by g.l.c.,⁸ of 99.97 mol % with pentafluorobenzene the probable impurity.

Results and Discussion

The molar excess enthalpies H_m^E and molar excess volumes V_m^E of CCl₄+C₆F₆ are given in Tables 1 and 2. The composition is expressed as the mole fraction x_2 of hexafluorobenzene.

TABLE 1
MOLAR EXCESS ENTHALPIES H_m^E /J mol⁻¹ OF CCl₄+C₆F₆

At 298.15 K									
x_2	0.1117	0.2219	0.3452	0.4606	0.5510	0.5728	0.6524	0.7295	0.8117
H_m^E	287	441	520	509	462	442	373	308	215
At 308.15 K									
x_2	0.2903	0.4417	0.5156						
H_m^E	486	498	462						

TABLE 2
MOLAR EXCESS VOLUMES V_m^E /cm³ mol⁻¹ OF CCl₄+C₆F₆

At 298.15 K									
x_2	0.1533	0.2187	0.2551	0.3767	0.3995	0.4472	0.5442	0.6870	0.7801
V_m^E	0.582	0.677	0.788	0.896	0.925	0.897	0.841	0.639	0.484
At 308.15 K									
x_2	0.3337	0.4366	0.4961	0.5812					
V_m^E	0.880	0.922	0.880	0.814					

The results at 298.15 K were fitted by a least-squares computer program to the expressions

$$H_m^E/\text{J mol}^{-1} = x_2(1-x_2) \sum_{n=0}^m h_n(1-2x_2)^n \quad (1)$$

$$V_m^E/\text{cm}^3 \text{ mol}^{-1} = x_2(1-x_2) \sum_{n=0}^m v_n(1-2x_2)^n \quad (2)$$

in which x_2 is the mole fraction of hexafluorobenzene and the h_n and v_n values are

⁵ Larkin, J. A., and McGlashan, M. L., *J. chem. Soc.*, 1961, 3425.

⁶ Fenby, D. V., Billing, G. J., and Smythe, D. B., *J. chem. Thermodynamics*, in press.

⁷ Lau, C. F., Wilson, P. T., and Fenby, D. V., *Aust. J. Chem.*, 1970, **23**, 1143.

⁸ Fuller, G., personal communication.

constants. The molar excess enthalpies could be fitted satisfactorily with three parameters and the molar excess volumes with two; these are as follows:

$$\begin{aligned} H_m^E: & \quad h_0 \ 1959, h_1 \ 1008, h_2 \ 200 \quad (\sigma \ 4.0 \text{ J mol}^{-1}) \\ V_m^E: & \quad v_0 \ 3.501, v_1 \ 1.249 \quad (\sigma \ 0.020 \text{ cm}^3 \text{ mol}^{-1}) \end{aligned}$$

where σ is the standard deviation defined in the usual way:

$$\sigma = [\text{sum of squared deviations}/(\text{No. of observations} - \text{No. of parameters})]^{1/2}$$

The molar excess enthalpy of the system $\text{CCl}_4 + \text{C}_6\text{F}_6$ is positive and its temperature coefficient (the molar excess heat capacity at constant pressure) is slightly negative. This is the usual situation for liquid mixtures involving no complex formation and consequently it is believed that this system should be amenable to interpretation in terms of current theories of nonelectrolyte solutions.

Hildebrand *et al.*² in discussing the behaviour of solutions containing aliphatic and alicyclic fluorocarbons as one component have noted that "... mixtures of fluorocarbons with certain substances (CCl_4 , C_6H_6 , etc.) show reasonable agreement with the predictions from their solubility parameters, as do the solid solubilities of I_2 and SnI_4 ; but with other substances (principally aliphatic hydrocarbons, but also including Kr), the disagreement is extreme". Solubility parameter theory was reasonably successful in accounting for the molar excess functions of the systems $\text{CCl}_4 + n\text{-C}_7\text{F}_{16}$ and $\text{CCl}_4 + \text{CF}_3\text{C}_6\text{F}_{11}$.¹ It is therefore of interest to compare our molar excess enthalpy results for $\text{CCl}_4 + \text{C}_6\text{F}_6$ with the predictions of solubility parameter theory.

According to the Scatchard-Hildebrand solubility parameter theory,² the molar excess energy at constant volume is given by

$$U_m^E = (x_1 V_{m1} + x_2 V_{m2})(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (3)$$

in which x_i , V_{mi} , ϕ_i , and δ_i refer to the mole fraction, molar volume, volume fraction, and solubility parameter, respectively, of the component i . From equation (3), the maximum U_m^E occurs at

$$x_2 = \sqrt{V_{m1}}/(\sqrt{V_{m1}} + \sqrt{V_{m2}}) \quad (4)$$

and has the magnitude

$$U_{m,\max}^E = (\delta_1 - \delta_2)^2 V_{m1} V_{m2} / (\sqrt{V_{m1}} + \sqrt{V_{m2}})^2 \quad (5)$$

According to equations (4) and (5) the maximum molar excess energy is 13 J mol^{-1} and occurs at $x_2 = 0.48$. The maximum in our molar excess enthalpy at 298.15 K is 520 J mol^{-1} and occurs at $x_2 = 0.39$. Correcting for the volume changes accompanying mixing we obtain, from our molar excess enthalpy results, a molar excess energy U_m^E at 298.15 K with a maximum of 227 J mol^{-1} occurring at $x_2 = 0.35$. Clearly the agreement between theory and experiment is unimpressive. For the system $\text{CCl}_4 + \text{C}_6\text{F}_6$ the deviations from ideal solution behaviour are very much larger than predicted.

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