Part I

CHEMICAL ENGINEERING

INORGANIC CHEMISTRY

PHYSICAL CHEMISTRY

Interaction in Nonelectrolyte Solutions

II. Solubility of Naphthalene at 25° in Some Mixed Solvents Containing Toluene, Ethylbenzene

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The solubility of naphthalene has been determined at 25° in the nine binary mixed solvents formed by combining toluene or ethylbenzene with each of the others in the series: ethylbenzene, toluene, carbon tetrachloride, cyclohexane, *n*-hexane and *n*-hexadecane. The determinations were made refractometrically under isothermal conditions. The average uncertainty in the solubilities is less than 0.001 in mole fraction naphthalene. Interaction in the ternary systems is related to that of the component pairs, using the approaches of Guggenheim and Hildebrand. The average errors in correlation by either approach are comparable, 0.002 to 0.003 in mole fraction naphthalene, for those systems of known solvent-solvent interaction effects. Solvent-solvent interactions obtained by present ternary solubility studies are compared to literature values based upon studies of the binary systems. The error introduced by approximating the interaction of a component pair in terms of the interaction of each member of the pair with a third component is considered. The approximation results in errors of the same magnitude as those which would be expected using the true pair interaction term.

THIS WORK is the second of a series concerning interactions in the ternary systems formed by naphthalene and benzene, toluene, ethylbenzene, carbon tetrachloride, cyclohexane, *n*-hexane and *n*-hexadecane. The previous work dealt with the six systems having benzene as a common solvent component (2), while the present work includes nine toluene and ethylbenzene systems.

Work on all these mixed solvent systems is consistent in approach and techniques. Thus, frequent reference will be made to the previously reported study of the benzene systems, both for a description of the experimental methods and a comparison of the results found there with those in other systems. To promote clarity, the numbering of the equations used in reporting the previous benzene systems will be maintained throughout.

EXPERIMENTAL

The interaction effects were investigated by determination of the solubility of naphthalene in the mixed solvent systems. A description of the reagents, equipment, and experimental procedure has been given (2).

RESULTS

Columns 4 and 5 of Table I list the experimental naphthalene solubilities corresponding to the initial solvent compositions given in Columns 2 and 3. Solubility dependence on initial solvent composition is shown in Figures 1 and 2 on an expanded scale as deviation plots. (For comparison purposes the benzene-toluene and benzene-

Table I. Solubility of Naphthalene in Mixed Solvents

Solvent Pair	Initial Solvent Composition: Toluene mole fraction	Initial Solvent Composition: Toluene volume fraction	Exptl. Naphthalene Solubility: Mole fraction	Exptl. Naphthalene Solubility: Volume fraction	10^3(Exptl. Solubility-Calcd. Solubility): Eq. 12	10^3(Exptl. Solubility-Calcd. Solubility): Eq. 13	10^3(Exptl. Solubility-Calcd. Solubility): Eq. 13, with assumption of Eq. 15
Toluene-Ethylbenzene	0.8332	0.8126	0.2921	0.316			0
	0.6135	0.5798	0.2916	0.309			0
	0.4117	0.3782	0.2919	0.303			0
	0.1591	0.1411	0.2923	0.297			0
Toluene-Carbon Tetrachloride	0.7942	0.8093	0.2867	0.320			0
	0.5899	0.6129	0.2800	0.317			−1
	0.4129	0.4365	0.2747	0.315			−1
	0.2057	0.2218	0.2665	0.311			−1
Toluene-Hexadecane	0.8399	0.6559	0.2674	0.247			−4
	0.5890	0.3424	0.2351	0.171			−8
	0.3968	0.1929	0.2199	0.136			−7
	0.1592	0.0644	0.2087	0.109			−3
Toluene-Cyclohexane	0.7928	0.7899	0.2765	0.305	−3	−5	2
	0.5952	0.5909	0.2564	0.281	−2	−5	5
	0.3733	0.3691	0.2246	0.248	−1	−4	6
	0.2071	0.2042	0.1948	0.215	1	−1	5
Toluene-Hexane	0.7910	0.7545	0.2681	0.286	−1	1	2
	0.5934	0.5422	0.2386	0.247	−1	4	5
	0.4076	0.3584	0.2018	0.203	−2	3	5
	0.2156	0.1824	0.1617	0.158	−1	3	4
	Ethylbenzene mole fraction	Ethylbenzene volume fraction					
Ethylbenzene-Carbon Tetrachloride	0.8408	0.8700	0.2873	0.294			−2
	0.6328	0.6859	0.2797	0.296			−3
	0.4095	0.4678	0.2720	0.299			−4
	0.1777	0.2150	0.2635	0.302			−3
Ethylbenzene-Hexadecane	0.8514	0.7057	0.2722	0.237			−3
	0.6190	0.4048	0.2440	0.174			−5
	0.4249	0.2362	0.2264	0.140			−6
	0.1874	0.0880	0.2113	0.112			−4
Ethylbenzene-Cyclohexane	0.7930	0.8126	0.2757	0.280			−1
	0.6006	0.6299	0.2534	0.262			−2
	0.4135	0.4438	0.2295	0.242			0
	0.1574	0.1745	0.1840	0.200			1
Ethylbenzene-Hexane	0.8445	0.8355	0.2756	0.273			0
	0.6053	0.5892	0.2423	0.237			1
	0.4185	0.4023	0.2063	0.200			2
	0.1663	0.1572	0.1526	0.145			1
Av. Dev.					2	3	3

ethylbenzene systems have been included in Figures 1 and 2.) The deviations are those from a linear dependence of naphthalene solubility on initial solvent composition, on a mole fraction basis. The deviations (Equation 11) are without theoretical significance, and are used only as a convenient means of summarizing the solubility results. The constants of the deviation functions (Table II) have been determined by least-squares treatment of the experimental solubilities. The maximum difference between experimental solubilities and those obtained with Equation 11 is 0.001 mole fraction naphthalene.

The activity coefficient of the solute, component 2, in the ternary systems may be expressed in terms of a mole fraction dependence (*1*), Equation 12, or a volume fraction dependence (*3*), Equation 13. Equation 13 may also be modified by the inclusion of Flory-Huggins entropy (*3*). Comparison (in terms of solubilities) of γ_2 predicted with Equations 12 and 13 and the experimental values is given in Columns 6 and 7 (Table I) respectively. Solvent-solvent W values used in Equation 12, listed in Table II, are those reported at $x = 0.5$. Corresponding W' used in Equa-

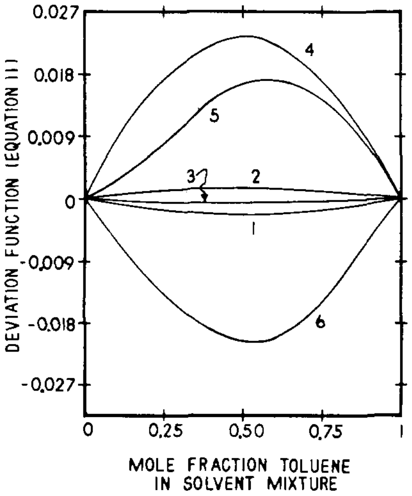

Figure 1. Dependence of deviation function on solvent composition in mixed solvents containing toluene

Legend for toluene systems:

1 = toluene-benzene
2 = toluene-carbon tetrachloride
3 = toluene-ethylbenzene
4 = toluene-cyclohexane
5 = toluene-hexane
6 = toluene-hexadecane

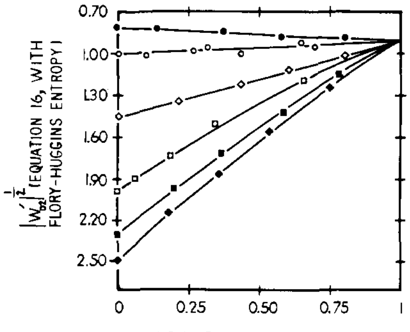

Figure 3. Dependence of $|W'_{02}|^{1/2}$ on solvent composition in mixed solvents containing toluene

Table II. Constants of Deviation Functions, Equation 11

Solvent Pair	10^3a	10^3b	10^3c
Toluene-Ethylbenzene	−2	0	3
Toluene-Carbon Tetrachloride	7	2	−3
Toluene-Hexadecane	−83	−9	21
Toluene-Cyclohexane	94	−10	−4
Toluene-Hexane	66	33	−20
Ethylbenzene-Carbon Tetrachloride	−3	6	−6
Ethylbenzene-Hexadecane	−62	0	7
Ethylbenzene-Cyclohexane	82	−16	10
Ethylbenzene-Hexane	73	27	−21

x_1° refers to the first-named solvent in each solvent pair.

tion 13 have been calculated from W values at that composition. The former are also listed in Table III. Literature values of W are available only for toluene-hexane and toluene-cyclohexane among the present systems. For those two systems the average errors by Equations 12 and 13 are comparable, 0.002 to 0.003 in mole fraction naphthalene.

Column 8 of Table I lists the comparisons between experimental solubilities and those obtained via Equation 13, assuming the approximation of Equation 15 for the solvent-solvent interaction. The solvent-solvent W' values obtained using Equation 15 are listed in Column 6 of Table III. The assumption of Equation 15 results in an average error of 0.004 in mole fraction naphthalene for the two systems of known solvent-solvent interaction. For all nine systems the average error is 0.003. For comparison, the square of the difference between the solubility parameters of the various solvent paris, equal to W'_{13} by solubility parameter theory (*3*), has been listed in Column 11 of Table III. The solubility parameters are from Column 9 of Table III (*2*). The validity of Equation 15 is also shown in Figures 3 and 4 in terms of the extent of linearity of the interchange energy of the pseudo-binary solute-mixed solvent system, defined by Equation 16. In discussing the benzene-solvent systems (*2*), it was erroneously concluded that the use of W'_{02} was less valid than that of W'_{13} via Equation 15. Rather, the two are related, and are equally effective. These figures are based upon a Flory-Huggins entropy. Modification to Raoult entropy has no consistent effect on the plots.

Equations 12 and 13 have been used for the determination of solvent-solvent interaction from measurements in ternary systems. Columns 2 and 4 of Table III contain the results by the respective equations. The corresponding mean in each system is given in Columns 3 and 5. The order of listing in each system in Table III is the same as that in Table I.

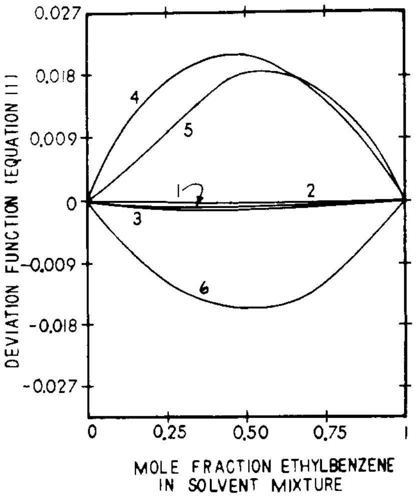

Figure 2. Dependence of deviation function on solvent composition in mixed solvents containing ethylbenzene

Legend for ethylbenzene systems:
1 = ethylbenzene-benzene
2 = ethylbenzene-toluene
3 = ethylbenzene-carbon tetrachloride
4 = ethylbenzene-cyclohexane
5 = ethylbenzene-hexane
6 = ethylbenzene-hexadecane

DISCUSSION

From Table I it is seen that, except for the toluene-ethylbenzene system, naphthalene solubility (as mole fraction) decreases continually from the solvent of greater to the solvent of lesser solvent action toward the solute. In the former system, the solubility is essentially constant within experimental error. The average departure of experimental solubilities from the smoothed values is comparable to that found in the benzene-solvent systems (*2*).

The errors incurred by the use of Equations 12 and 13 are similar (Columns 6, 7 of Table 1). The comparison is possible, however, for only two of the nine present systems. As with the benzene-hexane system, in the toluene-hexane system the sign of the error by the two equations is different.

In applying Equation 15, $|W'_{13}|^{1/2}$ has been obtained as the difference of the square roots of the solvent-solute interactions. The average error of 0.003 in mole fraction naphthalene thereby (Column 8, Table I) is essentially the same as that found in the two systems where the interactions between all components were known. This comparison must be qualified, however, as the known solvent-solvent interaction values are only estimates (*4*, *5*). The systematic increase in error as equimolal solvent composition is approached indicates that the error lies in theory rather than in experiment. As noted in the benzene systems, the presence of the relatively large hexadecane molecules in a system has no pronounced effect in causing greater error in predicted solubility when using Equation 15. The use of Equation 15, or the related solute-mixed solvent interchange energy of the pseudo-binary system appears to yield useful approximation to true interactions.

A comparison of: (1) W'_{13} obtained with Equation 15, (2) those predicted with solubility parameters (*2*), and (3) those calculated from the molar excess Gibbs free energy of mixing in binary systems may be made with Table III. The values by both (1) and (2) are less positive than those by (3), in both the systems where the comparison is possible. A measure of these differences is that 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.

The W_{13} values obtained by the application of Equation 12 to the results of solubility determinations in the present ternary systems (Columns 2 and 3, Table III) show a disagreement of about 30 cal. mole^{-1} with the two literature values, or about 1.5% in the solute activity coefficient. The average deviation of the present W_{13} from the mean for the nine systems is less than 20 cal. mole^{-1}, with six of the systems showing a deviation half that large. The systems showing large deviations are those having a trend in W_{13} with varying composition of the mixed solvent. A negative W_{13} is indicated by Equation 12 in four of the nine systems. Only in the hexadecane systems, however, is the interaction

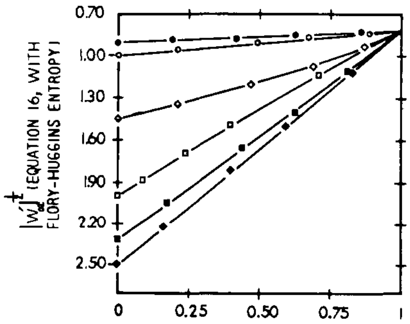

Figure 4. Dependence of $|W'_{02}|^{1/2}$ on solvent composition in mixed solvents containing ethylbenzene

Table III. Toluene and Ethylbenzene-Solvent Interaction Energies

	W (Cal. Mole^{-1})[a]		W' (Cal. Ml.$^{-1}$)[b]			
Solvent Pair	Exptl. Eq. 12	Mean ± av. dev. exptl.	Exptl. Eq. 13	Mean ± av. dev. exptl.	Eq. 15	$(\delta_1 - \delta_3)^2$ From ideal energies of vaporization[c]
Toluene-Ethylbenzene	−6	−6 ± 2	−0.022	−0.057 ± 0.020	0.0025	0.010
	−3		−0.069			
	−10		−0.085			
	−6		−0.053			
Toluene-Carbon Tetrachloride	23	20 ± 5	0.17	0.13 ± 0.05	0.28	0.096
	25		0.18			
	20		0.12			
	10		0.04			
Toluene-Hexadecane	−310	−286 ± 27	−0.009	−0.51 ± 0.30	0.56	0.83
	−311		−0.405			
	−291		−0.758			
	−233		−0.875			
Toluene-Cyclohexane	311	353 ± 30	2.55	2.88 ± 0.23	2.03	0.49
	335		2.76			
	366		2.98			
	400		3.24			
Toluene-Hexane	310	297 ± 12	3.06	3.32 ± 0.17	2.58	2.66
	308		3.24			
	295		3.47			
	275		3.51			
Ethylbenzene-Carbon Tetrachloride	−7	−21 ± 12	−0.27	−0.32 ± 0.07	0.33	0.044
	−12		−0.24			
	−22		−0.31			
	−43		−0.45			
Ethylbenzene-Hexadecane	−231	−226 ± 8	0.193	−0.13 ± 0.34	0.63	0.66
	−233		−0.029			
	−229		−0.203			
	−209		−0.548			
Ethylbenzene-Cyclohexane	270	320 ± 42	1.92	2.17 ± 0.23	2.18	0.36
	287		2.02			
	320		2.12			
	403		2.63			
Ethylbenzene-Hexane	312	317 ± 5	2.73	2.92 ± 0.10	2.74	2.34
	323		2.91			
	321		3.04			
	312		2.99			

[a] The lit. value of W estimated by Rowlinson (4, 5) for toluene-cyclohexane is 380 and for toluene-hexane is 330; the lit. minus exptl. value of W is 27 for toluene-cyclohexane and 33 for toluene-hexane. [b] From lit. W using ϕ which obtain at $x = 0.5$, the value for toluene-cyclohexane is 3.53 and for toluene-hexane is 2.80. The difference between the lit. and exptl. values for toluene-cyclohexane is 0.65 and for toluene-hexane is −0.52. [c] 1 = First named solvent, 3 = second named solvent.

pronounced. The decrease of some 80 cal. mole^{-1} in interchange energy from benzene to ethylbenzene toward hexadecane is beyond the average deviation of the results. The three aromatic solvents included in the study are insufficient in number to determine if this effect is one of increase in molecular size or decrease in aromaticity among the aromatics. The interaction effects involving hexadecane are in pronounced contrast to the strong positive interaction between naphthalene and hexadecane, 398 cal. mole^{-1} (2).

The W'_{13} calculated with Equation 13 and the solubility measurements in the ternary systems (Columns 4 and 5, Table III) show a disagreement with literature values of about 0.6 cal. ml.$^{-1}$, corresponding to W_{13} of 70 cal. mole^{-1} in the present systems. The average deviation in W'_{13} from the mean in a system is comparable to that in W_{13}. As in the benzene-solvent systems trends in either W' or W in a system are found only in those mixed solvents of the aromatic-aliphatic type. As noted with benzene-hexadecane, the hexadecane-systems with toluene and ethylbenzene pass from an indicated positive to negative interaction. The mean 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 with those by other methods (Columns 5 and 7, Table III) indicate that no one of the methods is consistently superior.

Results of the present work appear to indicate some systematic trends in behavior, when considered in conjunction with the benzene-solvent systems (2). An extension of the work to additional alkyl-substituted aromatic species should provide a broader basis for prediction of behavior in systems combining aliphatic and aromatic species. The existence of literature values for solvent-solvent interaction in only two of the present nine systems is representative of the lack of information concerning such behavior.

ACKNOWLEDGMENT

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NOMENCLATURE

a, b, c = constants of Equation 11
W = interchange energy, cal. mole^{-1}
W' = interchange energy, cal. ml.$^{-1}$
x = mole fraction
x^0 = mole fraction, solute-free basis
δ = solubility parameter
γ = activity coefficient
ϕ = volume fraction

LITERATURE CITED

(1) Guggenheim, E.A., "Mixtures," Oxford Univ. Press, London, 1952.

(2) Heric, E.L., Posey, C.D., J. Chem. Eng. Data **9**, 35 (1964).

(3) Hildebrand, J.H., Scott, R.L., "The Solubility of Nonelectrolytes," 3rd ed., Reinhold, New York, 1950; "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(4) Myers, H.S., *J. Am. Inst. Chem. Eng.* **3**, 467 (1957); *Ind. Eng. Chem.*, **47**, 2215 (1955).

(5) Rowlinson, J.S., "Liquids and Liquid Mixtures," Butterworths, London, 1959.

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Preparation and Properties of Two Strontium Orthophosphates—$Sr_3(PO_4)_2\cdot 4H_2O$ and $Sr_6H_3(PO_4)_5\cdot 2H_2O$

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Two new strontium orthophosphates have been prepared by precipitation from aqueous solution at room temperatures or below. $Sr_3(PO_4)_2\cdot 4H_2O$ was prepared by adding a $Sr(NO_3)_2$ solution to a solution containing an excess of K_2HPO_4 and made basic with KOH. This new compound, a gelatinous material, appears to have a layer structure. $Sr_6H_3(PO_4)_5\cdot 2H_2O$ was prepared by adding a $Sr(NO_3)_2$ solution to a KH_2PO_4 solution which had been adjusted to pH 7.7. X-Ray diffraction data are reported for both compounds.

IN THE COURSE OF STUDIES on mixed crystal formation between calcium and strontium hydroxyapatite, two phases of strontium phosphate have been found with characteristic x-ray diffraction patterns distinct from any previously reported. Both compounds precipitate from aqueous solution at room temperatures or below.

EXPERIMENTAL

All chemicals were reagent grade. The distilled water was boiled to remove excess CO_2 and was cooled under a soda-lime trap.

Preparation of $Sr_3(PO_4)_2\cdot 4H_2O$. This preparation, until the final drying period, was carried out at 10° to prevent hydrolysis of the compound to strontium hydroxyapatite. Precautions were taken to minimize CO_2 absorption during the precipitation and washing. To a vigorously stirred solution of 20 grams K_2HPO_4 and 15 ml. of 1*N* KOH was added to 100 ml. of a solution containing 1 gram $Sr(NO_3)_2$. The gelatinous precipitate was stirred for ½hr. and washed by centrifugation in cold water. Finally, the precipitate was either washed with ethanol and ether or dried in a vacuum desiccator over Drierite. The water content was variable and depended on the method of drying. The amount found by weight loss on heating to 900° varied between slightly under 4 to 5 moles of water per mole of $Sr_3(PO_4)_2$. The weight per cent analysis of a typical preparation was: calcd. for $Sr_3(PO_4)_2\cdot 4H_2O$—Sr, 50.08; P, 11.79; H_2O, 13.72. Found—Sr, 50.09; P, 12.09; H_2O (weight loss on heating to 900°), 12.84.

On heating the compound to 900° it transformed to pure $Sr_3(PO_4)_2$, as revealed by its x-ray pattern. X-Ray emission analysis showed a small potassium contamination amounting to less than 0.5%.

Precipitates showing identical diffraction patterns could be made using wide variations in amount of K_2HPO_4 and $Sr(NO_3)_2$, but it was noticed that, unless K_2HPO_4 was in excess of $Sr(NO_3)_2$, Sr/P ratios in the precipitate slightly greater than 1.5 could be obtained. Presumably the gelatinous precipitate has an affinity for strontium ions.

Preparation of $Sr_6H_3(PO_4)_5\cdot 2H_2O$. A solution of 20 grams KH_2PO_4 in 1 liter of water was adjusted to pH 7.70 with 1*N* KOH. To this vigorously stirred solution at room temperature was added 100 ml. of water containing 2 grams $Sr(NO_3)_2$. A large excess of KH_2PO_4 was used to keep the pH moderately constant during the precipitation. The gelatinous precipitate was allowed to stand quitely for at least 2 hours during which it transformed to a more crystalline form. The precipitate was washed extensively with water and finally with alcohol and ether. It was dried to constant weight at 150°. On heating this compound to 900° it broke down into a mixture of α-$Sr_2P_2O_7$ and $Sr_3(PO_4)_2$. The ratio of α-$Sr_2P_2O_7$ to $Sr_3(PO_4)_2$, as determined by a careful intensity estimate of characteristic x-ray lines of these compounds and a comparison with intensity estimates on known mixtures of α-$Sr_2P_2O_7$ and $Sr_3(PO_4)_2$, corresponded to a Sr/P ratio of 1.20 ± 0.005 in the original sample. Anal: Calcd. for $Sr_6H_3(PO_4)_5\cdot 2H_2O$—Sr, 50.57; P, 14.90; weight loss on conversion to α-$Sr_2P_2O_7$ and $Sr_3(PO_4)_2$, 6.06. Found—Sr, 50.36; P, 14.64; weight loss on heating to 900°, 5.53. Contamination by potassium was less than 0.5%.

RESULTS

$Sr_3(PO_4)_2\cdot 4H_2O$. The x-ray pattern from $Sr_3(PO_4)_2\cdot 4H_2O$ is shown in Figure 1. This pattern bears no similarity to that of strontium hydroxyapatite. Many of the peaks are