[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Enhanced Solubility in Solvent Mixtures. I. The System Phenanthrene–Cyclohexane–Methylene Iodide[1]

BY LEONARD J. GORDON[1a] AND ROBERT L. SCOTT

The Hildebrand theory of regular solutions predicts that whenever the internal pressure of a solid (or rather the metastable supercooled liquid) lies between those for two solvents, there will be a range of solvent mixtures in which the solubility of the solid is greater than in either solvent alone. This enhanced solubility has been observed in the system phenanthrene–cyclohexane–methylene iodide, although the maximum solubility of the phenanthrene in the optimum solvent mixture falls short of the ideal value predicted by the theory.

Introduction

Regular solution theory[2] when applied to the solubility of solid non-electrolytes gives solubility relationships in terms of the thermodynamic properties of the pure substances, principally the melting point and heat of fusion of the solute, and the so-called "solubility parameters" of the various components. The solubility parameter δ is usually defined as the square root of the internal pressure or cohesive energy density, and may be calculated for a given substance in various ways,[3] usually from the molar energy of vaporization and the molar volume

$$\delta = (\Delta E^V / v)^{1/2} \qquad (1)$$

Where the solubility parameter of a solid solute (calculated for the supercooled liquid) is between those of two solvents, the theory predicts that there will be a range of solvent mixtures in which the solid is more soluble than in either pure solvent. As far as we know this effect has not heretofore been reported for three component systems of normal non-polar or slightly polar liquids, although an analogous enhanced solubility in solvent mixtures has previously been observed in the case of high polymers.[4,5]

The system chosen for studying this enhanced solubility consisted of phenanthrene ($\delta = 9.8$, estimated), cyclohexane ($\delta = 8.2$) and CH_2I_2 ($\delta = 11.8$). In addition to satisfying the necessary solubility parameter conditions, this system is reasonably free from the complications of hydrogen bonding and high polarity[6] and the thermodynamic properties of the components make the system a convenient one for experimental measurements.

It was of interest to investigate the system further and, therefore, the two phase solvent–solvent phase diagram was determined, and some aspects of the three-phase freezing diagram were determined.

Theory

The ideal solubility of a solid (expressed as mole fraction x^i in its saturated solution) is given by the equation

$$RT \ln x^i = -\Delta H^F (1 - (T/T_m)) \qquad (2)$$

where ΔH^F is its heat of fusion, and T_m its melting point.

If the solution is not ideal, $RT \ln x^i$ is replaced by $RT \ln a$, where a is the activity of the solute in the saturated solution. According to regular solution theory, the deviations from ideality are related to the partial molal heat of mixing ΔH_1 of the supercooled liquid solute with the solvent

$$RT \ln (x_1^i/x_1) = RT \ln (a_1/x_1) = \Delta H_1 = v_1 \phi_0^2 (\delta_1 - \delta_0)^2 \qquad (3)$$

where the δ's are solubility parameters, the ϕ's volume fractions and the v's molar volumes of components 0 (solvent) and i (solute).

For three component systems the theory[7] leads (with no further assumptions than those involved in the two-component case) to equations which are identical with Equation 3 if ϕ_0 is taken as the total volume fraction of solvents 2 and 3 and δ_0 is taken as the volume fraction average of δ_2 and δ_3

$$\delta_0 = \frac{\phi_2 \delta_2 + \phi_3 \delta_3}{\phi_2 + \phi_3} \qquad (4)$$

$$\phi_0 = \phi_2 + \phi_3 \qquad (5)$$

Consequently the thermodynamic behavior of the solute should not be affected by the fact that the solvent is a mixture[8] and its solubility should be equal to that in a hypothetical "single liquid" of average properties. It is easily seen that if δ_1 for the supercooled liquid solute lies between δ_2 and δ_3, a proper choice of solvent ratios will make δ_0 approach δ_1 and for the solvent mixture such that $\delta_0 = \delta_1$, the ideal solubility should be observed.

Experimental

All materials were Eastman Kodak Co. "white label," and were not further purified. (Small traces of impurities should have no effect except to depress all temperatures slightly in a more or less uniform way.)

Liquid mixtures were prepared having different ratios of cyclohexane to methylene iodide. For each "single liquid" a series of measurements of the solubility of phenanthrene were made by the "synthetic" method: Solid and solvent were weighed and then sealed in a glass ampule. The ampule was warmed until the solid dissolved and then cooled quickly so that the solid precipitated as finely divided crystals. The ampule was again heated this time at a rate not exceeding one-half degree per minute and the temperature at which the last crystal of solid dissolved was noted. Figure 1 gives the experimental results plotted in the usual manner. The precision of the temperature measurement was within one-half degree. From the best straight line for each liquid mixture the solubility at a given temperature was determined. A series of solubility curves at different

(1) First presented at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 11, 1951.

(1a) Present address: Aerojet Engineering Corporation, Azusa, Calif.

(2) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Third Edition, ACS Monograph #17, Reinhold, 1950.

(3) Reference 3, Chapter XXIII.

(4) G. Gee, Trans. Faraday Soc., 40, 468 (1944).

(5) R. L. Scott, J. Chem. Phys., 17, 268 (1949).

(6) According to C. P. Smyth and H. E. Rogers (THIS JOURNAL, 52, 2227 (1930)), the dipole moment of CH_2I_2 is 1.1 Debye units.

(7) Reference 3, Chapter XIII, p. 201.

(8) This conclusion is valid only if the solid phase in equilibrium with the solution is pure component 1; solid solutions introduce complications.

temperatures are shown in Fig. 2; the enhanced solubility in certain mixtures is obvious.
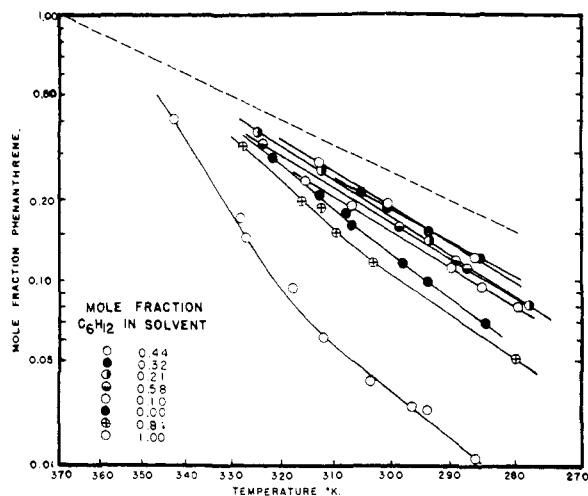

Fig. 1.—Solubility of phenanthrene in mixtures of cyclohexane and methylene iodide. Dotted line represents ideal solubility.
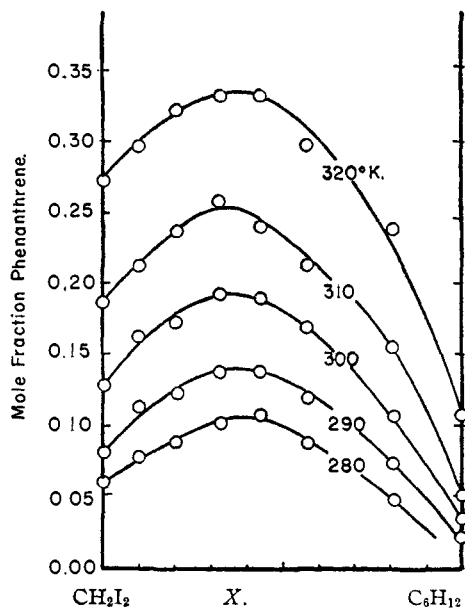

Fig. 2.—Solubility of phenanthrene at selected temperatures as a function of composition of the cyclohexane–methylene iodide mixture. (Circles are not the original experimental measurements, but are taken from the smoothed curves of Fig. 1.)

The two component system methylene iodide–cyclohexane was investigated by cooling various mixtures and observing the temperature at which heterogeneity (milkiness) appeared. The resulting phase diagram is given in Fig. 3.

The freezing points of various two-component mixtures were determined by inserting a thermocouple in the mixture and recording the maximum temperature obtained after supercooling. The experimental three-component diagram is given in Fig. 4, in addition to the experimental points shown. The freezing points in the three-component region were obtained in part from interpolation between two two-component curves.

Approximately forty solubility determinations were made for eight different solvent ratios including the two pure solvents and another forty experimental points were determined in the solvent separation and freezing regions of the phase diagram.
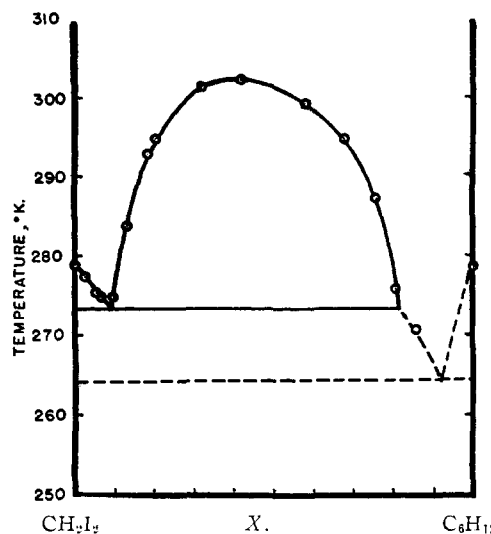

Fig. 3.—Experimental phase diagram for the binary system methylene iodide–cyclohexane.
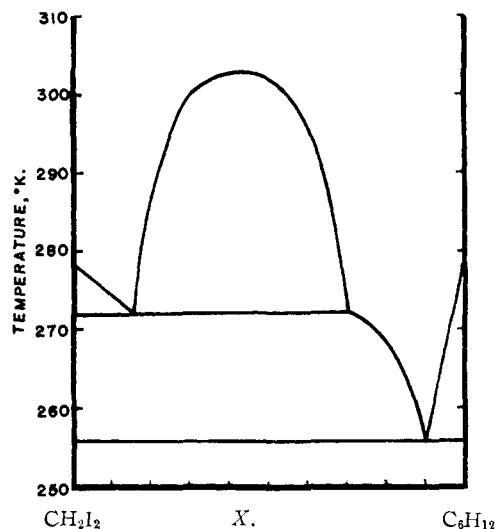

Fig. 3A.—Calculated phase diagram for the binary system methylene iodide–cyclohexane (using thermodynamic parameters of Table I).

The solubility points were found to fall fairly well on straight lines on a log mole fraction vs. temperature plot (Fig. 1). Each straight line was drawn to best fit the points for that particular solvent mixture and no attempt was made to draw the lines so as to represent a consistent family; however, the lines are nearly parallel. The effect of the slight differences in slopes is somewhat evident in Fig. 2; if the lines had been made consistent, these curves would be smoother.

Discussion

For comparison of experimental results with theory, the phase diagram Figs. 3a and 4a were calculated using the values in Table I. The properties of the three components were taken as constants independent of temperature. The solvent–solvent diagram was calculated by the method of Scatchard.[9]

The ideal solubility of phenanthrene was calculated using its heat of fusion[10] ΔH^F = 4300 cal./

(9) G. Scatchard, THIS JOURNAL, 62, 2426 (1940).

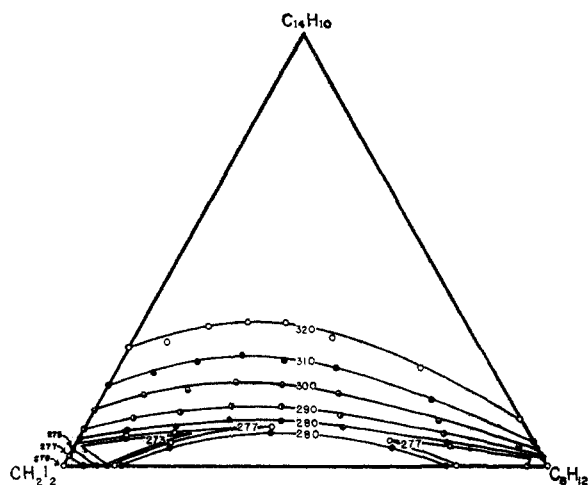(10) International Critical Tables, 5, 134 (McGraw-Hill, 1929)

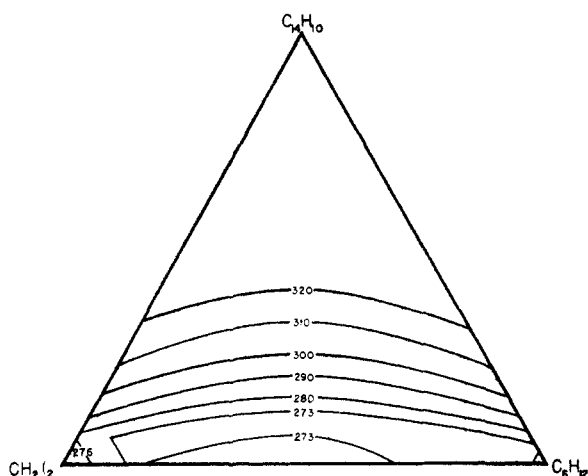Fig. 4.—Experimental phase diagram for the ternary system phenanthrene–methylene iodide–cyclohexane.

Fig. 4A.—Calculated phase diagram for ternary system phenanthrene–methylene iodide–cyclohexane.

mole at 96.3.[11] No correction for change of ΔH^F with temperature was made.

TABLE I

Component	v, cc./mole	δ
CH$_2$I$_2$	80	11.8
Cyclohexane	108	8.2
Phenanthrene (solid at m.p.)	143	
(supercooled liquid at 25°)	150[a]	9.8[b]

[a] A somewhat arbitrary value estimated from expansion of solid upon melting. [b] Estimated from solubility data: J. H. Hildebrand, E. T. Ellefson and C. W. Beebe, This Journal, 39, 2301 (1917).

There is complete qualitative agreement between the calculated and observed phase diagrams; however, there are several quantitative differences.

Table II gives a comparison of the maximum observed solubility at each temperature, taken from Fig. 2, with the predicted ideal.

The observed solubility of phenanthrene in CH$_2$I$_2$

(11) G. S. Parks, Ind. Eng. Chem., 23, 1138 (1931). There is some variation in the value of the melting point reported in the literature. Use of a melting point of 100° would make the ideal solubility at 25° 0.227 instead of 0.244.

TABLE II

SOLUBILITY OF PHENANTHRENE

(All concentrations expressed as mole fractions)

T, °K.	Calculated		Observed	
	Ideal solubility C$_{14}$H$_{10}$	$x_{C_6H_{10}}$ in "ideal" solvent	Maximum solubility C$_{14}$H$_{10}$	$x_{C_6H_{12}}$ in best solvent
280	0.153	0.49	0.108	0.42
290	.200	.49	.141	.38
300	.256	.49	.196	.38
310	.324	.49	.255	.35
320	.403	.49	.336	.39

Average   0.38 ± 0.02

agrees with the theoretical prediction. The solubility in cyclohexane is far below that predicted.

The solubility curve found here, however, is still "regular" and if $\delta = 9.8$ is accepted as correct for phenanthrene, the apparent δ of cyclohexane can be calculated from the theory (see Table III). Using the value 7.0, the predicted "ideal" solvent is found to have the molar composition 0.37 cyclohexane, 0.63 CH$_2$I$_2$. This agrees with the observed value within experimental error.

TABLE III

SOLUBILITY OF PHENANTHRENE IN CYCLOHEXANE

T, °K.	Mole fraction phenanthrene, $x_{C_{14}H_{10}}$	$\delta_1 - \delta_0$	δ_0 (cyclohexane)
286.0	0.0217	2.92	6.9
293.7	.0328	2.86	6.9
296.1	.0337	2.89	6.9
302.8	.0418	2.92	6.9
311.7	.0608	2.89	6.9
317.6	.0939	2.79	7.0
326.7	.144	2.84	7.0
328.2	.173	2.71	7.1
341.9	.404	2.74	7.1

7.0 ± 0.1

It should be noted however that the δ value 8.2 for cyclohexane gives almost exact agreement between theory and experiment for the solvent–solvent critical temperature.

The theory predicts that the ideal solubility will occur in a liquid having a composition such that $\delta_0 = \delta_1$. Examination of the complete three-phase diagram reveals that no such "ideal" solvent exists. The mixture of solvents having the desired stoichiometric composition is near enough to the solvent–solvent critical composition and temperature that extensive clustering must occur; consequently the solute is actually dissolved not in a homogeneous "ideal" solvent, but rather in a solvent which consists of microscopic regions richer either in cyclohexane or methylene iodide than the over-all average composition would indicate. At higher temperatures where clustering is less significant we may expect the mixed solvent to be more nearly "ideal."

We may try to allow for this clustering effect by using the more refined "quasi-chemical" equations for the free energies. Preliminary calculations (to be published later) indicate that this will account for part but not all of the discrepancy between the "ideal" solubility and the observed maximum solubility in the best mixed solvents.

Los Angeles, California