

Figure 3. Effect of carbon dioxide on the K -values of the components at various pressures and at 40° F.

diagrams are shown in Figures 1 and 2. Figure 3 shows the effect of carbon dioxide on the K -values of each of the components.

The accuracy of the actual temperature measurements is within $\pm 0.05^\circ$ F. at 100° F. and $\pm 0.5^\circ$ F. at -140° F. The gage readings are accurate within 2 parts per 1000 parts (0.2%). The study shows that the actual analyses are reproducible to within ± 0.1 mole %.

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LITERATURE CITED

- (1) Clark, A.M., Din, F., *Discussions Faraday Soc.* 15, 202 (1953).
- (2) Roberts, L.R., Wang, R.H., Azamoosh, A., McKetta, J.J., *J. CHEM. ENG. DATA* 7, 484 (1962).
- (3) Wang, R.H., "Vapor-Liquid Equilibrium of the Methane-*n*-Butane-Carbon Dioxide System at Low Temperatures," Ph.D. dissertation, University of Texas, Austin, Texas, 1963.

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Interaction in Nonelectrolyte Solutions

Solubility of Naphthalene in Some Mixed Solvents Containing Benzene

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The solubility of naphthalene has been determined in benzene and other solvents, and in solvent mixtures. The average uncertainty in the solubilities is 0.0005 mole fraction naphthalene in the binary systems and less than 0.001 mole fraction in the ternary systems. Ternary systems were investigated using the approaches of Guggenheim and Hildebrand. The average error in correlating predicted with experimental results is the same by either approach, 0.002 in mole fraction naphthalene. Better correlation of ternary with binary behavior is obtained with Raoult entropy than with that of Flory-Huggins. Data obtained from binary solution studies are used to predict behavior in ternary systems.

CORRELATION of solution behavior with molecular parameters has been considered in some detail for binary systems of nonelectrolytes (6-8, 16, 19). A related problem is the prediction of behavior in multicomponent nonelectrolyte systems from that of the various component pairs. The present work describes a study of solute solubility in mixed solvent systems. The components considered—naphthalene, benzene, toluene, ethylbenzene, carbon tetrachloride, cyclohexane, *n*-hexane and *n*-hexadecane—are characterized by the absence of pronounced polarity.

EXPERIMENTAL

Reagents. Naphthalene used was Eastman (recrystallized from alcohol) and Baker (reagent grade). Since both had indistinguishable properties, which were unchanged upon further recrystallization, they were used as received.

All solvents were purified by distillation at a recovery rate of 1 ml. min.⁻¹ and the middle half of the starting material of each distillation was used. Each solvent was double-distilled except for ethylbenzene (single) and *n*-hexadecane (triple). Distillations, except that of *n*-hexadecane at 5mm., were conducted at atmospheric pressure

under an atmosphere of nitrogen purified with sulfuric acid and sodium hydroxide. Phosphorus (V) oxide was used as drying agent prior to distillation for all solvents except benzene (sodium) and ethylbenzene (calcium hydride).

Refractive indices of the purified solvents were measured at $25 \pm 0.01^\circ \text{C}$. with a Bausch and Lomb Precision Refractometer, their infrared spectra were determined with a Perkin Elmer Model 421 Spectrometer, and their chromatographs were obtained with a Beckman GC-2 Gas Chromatograph. Table I contains a comparison of experimental and literature refractive indices, and an estimation of the purity based upon chromatography. It has been assumed that the ratio of area under an impurity peak to that under the peak of the major component is the same as the ratio of masses of the two substances in the sample. No significant impurity spectral peaks were found upon comparison with standard spectra (2).

Equipment. All analytical equipment was calibrated against certified standards. The systems were studied in a bath thermostated to $\pm 0.01^\circ \text{C}$. Solubility determinations were based upon refractometric measurements.

Procedure. Solubility was determined in both individual solvents and binary solvent mixtures. In the latter, determinations were made using a minimum of four (usually approximately equal) intervals of mixed solvent composition.

Mixtures of known composition were placed in small (ca. 65-ml.) glass bottles having TS glass stoppers carefully hand lapped to the extent that leak rates tested negligible. Solids were dissolved by gentle agitation with a magnetic stirrer. The refractive index of a fraction of the resulting solution was determined in duplicate. Additional naphthalene was added to achieve a second mixture of known composition, and the refractive index again measured after solution was complete. This procedure was continued until an amount of solute beyond that needed for saturation had been added.

Twelve hours of agitation were allowed for saturation, and this period was always found sufficient. The refractive index of the saturated solution was measured, and the observation was re-checked after adding more naphthalene and allowing an additional hour of agitation. Duplicate measurements ensured saturation and established that the saturating solid phase was unsolvated naphthalene.

Solute solubility for a given solvent composition was found by extrapolation of a plot of refractive index *vs.* solute concentration to the refractive index of the saturated solution. Prior to being plotted, solution compositions were corrected for the mass of components in the vapor phase. Mixtures of sufficient quantity were prepared so that this mass was comparably small, and corrections were

made assuming ideal solution behavior. The maximum correction to any mixture composition was 0.02 wt. % naphthalene.

The number of unsaturated solutions prepared for a given solvent composition was variable. Solubilities in the individual solvents were determined and served as a guide in the study of the solvent mixtures. Thus for an individual solvent, from six to 12 measurements of refractive indices of unsaturated solutions were made, ranging from pure solvent to near-saturation. In each of these systems, at least one point represented a replication.

The ethylbenzene, cyclohexane, and hexane binary systems are totally linear in refractive index *vs.* mole fraction solute. The other binary systems show a small curvature. The data summarized in Table II indicate that an uncertainty of more than 0.0005 in mole fraction solute at saturation is unlikely. Each curve is well defined, and the nonlinear systems involve a minor extrapolation.

For the ternary systems, it was assumed that extrapolation errors were similar to those of the binary systems. In these, extrapolation of the complete curve to the saturation refractive index value gave results differing by less than 0.001 mole fraction naphthalene from those obtained by extrapolation of the apparent straight line defined by a few points quite near saturation. The linear extrapolation approach was used for ternary systems. No actual test of linearity was made in ternary systems for the range from pure solvent mixture to saturation. For these solutions, usually four measurements of refractive indices were made, although in a few instances three were accepted if they were in a range quite near saturation, and required only slight extrapolation. No attempt at replication was made in ternary systems because of the difficulty in synthesis of ternary mixtures of a specified composition. An uncertainty of less than 0.001 in mole fraction naphthalene at saturation in mixed solvents is indicated.

BINARY SYSTEMS

Results. Experimental solubilities of naphthalene in mole and volume fractions are shown, respectively, in the third and fifth columns in Table III. Literature values (Column 4) were taken by the present authors from plots of the reported temperature dependence of solubility. There is considerable spread in the results of different workers, and the use of visually smoothed plots was considered adequate.

The molar excess Gibbs free energy of mixing (ΔG^E) in binary systems of nonelectrolytes is commonly expressed as a power series in the difference of component mole fractions (20).

Table I. Solvent Properties

Solvent	Source ^a	Refractive Index		Estimated Purity by Chromatography, Wt. %
		Exptl.	Lit.	
Benzene	MCB-S	1.49776	1.49790(15)	99.95
Ethylbenzene	MCB-S	1.49320	1.49330(15)	99.9
Toluene	MCB-A	1.49420	1.49413(15)	99.99
			1.49405(25)	
Carbon tetrachloride	MCB-S	1.45736	1.45704 (3)	99.99
			1.45732(25)	
			1.45759(27)	
<i>n</i> -Hexadecane	EOC-P	1.43267	1.43250 (3)	99.1
Cyclohexane	MCB-S	1.42325	1.42354(15)	99.8
<i>n</i> -Hexane	MCB-S	1.37256	1.37226(15)	99.99

^aEOC, Eastman Organic Chemicals; MCB, Matheson, Coleman and Bell; A, ACS Grade; P, Practical Grade; S, Spectroquality Grade.

Table II. Solubility Determination in Individual Solvents

Solvent	Extrapolation Factor ^a	10 ⁵ × Av. Dev. of n _D ^b	Naphthalene Equivalent ^c
Benzene	0.04	2	7
Ethylbenzene	0.11	3	8
Toluene	0.01	4	7
Carbon tetrachloride	0.02	6	5
n-Hexadecane	0.07	2	11
Cyclohexane	0.21	3	5
n-Hexane	0.04	4	4

^a Let the refractive index of pure solvent be n_D , that of the last solution prior to saturation with solute be n'_D and that of the saturated solution be n''_D . Then extrapolation factor $\equiv n''_D - n'_D/n'_D - n_D$. ^b From smoothed n_D vs. mole fraction naphthalene plot. ^c 10⁵ × mole fraction per 10⁻⁵ n_D unit.

$$\Delta G^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] \quad (1)$$

where A, B, C , are empirical constants specific to the system. The terms in the brackets of Equation 1 represent the molar energy of interaction of the components. Guggenheim (6) has shown that for s-regular systems (16) the constants beyond A are zero leaving:

$$\Delta G^E = x_1 x_2 W \quad (2)$$

W is the interchange energy of components 1 and 2.

Hildebrand and Scott (7) have obtained an expression for regular solutions (16) comparable to Equation 2:

$$\Delta G^E = (n_1 V_1^0 + n_2 V_2^0) \phi_1 \phi_2 (c_{11} + c_{22} - 2c_{12}) \quad (3)$$

Where

- n_i = moles of i
- V_i^0 = molar volume of i
- ϕ_i = volume fraction of i
- c_{ij} = interaction energy density (the negative of the potential energy per unit volume)

For brevity, the combination of interaction energy densities in Equation 3 will be expressed here as W' , so that the equation may be re-stated as:

$$\Delta G^E = V_{12}^0 \phi_1 \phi_2 W' \quad (4)$$

Equations 2 and 4 may be applied to mixtures showing either positive or negative deviations from ideal behavior. They differ in the assumed dependence of ΔG^E on composition unless V_1^0 equals V_2^0 .

For endothermic solutions, Hildebrand has shown (7) that the assumption of the interaction of unlike components as the geometric mean (17) allows a restatement of Equations 2 and 4 in terms of the solubility parameters of the individual components, δ_i ;

$$\Delta G^E = V_{12}^0 \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (5)$$

δ_i may be calculated from (7):

$$\delta_i = (\Delta E_i^{\text{ideal}} / V_i^0)^{1/2} \quad (6)$$

where $\Delta E_i^{\text{ideal}}$ is the ideal energy of vaporization.

By partial differentiation of Equations 2, 4, and 5 with respect to the moles of a component (the solute, component 2, here) at constant temperature, pressure and moles of other components, equations relating interaction to the variable component's activity coefficient, γ_2 , may be obtained:

$$\ln \gamma_2 = (x_2^2 W) / RT \quad (7)$$

$$\ln \gamma_2 = (V_2^0 \phi_1^2 W') / RT \quad (8)$$

$$\ln \gamma_2 = \frac{V_2^0 \phi_1^2 (\delta_1 - \delta_2)^2}{RT} \quad (9)$$

Equation 9 has been modified by inclusion of a Flory-Huggins entropy factor to account for effects arising from dissimilar molecular sizes of solution components (7);

$$\ln \frac{\gamma_2 x_2}{\phi_2} = \left(1 - \frac{V_2^0}{V_1^0}\right) \phi_1 + \frac{V_2^0 \phi_1^2 (\delta_1 - \delta_2)^2}{RT} \quad (10)$$

Solubility determinations provide a means of evaluating γ_2 . At saturation with solid solute, $\gamma_2 = (x_2^{\text{ideal}} / x_2)_{\text{sat}}$, with the ideal solubility calculated via Raoult's law (10). Equations 7 to 10 have been applied to the present work. The ideal naphthalene solubility used is 0.312, based upon thermal data of Ward (26). Other values reported by various workers range from 0.298 to 0.322, depending upon the source of thermal data. A molal volume of 123 ml. at 25° C. was assumed for supercooled naphthalene (11). W values of solvent-solute (Equation 7) are listed in column 6 of Table III. Column 7 lists W' values for solvent-solute, based on Equation 8. Columns 8 and 9 contain δ_2 values (Equations 9 and 10, respectively) obtained in conjunction with the δ_1 listed in Column 10. The latter were calculated from the molal volumes in column 2 and the most recent tabulation of thermal data (3), using Equation 6.

Discussion. Isothermal instrumental methods appear more precise than those involving either cooling curves or visual observation of saturation. Experimental results in the binary systems indicate a range of solvent-solute interaction. The W values may be used to divide the solvents

Table III. Binary Naphthalene-Solvent Systems at 25°

Solvent	V ₁ ⁰ (ml.)	Naphthalene Solubility		Volume fraction	W by Eq. 7, cal. mole ⁻¹	W' by Eq. 8, cal. ml. ⁻¹	δ ₂ by Eq. 9	δ ₂ by Eq. 10	δ ₁ by Eq. 6
		Mole Fraction							
		This work	Lit. (24)						
Benzene	89.40(15)	0.2946	0.292-.296	0.366	68.5	0.686	9.98	10.14	9.15
Ethylbenzene	123.06(15)	0.2926	0.302	0.293	75.8	0.615	9.58	9.58	8.80
Toluene	106.84(15)	0.2920	0.286-.295	0.322	78.1	0.695	9.73	9.77	8.90
Carbon tetrachloride	97.11(26)	0.2591	0.257-.264	0.307	200	1.86	9.95	10.01	8.59
n-Hexadecane	294.08 (3)	0.2043	...	0.0970	398	2.50	9.57	9.94	7.99
Cyclohexane	108.75(15)	0.1487	0.18	0.165	606	5.12	10.46	10.47	8.20
n-Hexane	131.59(15)	0.1168	0.125	0.110	746	5.97	9.71	9.72	7.27

Av., all values ± av. dev.

Av. (cyclohexane-naphthalene omitted) ± av. dev.

9.85 ± .24 9.95 ± .22

9.75 ± .14 9.86 ± .17

into two relatively distinct groups according to their interaction with naphthalene. One group composed of benzene, ethylbenzene, toluene, and carbon tetrachloride, in which the interaction is relatively small; the other of hexadecane, cyclohexane, and hexane, in which the interaction is greater. This difference in interaction has been previously noted for similar systems (19).

The small difference in naphthalene solubility in benzene, toluene, and ethylbenzene is striking, and amounts to only 0.003 in mole fraction, or about 1% on a relative basis. While the difference appears considerably greater on a volume fraction basis, about 25%—this is, essentially, a result of differing solvent molar volumes. The results indicate that neither the methyl nor ethyl group has much effect upon what may be the major factor in the interaction, a tendency for fused-ring aromatic molecules to assume a quasi-parallel configuration in the liquid state over limited regions (12). The similarity of interaction is indicated by the small range of 10 cal. mole⁻¹ in *W* values. The benzene-naphthalene *W*, 68.5, may be compared with the value of 52 estimated by McLaughlin and Zainal on the basis of extrapolation from solubility measurements between 35° and 75° C. (13).

The solubility of naphthalene in carbon tetrachloride may be determined by attractive forces associated with the polarizability of chlorine atoms by pi-electron clouds—the species CCl₄·C₁₀H₈ has been established by freezing point measurements (5), and repulsive forces caused by the resistance of the quasi-parallel naphthalene structure to disruption. The increased value of *W* in this system, 200 cal. mole⁻¹, indicates that the latter predominates.

Cyclohexane and carbon tetrachloride are similar in the absence of pi electrons, linearity, and planarity. They differ in molecular size and in that carbon tetrachloride has nonbonding outer electron pairs. These properties effect a larger *W*, 606 cal. mole⁻¹.

The combination of linearity and an absence of non-bonding electron pairs results in considerable interaction in the systems involving hexane and hexadecane. The difference of 300 cal. mole⁻¹ in the two *W* values may be caused by the difference in solvent molecular size. The increasing loss of randomness in liquid structure owing to increasing molecular alignment as the chain increases in length should offer less opportunity for contact between unlike species. A volume fraction comparison indicates that the solubilities in these two solvents differ by only 10%. The solubility of naphthalene in hexadecane has been reported to four significant figures despite lesser solvent purity. In the chromatogram of this solvent, the impurity was eluted over an interval overlapping that of the solvent, suggesting a highly similar solvent action.

Except for the ethylbenzene-naphthalene system, *W'* and *W* values follow the same order.

The mean value of δ_2 found is $9.75 \pm .14$ by Equation 9, and $9.86 \pm .17$ by Equation 10. In each case, the cyclohexane-naphthalene system was omitted in averaging. The anomalous behavior of cyclohexane encountered in this work resembles that noted previously in a study of methanol solubilities (9). Hildebrand and Scott have reported $\delta_2 = 9.9$, using earlier solubility data (7).

The presence of dipolar forces requires a modification of Equations 9 and 10 to include this effect (7). The present work has followed common practice, however, in extending these equations directly to molecules of low polarity, toluene and ethylbenzene. While both of these solvents indicate δ_2 values below the average, the values are comparable with those indicated by nonpolar hexane. Spread in δ_2 thus appears to arise from factors other than polarity.

Guggenheim has pointed out limitations in determining *W* by solubility measurements (6)—the thermal properties of supercooled solutes are not generally well known and *W* is determinable at only one concentration for a given

temperature. The second limitation may be especially serious in a system of highly dissimilar components. The terms beyond *A* in Equation 1 reflect a departure from the parabolic form of Equation 2. The assumption of Equation 2 is an oversimplification for most systems, because *W* is actually the concentration dependent term in the brackets of Equation 1. Omission of the terms in *B* and *C* introduces an error in *W* (assuming its equivalence to *A*) of $100[(x_1 - x_2)B/A + (x_1 - x_2)^2C/A]\%$. In the present system, $(x_1 - x_2)$ ranges from 0.8 to 0.4, which could introduce significant error. However, studies of comparable systems (19) indicate probable small *B/A* and *C/A* values. Results of the ternary studies below, in which each solvent-solute ratio is varied considerably, confirm this. The function *W'* is similarly subject to the limitations noted by Guggenheim.

Guggenheim has proposed equations which may better correlate *W* with experimental observations (6). These have not been applied here for several reasons. Theoretical justification for the uncertain coordination numbers of the lattice theory of solutions is questionable (8), and the interpretation of this quantity in multicomponent systems containing variable ratios of both homogeneous and heterogeneous molecules (6) is particularly indefinite. This difficulty has been ignored here by adoption of the zeroth approximation of solution structure (6). The present work deals with equations applicable across broad lines, without excessive mathematical manipulation, to predictions of ternary systems from the component binary systems' behavior. On this basis, the corresponding states principle of Prigogine (16) was also considered less suitable, despite the degree of agreement obtained when it is applied to systems of essentially spherical components.

TERNARY SYSTEMS

Results. Columns 4 and 5 of Table IV list the experimental naphthalene solubilities corresponding to the initial solvent compositions given in columns 2 and 3. Solubility behavior with varying solvent composition is shown in Figure 1 on an expanded scale as a deviation plot. The deviations are those from a linear dependence of naphthalene solubility on solvent composition, the latter expressed as mole fraction of either solvent in the solvent mixture—i.e., on a solute-free basis. The deviations are without theoretical significance, and are intended only to depict the trend in solubilities. In form, the plots are quite similar to those of excess molar thermodynamic solution properties, such as in Equation 1. Accordingly, the deviations, *D*, may be represented by:

$$D = x_1^2 x_3^2 [a + b(x_1^2 - x_3^2) + c(x_1^2 - x_3^2)^2] \quad (11)$$

where x_i^0 is the mole fraction of solvent *i* in the solvent mixture (solute-free), and *a*, *b*, *c* are empirical constants (Table V) which have been determined by least-squares treatment of the experimental solubilities. The maximum difference between experimental solubilities and those predicted with Equation 11 is less than 0.0010 mole fraction naphthalene.

In ternary systems, corresponding to Equations 7 and 8 above are, assuming interaction between component pairs only (7);

$$RT \ln \gamma_2 = x_1^2 W_{12} + x_3^2 W_{23} + x_1 x_3 / (W_{12} + W_{23} - W_{13}) \quad (12)$$

$$RT \ln \gamma_2 = V_2^0 [\phi_1^2 W_{12} + \phi_3^2 W_{23} + \phi_1 \phi_3 (W_{12} + W_{23} - W_{13})] \quad (13)$$

Equation 13 may be modified by the inclusion of Flory-Huggins entropy.

In principle, Equations 12 and 13 may be used to predict solubility in solvent mixtures by substitution of the relationships $x_1/x_1^0 = x_3/x_3^0 = 1 - x_2$ or $\phi_1/\phi_1^0 = \phi_3/\phi_3^0 = 1 - \phi_2$. This provides a means of evaluating the effectiveness of the former indescribing departures from ideality in the

Table IV. Solubility of Naphthalene in Mixed Solvents

Solvent Pair	Initial Solvent Composition		Exptl. Naphthalene Solubility		10 ³ (Exptl. Solubility - Calculated Solubility)		
	Benzene mole fraction	Benzene vol. fraction	Mole fraction	Vol. fraction	Eq. 12	Eq. 13	Eq. 13, with assumption of Eq. 15
Benzene-ethylbenzene	0.8400	0.7923	0.2940	0.356	-0	0	0
	0.5872	0.5082	0.2931	0.330	-1	-1	-1
	0.4089	0.3335	0.2928	0.318	-1	-1	-1
Benzene-toluene	0.1505	0.1140	0.2930	0.302	0	0	0
	0.9223	0.9085	0.2940	0.361	0	0	0
	0.7759	0.7434	0.2931	0.354	-2	-1	-1
	0.6113	0.5682	0.2913	0.344	-3	-2	-2
	0.4014	0.3594	0.2908	0.336	-2	-2	-2
Benzene-carbon tetrachloride	0.3497	0.3103	0.2921	0.335	-1	-1	-1
	0.8604	0.8501	0.2904	0.358	-2	-2	0
	0.6634	0.6447	0.2828	0.345	-4	-5	-2
	0.3866	0.3672	0.2723	0.328	-4	-5	-3
Benzene-hexadecane	0.2880	0.2714	0.2702	0.324	-3	-4	-1
	0.8603	0.6518	0.2734	0.282			-2
	0.6023	0.3153	0.2375	0.184			-5
	0.4219	0.1816	0.2217	0.144			-6
Benzene-cyclohexane	0.1743	0.0603	0.2075	0.111			-4
	0.9411	0.9291	0.2915	0.358	1	0	2
	0.7967	0.7631	0.2818	0.341	3	1	6
	0.6006	0.5528	0.2609	0.309	4	2	9
	0.4034	0.3572	0.2306	0.268	4	3	9
	0.2045	0.1744	0.1935	0.220	3	3	7
Benzene-hexane	0.0614	0.0510	0.1622	0.181	0	1	2
	0.9506	0.9289	0.2905	0.355	0	1	2
	0.8219	0.7582	0.2744	0.325	0	3	3
	0.5960	0.5006	0.2400	0.267	0	7	8
	0.4109	0.3215	0.2028	0.215	-1	8	8
	0.2121	0.1546	0.1590	0.159	-2	4	4
	0.0743	0.0517	0.1313	0.126	0	1	2
				Av. dev.	2	2	4

ternary systems. The comparisons are given in columns 6 and 7 of Table IV for Equations 12 and 13, respectively. Benzene-solvent W values used in Equation 12, listed in column 2 of Table VI, are those reported at $x = 0.5$. Corresponding W' have been calculated from W values at that composition. The former are listed in column 6 of Table VI. No literature W are available for benzene-hexadecane.

The Flory-Huggins modification of Equation 13 was also used to predict solubilities. The results, not included here, show poorer agreement with experiment than those obtainable with Equation 13. The error in the former is typically about double that found in the latter.

The solubility parameter approach to ternary systems is convenient in that it makes possible the elimination of one of the interaction energies by means of (7):

$$|\delta_1 - \delta_3| = |\delta_1 - \delta_2| \pm |\delta_3 - \delta_2| \quad (14)$$

With the paucity of data concerning interaction energies, it appears worthwhile to consider treating W' in a similar manner. The validity of this assumption;

$$|W_{13}|^{1/2} = |W_{12}|^{1/2} \pm |W_{23}|^{1/2} \quad (15)$$

is considered in the present work. Equations 14 and 15 differ in that the latter is not restricted to the geometric mean of interaction assumption. The additivity assumption of Equation 15 might be expected to hold best, however, when interaction between each pair of 1, 2, and 3 is of the same type.

Column 8 of Table IV lists the comparisons between experimental solubilities and those obtained from Equation 13, assuming the approximation of Equation 15 for the benzene-solvent interaction. The latter W' values are listed in Column 10 of Table VI. The assumption of Equation 15 results in an average error of 0.004 in mole fraction naphthalene, with the effect on individual systems

varying. Increase in error is a reflection of the poorer fit of the assumption to the benzene-aliphatic systems.

An equation in W similar to Equation 15 might be proposed. Such an equation was considered briefly for the systems of benzene with the aliphatic solvents. The effect was variable. In the cyclohexane and hexane systems the use of W in place of W' reduced the disagreement by 1 or 2 $\times 10^{-3}$ in mole fraction naphthalene for the several points considered. In the hexadecane system, however, the error was approximately quadrupled. In each case, the interactions between naphthalene and the solvents were combined by summing (c.f. Equation 15) rather than subtracting.

For comparison, the square of the difference between the solubility parameters of benzene and the second solvent, equal to W_{13} by solubility parameter theory, has been listed in column 11 of Table VI. The solubility parameters are from column 9 of Table III.

Hildebrand has considered the treatment of ternary one-phase systems as pseudo-binary systems (7). This is possible by defining the solubility parameter of a component pair, δ_{e_2} , as:

Table V. Constants of Deviation Functions

Solvent Pair	10 ³ _a	10 ³ _b	10 ³ _c
Benzene-ethylbenzene	-4	-4	2
Benzene-toluene	-10	-8	14
Benzene-carbon tetrachloride	0	0	0
Benzene-hexadecane	-87	2	15
Benzene-cyclohexane	98	8	-13
Benzene-hexane	61	42	-27

where $D = x_1^0 x_3^0 [a + b(x_1^0 - x_3^0) + c(x_1^0 - x_3^0)^2] \cdot x_2^0$ refers to benzene in each solvent pair.

$$\delta_c = \frac{\phi_1 \delta_1 + \phi_3 \delta_3}{\phi_1 + \phi_3}$$

In terms of W' , an equivalent expression is:

$$W'_{02}{}^{1,2} = \frac{\phi_1 W'_{02}{}^{1,2} \pm \phi_3 |W'_{23}|^{1,2}}{\phi_1 + \phi_3} \quad (16)$$

Equation 16 leads to:

$$RT \ln \gamma_2 = V_2^0 (1 - \phi_2)^2 W'_{02} \quad (17)$$

assuming Raoult entropy of mixing. Equation 17 may also be modified by the assumption of Flory-Huggins entropy.

W'_{02} values in the various systems were calculated with both Equation 17 and the Flory-Huggins modification thereof. Results via the latter are shown in Figure 2, which indicates both the spread in W'_{02} and the departure from linearity in volume fraction of either solvent. This figure also shows the shift in solvent-solute W' order among the aromatic solvents from that of column 7, Table III due to their different molar volumes. If Raoult entropy of mixing is assumed, the effect upon $|W'_{02}|^{1,2}$ is not uniform. While the curvature of the three nonlinear systems is thereby somewhat lessened, linearity in the benzene-toluene system is lost. Similar results are obtained when equations in W parallel to Equations 16 and 17 in W' are considered. For some systems, the former shows greater curvature than do the latter; for others, the curvature is less.

Interaction between a pair of liquids is commonly determined by binary vapor-liquid equilibrium studies. Either lack of necessary P - V - T data or low vapor pressures of the components may render this method impractical in a given system. Thus Equations 12 and 13 have been considered as alternate means of determining this interaction. Columns 3 and 7 of Table VI contain the results by the

respective equations. The corresponding mean in each system is given in columns 4 and 8, and the comparison of the mean with the literature value is located in columns 5 and 9. The order of listing in each system in Table VI is the same as that in Table IV.

Discussion. Table IV shows that, except for the systems involving toluene and ethylbenzene, naphthalene solubility (as mole fraction) decreases continually from the solvent of greater to the solvent of lesser solvent action toward the solute. In the toluene system, a solubility minimum occurs at about 0.5 in x_{benzene}^0 . The solubility is essentially constant in the ethylbenzene system from about 0.5 in $x_{\text{ethylbenzene}}^0$ to pure ethylbenzene. In both the latter systems, the range of solubilities is very small, less than 0.003.

The constants of the deviation functions (Table V) represent the solubility well. The difference between experimental and smoothed solubilities, less than 0.001 in mole fraction naphthalene, is consistent with the estimated accuracy of the analytical procedures used. Such agreement between smoothed and experimental values does not constitute proof that the function selected is the most suitable for representation of the data. That b/a and c/a are relatively small in each system is a desirable feature and shows that the higher powered terms in $x_1^0 - x_3^0$ are of decreasing importance. While the function is without particular theoretical significance concerning molecular interaction in the ternary systems, it is evident from Figure 1 that the degree of curvature of the solubility curves is greater in benzene-aliphatic solvent pairs than it is in benzene-aromatic pairs.

The interactions predicted with Equations 12 and 13 are comparable (columns 6 and 7 of Table IV). The average error with either is 0.002 in mole fraction naphthalene, and the maximum error is three to four times that. In a given system, the use of either equation leads to predicted

Table VI. Benzene-Solvent

Solvent Pair	W , Cal. Mole ⁻¹			
	Lit.	Exptl. Eq. 12	Mean \pm Av. Dev. Exptl.	Lit. - Exptl.
Benzene-ethylbenzene	(5) ^c	-5.4 -13.0 -12.1 3.1	-7 \pm 6	12
Benzene-toluene	2.0 ^d	-16.0 -16.7 -36.7 -36.6 -13.4	-24 \pm 10	26
Benzene-carbon tetrachloride	78.0 ^e	24.2 -1.2 -14.2 8.4	4 \pm 12	74
Benzene-hexadecane	...	-279 -329 -307 -310	-306 \pm 14	...
Benzene-cyclohexane	304 ^f	362 377 372 359 374 356	367 \pm 8	-63
Benzene-hexane	(306) ^g	381 304 308 274 224 254	291 \pm 40	15

^c From Literature W , using ϕ which obtain at $x = 0.5$. ^d From Column 10, Table III. ^e Present authors' estimate from meager data at 20° (1); estimated uncertainty ± 50 cal. mole⁻¹. Temperature correction

omitted. ^d Ref. (10, 18). ^e Ref. (10, 23). ^f Ref. (10, 21). ^g Ref. (19, 14).

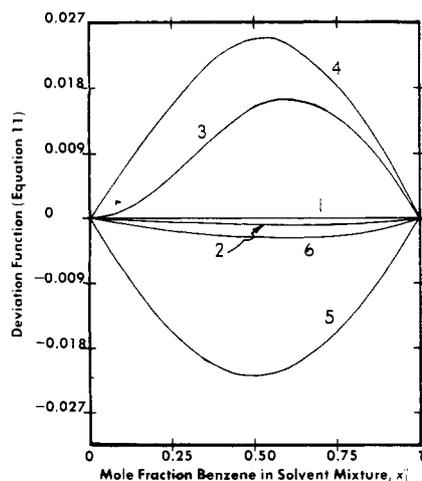
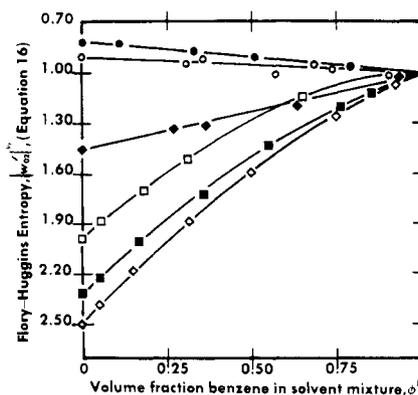


Figure 1. Dependence of deviation function on solvent composition.

Figure 2. Dependence of $|W'_{12}|^{1/2}$ on solvent composition

- Systems represented:
- 1. Benzene-carbon tetrachloride
 - 2. Benzene-ethylbenzene
 - ◇ 3. Benzene-hexane
 - 4. Benzene-cyclohexane
 - 5. Benzene-hexadecane
 - 6. Benzene-toluene



solubilities which are either consistently high or low, with a maximum error as x_1^1 approaches x_2^1 . In only one system, benzene-hexane, is the sign of the error by the two equations different. The increase in error as equimolar solvent composition is approached indicates that the source of disagreement between predicted and experimental results lies in theory rather than experimental error. It is unfortunate that solvent-solvent interaction is not known for the benzene-hexadecane system which might be expected to show a sharper difference in the effectiveness of the mole fraction *vs.* volume fraction approach. Interaction of benzene and its homologs with higher normal aliphatic hydrocarbons has not been reported in the literature.

Frequently, the power series expression for ΔG^E (Equation 1) is unavailable, and a constant W or W' must be assumed. This situation might even be considered prevalent. The

present work assumes this restriction, and a constancy of the W functions has been adopted in each system. This cannot be correct, however, as a constancy of either W function requires that the other shall be a variable when molal volumes of the components are unequal. More commonly, in reality, both W and W' are variables in a system. The systems included in the present work are among those in which the binary solvent-solvent interaction is known to be essentially regular—with the exception of the unknown benzene-hexadecane system.

When a Flory-Huggins entropy is assumed in Equation 13 poorer agreement with experiment is obtained than when Equation 13 itself is used. Previous studies of systems of quasi-spherical molecules which differ in size by up to a nine-to-one ratio (4, 22) also show this.

While the errors incurred by the assumption of Equation 15 (column 8, Table IV) are not uniform, the approximation may serve a useful purpose when it is required. In the present work, the errors in the benzene-hexadecane system

Interaction Energies

Solvent Pair	Lit. ^a	Exptl. Eq. 13	W' , Cal. Mole ⁻¹			$(\delta$ Benzene - δ sec-ond solvent) 2b
			Mean \pm Av. dev. exptl.	Lit - exptl.	Eq. 15	
Benzene-ethylbenzene	(0.05) ^c	-0.033 -0.103 -0.104 0.010	$-0.058 \pm .046$	0.11	0.0019	0.12
Benzene-toluene	0.021 ^d	-0.138 -0.154 -0.324 -0.341 -0.114	$-0.214 \pm .095$	0.235	0.00004	0.062
Benzene-carbon tetrachloride	0.836 ^e	0.224 -0.004 -0.116 0.103	$0.052 \pm .112$	0.784	0.28	0.31
Benzene-hexadecane	...	0.374 -0.223 -0.496 -1.71	-0.52 ± 0.60	...	0.56	1.35
Benzene-cyclohexane	3.10 ^f	3.14 3.37 3.51 3.59 3.95 3.90	$3.58 \pm .24$	-0.48	2.04	0.90
Benzene-hexane	(2.87) ^g	3.57 3.32 3.81 4.19 4.27 4.89	$4.01 \pm .44$	-1.14	2.59	3.53

are not excessive by comparison with the other systems and the choice of signs in Equations 14 and 15 are consistent with one another.

A comparison of W_{13} values 1, obtained with Equation 15; 2, those predicted with solubility parameters, and 3, those calculated from ΔG^E in binary systems may be made with columns 10, 11, and 6 of Table IV. The values by 1 are consistently less positive than those by 3, while those by 2 are neither consistently less nor more positive than the latter. There is a tendency with either 1 or 2 for the error in W_{13} to increase as the solvent-solute interactions become increasingly different. Error incurred by the use of 1 or 2 is comparable in the present systems, suggesting the alternative use of either in the absence of known solvent-solvent interactions. (The use of the term "solvent-solvent" is used here only for continuity with the remainder of the discussion. There is no distinction between solvent and solute in terms of interaction between pairs.) A measure of the significance of these differences is given by the following: In a binary system of near equal volume fractions, 0.1 in W' is equivalent to about 10 cal. mole⁻¹ in W , or to a change of about 0.5% in the activity coefficient of the present solute.

Predicted values of naphthalene solubility obtained from W_{12} (calculated with Equation 16) in Equation 17 have not been tabulated because of the evident failure of the assumption in systems of significant solvent dissimilarity, as indicated by Figure 2. The assumption of this equation appears invalid, whether the entropy assumed is either Raoult or Flory-Huggins. Neither the use of W nor W' leads to results comparable with those obtainable without the assumption.

The W_{13} obtained by applying Equation 12 to the results of solubility determinations in ternary systems (columns 3 to 5, Table VI) show a disagreement of 12 to 74, and an average disagreement of 38, in cal. mole⁻¹ from the literature values. For the present solute, the latter two differences are equivalent to 3.3 and 1.7% in the activity coefficient. The average deviation of the present W_{13} from the mean, excluding the benzene-hexane system, is about 10 cal. mole⁻¹. This compares with many of the binary interaction studies reported in the literature. The significantly greater deviation in the benzene-hexane system results from a trend in W_{13} with varying composition of the mixed solvent.

A negative W_{13} is indicated by Equation 12 in three of the six systems. Only in the benzene-hexadecane system, however, is the interaction pronounced, -306 cal. mole⁻¹. In contrast, the present work indicates a strong positive interaction between naphthalene and hexadecane, 398 cal. mole⁻¹. The benzene-hexadecane interaction is unusual among the present component pairs. The effect is greater than those found in mixtures of hexadecane with hexane and with heptane, which show small negative deviations from ideality (19). Present Conclusions regarding hexadecane interactions assume pairwise interaction, the validity of which is unproved in this work. The assumption may be particularly invalid between solvent components of the greatest dissimilarity in molar volume among those of the present work. If the assumption is invalid, the average deviation of only 14 cal. mole⁻¹ from the mean W_{13} is surprisingly small.

The contrast between the relative constancy of W_{13} for a given benzene-solvent system as determined by solubility in the ternary systems and the significant disagreement between these values and literature values emphasizes the question of which are more pertinent to systems of a yet higher number of components. (This problem is currently being studied.) Values obtained by the study of the particular binary systems are undoubtedly more significant in elucidating the pairwise interaction of the particular pair concerned. Perturbation of these interaction effects by

other components may lead to significant error, however, which might be avoided by the use of modified interactions between the given pair indicated in higher systems. Prediction of the latter may be assumed to be yet more difficult than the already formidable problem of predicting interaction of the isolated pair itself.

The W_{13} calculated with Equation 13 and the solubility measurements in the ternary systems (columns 7-9, Table VI) show a range of disagreement with literature values of 0.11 to 1.14, and an average disagreement of 0.55 cal. ml.⁻¹, corresponding to W_{13} of 13, 140 and 68 cal. mole⁻¹, respectively, in the present systems. The average deviation in W_{13} from the mean in each system is about the same as that in W_{13} , except for the systems of benzene with an aliphatic solvent. In the latter systems, there is a definite dependence of W_{13} on mixed solvent composition, as there is with W_{13} in the benzene-hexane system. The trend results in a rather large average deviation in W_{13} . In the benzene-hexadecane system, the trend passes from an indicated positive to negative interaction. The mean solvent-solvent interchange energy in a given system has the same sign whether evaluated on the mole or volume fraction basis.

Comparison of W_{13} by ternary solubility measurements to those by other methods (columns 10 and 11, Table VI) indicate about the same disagreement with literature values.

These results contribute little to the theoretical justification of either of the interaction approaches considered. The extent of agreement may be considered merely that between empirical parameters in binary and ternary systems. Even with this limitation, these ternary systems' solution behavior may be predicted with considerable confidence from that of the component pairs. A mole or volume fraction approach appears to have no consistent effect upon the results.

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NOMENCLATURE

- A, B, C = constants of Equation 1
- D = deviation function, Equation 11
- ΔG^E = molar excess Gibbs free energy of mixing
- V^o = molar volume
- a, b, c = constants of Equation 11
- n_D = refractive index
- W = interchange energy, cal. mole⁻¹
- W' = interchange energy, cal. ml.⁻¹
- x = mole fraction
- x^o = mole fraction, solute-free basis
- δ = solubility parameter
- γ = activity coefficient
- ϕ = volume fraction
- ϕ^o = volume fraction, solute-free basis

LITERATURE CITED

- (1) Bell, T., Wright, R., *J. Phys. Chem.* **31**, 1884 (1927).
- (2) Catalog of Infrared Spectral Data, API Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.
- (3) Dreisbach, R.R., "Advances in Chemistry Series," Vol. I, II, (1955, 1959).
- (4) Dyke, D.E.L., Rowlinson, J.S., Thacker, R., *Trans. Faraday Soc.* **55**, 903 (1959).
- (5) Goates, J.R., Sullivan, R.J., Ott, J.B., *J. Phys. Chem.* **63**, 589 (1959).
- (6) Guggenheim, E.A., "Mixtures," Oxford Univ. Press, London, 1952.
- (7) Hildebrand, J.H., Scott, R.L., "The Solubility of Non-electrolytes," 3rd ed., Reinhold, New York, 1950.

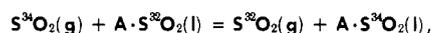
- (8) Hildebrand, J.H., Scott, R.L., "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.
- (9) Kiser, R.W., Johnson, G.D., Shetlar, M.D., *J. Chem. Eng. Data* **6**, 338 (1961).
- (10) Lewis, G.N., Randall, M., "Thermodynamics," 2nd ed. revised by K.S. Pitzer, L., Brewer, McGraw-Hill, New York, 1961.
- (11) Lumsden, J.S., *J. Chem. Soc.* **91**, 24 (1907).
- (12) McLaughlin, E., Ubbelohde, A.R., *Trans. Faraday Soc* **53**, 628 (1957).
- (13) McLaughlin, E., Zainal, H.A., *J. Chem. Soc.* **1959**, p. 863.
- (14) Myers, H.S., *J. Am. Inst. Chem. Eng.* **3**, 467 (1957); *Ind. Eng. Chem.* **47**, 2215 (1955).
- (15) Natl. Bur. Std. (U. S.) Circ. C-461, "Selected Values of Properties of Hydrocarbons," November, 1947.
- (16) Prigogine, I., "The Molecular Theory of Solutions," Interscience, New York, 1957.
- (17) Reed, T.M., *J. Phys. Chem.* **59**, 425 (1955).
- (18) Rollet, A.P., Elkaim, G., Toledano, P., Senez, M., *Compt. rend.* **242**, 2560 (1956); Cheesman, G.H., Ladner, W.R., *Proc. Roy. Soc. (London)*, **A229**, 387 (1955).
- (19) Rowlinson, J.S., "Liquids and Liquid Mixtures," Butterworths, London, 1959.
- (20) Scatchard, G., *Chem. Rev.* **44**, 7 (1949).
- (21) Scatchard, G., Wood, S.E., Mochel, J.M., *J. Phys. Chem.* **43**, 119 (1939).
- (22) Shinoda, K., Hildebrand, J.H., *Ibid.*, **62**, 292 (1958).
- (23) Staveley, L.A.K., Tupman, W.I., Hart, K.R., *Trans. Faraday Soc.* **51**, 323 (1955).
- (24) Timmermans, J., "The Physico-chemical Constants of Binary Systems in Concentrated Solutions," Interscience New York, 1959.
- (25) Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
- (26) Ward, H.L., *J. Phys. Chem.* **38**, 761 (1934).
- (27) Weissberger, A., Proskauer, E.S., Riddick, J.A., Toops, E.E., "Organic Solvents," 2nd ed., Interscience, New York, 1955.

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Some Isotope Fractionation Factors for Sulfur

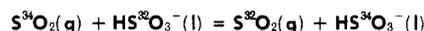
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Isotopic fractionation factors were measured for the reaction:



where **A** was aniline, dimethylaniline, triethylamine, pyridine, and ethylene oxide.

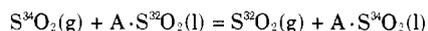
Similar measurements were made for the KH_2PO_4 buffered reaction:



and for the distillation of SO_3 . The fractionation factors ranged from 1.0005 to 1.005 with the heavy isotope concentrating in the liquid phase.

ALTHOUGH the fractionation of sulfur isotopes has been studied by a number of investigators (2, 5-7), no satisfactory separation method has been developed. This situation provided the incentive for further studies of the isotopic fractionation which may be achieved in sulfur systems.

A group of reactions, interesting for this purpose, is described by the equation:



where $A \cdot SO_2$ is a 1:1 molecular addition compound of SO_2 . A number of amines, ethers, and heterocycles are known to form such compounds (1, 3, 4). In the first part of this study, the isotopic fractionation achievable was measured through the exchange of sulfur between these compounds and SO_2 . In succeeding parts of the study, the isotopic fractionation resulting from the distillation of SO_3 , and the exchange of sulfur between SO_2 and HSO_3^- in a buffered solution (from which the SO_2 could be recovered thermally) was measured.

EXPERIMENTAL

Materials. Matheson's Anhydrous Grade SO_2 was used; the SO_3 was B & A Sulfan B sulfuric anhydride. The following were J.T. Baker Reagent Grade, Fischer Scientific

Reagent Grade, or Eastman White Label: aniline, dimethylaniline, triethylamine, pyridine, ethylene oxide, propylene oxide, tetrahydrofuran, dimethyl sulfide, thiophene, phenol, and KH_2PO_4 . All were used without further purification.

Apparatus and Procedure. MOLECULAR ADDITION EXCHANGE REACTIONS. A vacuum jacketed, borosilicate glass, 30-plate bubble cap exchange column, 84 cm. long and 2.5 cm. I.D., was used. Its plate efficiency was 50 to 55% for a wide variety of aqueous and organic systems. Above the exchange column was a jacketed glass tube 26 cm. long and 3.4 cm. I.D., packed with 0.3 cm. glass helices. In this recombiner, SO_2 gas from the exchange column was reacted with fresh solvent to form the liquid molecular addition compound. The liquid flow rate (under gravity) was set at a fixed value; the SO_2 flow was adjusted to maintain the recombination interface at the desired level in the recombiner.

Gradient studies established that seven hours was sufficient to achieve isotopic equilibrium. Samples of SO_2 gas were collected in evacuated tubes at a capillary sampling port between the column and the recombiner. These were frozen in liquid nitrogen, evacuated, and then distilled from dry ice to a liquid nitrogen trap. Representative samples were analyzed with a mass spectrometer and found essentially free of impurities.

Isotopic analyses were obtained from the m/e 64 and