# Interaction in Nonelectrolyte Solutions

## Solubility of Naphthalene at 25° C. in Some Ternary Solvent Mixtures

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**The solubility of naphthalene has been determined at 25° C. in some ternary solvent systems at approximately equimolal solvent compositions. The solvent mixtures consisted of hexadecane in combination with various pairs from among benzene, toluene, ethylbenzene, carbon tetrachloride, hexane, and cyclohexane. The determinations were made refractometrically under isothermal conditions. Experimental results are compared with predicted values.**

SOME PREVIOUS WORKS (*3*, *4*) were concerned with a comparison of experimentally determined solubilities of naphthalene in binary mixed solvents with those calculated by equations based upon the s-regular solution concept of Guggenheim (*2*) and the regular solution concept of Hildebrand (*5*). While neither theoretical approach consistently predicted experimental results correctly, the agreement was sufficient to establish either as a useful first approximation to the actual behavior. The present work is an extension of the previous investigations, in this instance concerned with quaternary systems of naphthalene dissolved in ternary solvent mixtures. The solvents used are those involved in the prior work (*3*, *4*).

Sixteen approximately equimolal ternary solvent mixtures in eight different systems have been used. Observation of solubility behavior across this series of systems provides both an indication of the range of behavior to be expected in systems of similar molecular types, and a basis for selection of systems best suited for planned studies of more detail over extended ranges of mixed solvent composition.

In the present work, the experimental results are compared with predicted values based upon several possible approaches to the evaluation of interaction between the components:

I. The solvent mixture is treated as a pseudo-single component, the solubility parameter (*5*) of which is combined with that of naphthalene. The latter value is the average found in the binary naphthalene-solvent studies previously reported (*3*).

II. Same as the first approach, except that the solubility parameter of naphthalene is considered specific to each mixed solvent system, and is determined by the values appropriate to the solvents of the solvent mixture.

III. Specific solvent-solute interaction from the binary studies (*3*) is combined with apparent solvent-solvent interaction calculated from measurements in ternary systems (*3*, *4*). The interactions are assumed to be expressible in terms of volume fraction as the concentration variable.

IV. As in the third approach, except that mole fraction is used as the concentration variable.

A priori objections to some of the above proposed ways of treating the quaternary data are evident. Thus, one is inclined to suspect that it is unlikely that a quaternary system will behave in a certain manner if it has already been shown that the ternary subsystems do not exhibit this behavior. As the literature is essentially devoid, however, of data suitable for evaluating behavior in quaternary systems that approach regular behavior, a consideration of the above variety of approaches may serve a useful purpose in this instance.

## EXPERIMENTAL

The method of solubility determination, based upon refractometric measurements, has been described (*3*). Most of the solvent portions used, consisting of benzene, toluene, ethylbenzene, hexane, cyclohexane, hexadecane, and carbon tetrachloride, were the remainder of batches purified previously; additional required amounts of solvents were purified as before. For different batches of a solvent, purities were quite similar, and solubility behavior was consistent.

Difficulty in the synthesis of identical ternary solvent mixtures made replication of solubility measurements impractical. The results, however, show that the uncertainty in the data is consistent with that noted previously (*3*).

## RESULTS

The composition of the solvent mixtures is given in columns 1 to 4 of Table I. The measured solubility of naphthalene in these mixtures is given in columns 5 and 6.

Hildebrand has proposed a simplified solubility parameter equation for the activity coefficient, $\gamma_i$, of the solute in a mixed solvent system (*5*)

$$RT \ln \gamma_i = V_i^0(1 - \phi_i)^2(\delta_o - \delta_i)^2 \qquad (1)$$

where $V_i^0$ = molal volume of solute
$\phi_i$ = volume fraction of solute
$\delta_i(\delta_o)$ = solubility parameter of solute (mixed solvent)

For the mixed solvent of $j$ components,

$$\delta_o = \frac{\sum \phi_j \delta_j}{\sum \phi_j}$$

with the summation extending over all solvent species.

Equation 1 is the basis of predicting naphthalene solubility by I, as $\gamma_i$ is equal to the ratio $x_i^{\text{ideal}}/x_i$ at saturation of the solution by the solid solute. The solubility parameters used in these equations have been tabulated previously (*3*). For naphthalene, the value used is 9.85 $\text{cal.}^{\frac{1}{2}}\ \text{ml.}^{-\frac{1}{2}}$. This is the average in the seven individual solvents, assuming a Raoult entropy contribution. The errors by method I are listed in column 7. The average error among the 16 determinations is $10 \times 10^{-3}$ in mole-fraction naphthalene, and the maximum error is $16 \times 10^{-3}$.

The spread of naphthalene solubility parameters among the seven solvents is 0.89 $\text{cal.}^{\frac{1}{2}}\ \text{ml.}^{-\frac{1}{2}}$, or about 9% of the average value. Such disagreement is frequently found when the solubility parameter of a substance is determined by interaction measurements with a number of different species (*5*). Method II of treating the present work is an attempt to lessen the effect of the spread of the naphthalene solubility parameters by using only those values appropriate to the three solvents in each system.

If

$$W'_{ij} = (\delta_i - \delta_j)^2$$

and

$$W'^{\frac{1}{2}}_{oi} = \frac{\sum \phi_j W'^{\frac{1}{2}}_{ji}}{\sum \phi_j}$$

where the summation extends over only the $j$ components of

### Table I. Solubility of Naphthalene in Mixed Solvents

| Solvent Composition (No Solute) | | | | Experimental Naphthalene Solubility | | $10^3$ Solubility (Experimental − Calculated) as Mole Fraction | | | |
|---|---|---|---|---|---|---|---|---|---|
| Mole fraction of hexadecane | Mole fraction of 2nd named solvent | Volume fraction of hexadecane | Volume fraction of 2nd named solvent | Mole fraction | Volume fraction | Eq. 1 | Eq. 2 | Eq. 3 | Eq. 4 |
| Hexadecane–ethylbenzene–benzene–naphthalene | | | | | | | | | |
| 0.3299 | 0.3385 | 0.5764 | 0.2475 | 0.2484 | 0.194 | +13 | −4 | 3 | 0 |
| 0.3284 | 0.3386 | 0.5748 | 0.2480 | 0.2480 | 0.195 | +14 | −4 | 3 | 0 |
| Hexadecane–ethylbenzene–toluene–naphthalene | | | | | | | | | |
| 0.3314 | 0.3368 | 0.5590 | 0.2377 | 0.2472 | 0.188 | +16 | −6 | 2 | −1 |
| 0.3360 | 0.3240 | 0.5641 | 0.2278 | 0.2451 | 0.186 | +15 | −7 | 1 | −2 |
| Hexadecane–toluene–benzene–naphthalene | | | | | | | | | |
| 0.3333 | 0.3387 | 0.5994 | 0.2213 | 0.2453 | 0.197 | +9 | −5 | 4 | 0 |
| 0.3255 | 0.3326 | 0.5915 | 0.2196 | 0.2469 | 0.199 | +10 | −4 | 5 | 1 |
| Hexadecane–carbon tetrachloride–cyclohexane–naphthalene | | | | | | | | | |
| 0.3312 | 0.3371 | 0.5860 | 0.1970 | 0.1864 | 0.145 | −15 | −16 | 1 | −3 |
| 0.3340 | 0.3335 | 0.5890 | 0.1942 | 0.1865 | 0.145 | −16 | −17 | 0 | −3 |
| Hexadecane–hexane–cyclohexane–naphthalene | | | | | | | | | |
| 0.3341 | 0.3349 | 0.5510 | 0.2472 | 0.1598 | 0.116 | −3 | −10 | 8 | 0 |
| 0.3426 | 0.3185 | 0.5612 | 0.2335 | 0.1602 | 0.116 | −4 | −11 | 7 | 0 |
| Hexadecane–benzene–cyclohexane–naphthalene | | | | | | | | | |
| 0.3554 | 0.3233 | 0.6208 | 0.1717 | 0.2063 | 0.160 | −7 | −9 | 4 | −6 |
| 0.3525 | 0.3146 | 0.6107 | 0.1674 | 0.2046 | 0.160 | −8 | −9 | 3 | −7 |
| Hexadecane–benzene–hexane–naphthalene | | | | | | | | | |
| 0.3300 | 0.3357 | 0.5674 | 0.1754 | 0.2006 | 0.153 | +13 | −5 | 10 | −4 |
| 0.3298 | 0.3335 | 0.5668 | 0.1742 | 0.2000 | 0.152 | +13 | −5 | 10 | −4 |
| Hexadecane–carbon tetrachloride–benzene–naphthalene | | | | | | | | | |
| 0.3397 | 0.3303 | 0.6187 | 0.1987 | 0.2300 | 0.186 | +4 | −8 | −2 | 1 |
| 0.3328 | 0.3322 | 0.6113 | 0.2015 | 0.2312 | 0.187 | +5 | −8 | −1 | 1 |
| Average deviation | | | | | | 10 | 9 | 4 | 2 |

the solvent mixture, are introduced into Equation 1, there results

$$RT \ln \gamma_i = V_i^0(1 - \phi_i)^2 W'_{oi} \tag{2}$$

Equation 2 thus avoids the necessity of assuming a single averaged $\delta_i$ value for the solute. Column 8 lists the errors resulting from the use of Equation 2. The average error thereby is $9 \times 10^{-3}$, while the maximum error is $17 \times 10^{-3}$.

Both methods I and II involve an averaging principle in treating solvent-solvent interactions. By III and IV the averaging is omitted, and the interaction specific to each solvent pair is considered. For III, the relationship (from which Equation 1 is also obtained) is (*5*), letting 1, 2, 3 indicate the solvents,

$$RT \ln \gamma_i = V_i^0[\phi_1(1 - \phi_i)W'_{1i} + \phi_2(1 - \phi_i)W'_{2i} + \phi_3(1 - \phi_i)W'_{3i} - \phi_1\phi_2W'_{12} - \phi_1\phi_3W'_{13} - \phi_2\phi_3W'_{23}] \tag{3a}$$

or, alternatively,

$$RT \ln \gamma_i = V_i^0[\phi_1^2W'_{1i} + \phi_2^2W'_{2i} + \phi_3^2W'_{3i} + \phi_1\phi_2(W'_{1i} + W'_{2i} - W'_{12}) + \phi_1\phi_3(W'_{1i} + W'_{3i} - W'_{13}) + \phi_2\phi_3(W'_{2i} + W'_{3i} - W'_{23})] \tag{3b}$$

The $W'_{ij}$ used in Equation 3 have been obtained from binary solubility studies for solvent-solute (*3*), while for solvent-solvent, they are values calculated from naphthalene solubility in mixed solvent pairs under the assumption of regular behavior and pairwise interaction (*3*, *4*). Column 9 lists the errors in this approach. The average error is $4 \times 10^{-3}$ and the maximum error is $10 \times 10^{-3}$.

The equations pertinent to method IV are similar in form to Equation 3, except that the concentration variable is mole fraction rather than volume fraction. Thus, comparable to Equation 3b, one may obtain from Guggenheim (*2*)

$$RT \ln \gamma_i = x_1^2W_{1i} + x_2^2W_{2i} + x_3^2W_{3i} + x_1x_2(W_{1i} + W_{2i} - W_{12}) + x_1x_3(W_{1i} + W_{3i} - W_{13}) + x_2x_3(W_{2i} + W_{3i} - W_{23}) \tag{4}$$

Again the various interaction parameters, $W_{ij}$, are taken from the previous works, as described under method III above. Column 10 lists the errors by IV, with the average and maximum errors, respectively, 2 and $7 \times 10^{-3}$.

## DISCUSSION

The disadvantage of using the averaging principle of method I is apparent from column 7. Moreover, the use of II yields little improvement over I. The results by the former are all high in predicted solubility (column 8), indicating that the approach represents an overcompensation in the present systems.

Table I shows that the errors by I or II are quite consistently larger than those by III or IV (columns 9, 10). This was also found in the binary mixed solvents (*3*, *4*). In the present work, solvent-solvent interactions used in I and II are not necessarily the same as those used in III and IV, however. The former are obtained from the ideal energies of vaporization, $\Delta E^{\text{ideal}}$, (*5*),

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

while the latter are values obtained from measurements of interaction in ternary systems (*3*, *4*). While component pair interactions based upon studies of that isolated binary system are more desirable, this information often is not available. The present procedure was adopted in III and IV because only with hexane is the free energy of mixing hexadecane known.

The greatest known difference among the present systems between the interchange energy obtained from binary system data and that obtained from the ternary studies is found for the hexadecane-hexane pair (*1*) ( − 70 and 163 cal. mole$^{-1}$, respectively). Use of the interchange energy based on binary data produces a maximum change of 0.005 mole-fraction naphthalene solubility from that of the ternary data. This is observed in the hexadecane-hexane-cyclohexane system. A smaller difference, 0.003 mole fraction, is found with the hexadecane-hexane-benzene system. In the first system, the change decreases the agreement between present experimental and predicted solubilities, while in the latter the agreement is improved.

The use in the present study of apparent interaction parameters from measurements in ternary systems lessens the theoretical significance of the results by methods III and IV. The question with which the work is concerned may be reduced to one of whether apparent interaction parameters derived from measurements in ternary systems may be of use in approximate calculations in higher systems.

On theoretical grounds, the assumption of s-regular behavior (Equation 4) in the present systems is more objectionable than is that of regular behavior (Equation 3). In the ternary systems (*3*, *4*), however, there was little difference in the ability of either of the two models to predict behavior. A similar situation exists in the present quaternary systems. A distinction between methods III and IV lies in the fact that the former tends to predict a rather consistently low solubility in the present work.

## NOMENCLATURE

$V^0$ = molar volume
$W$ = interchange energy, cal. mole$^{-1}$
$W'$ = interchange energy, cal. ml.$^{-1}$
$x$ = mole fraction
$\delta$ = solubility parameter
$\gamma$ = activity coefficient
$\phi$ = volume fraction

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RECEIVED for review March 8, 1965. Accepted November 1, 1965.

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# Stabilization of Silicone Lubricating Fluids at 300° to 400° C. by Soluble Cerium Complexes

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**The discovery that the Si—H bond is involved in the formation of a stable cerium-silicone inhibitor system has been applied to the development of improved methods for stabilizing silicones. The inhibitory process uses initial reactions between hydrous cerous acetylacetonate and a methylhydrogen silicone which proceed and terminate in aerated refluxing benzene to provide a silicone-soluble adduct. The chemistry of the hydride group has been followed quantitatively and some features of structure are postulated for the adduct. Stabilization is completed by aerating a mixture of the cerium adduct and a silicone oil for one hour at 270° to 280° C. There is an optimum concentration of cerium adduct for the stabilization of lightly phenylated dimethyl silicones. The same concentration achieves improvement factors of 100 to 500 in the 300° C. stability of dimethyl silicones and their chlorophenyl- and phenyl-substituted types; with more highly phenyl-substituted silicones, stabilization temperatures are raised to 400° C. and relative improvement factors roughly parallel those observed at 300° C.**

IRON, cobalt, nickel, and copper soaps were patented as stabilizers for silicones in 1948 (*14*). These stabilizers were difficult to solubilize in stable form (*12*, *13*). Solubilization of iron as a silicone-substituted ferrocene has been reported (*5*, *20*, *22*).

Other work has demonstrated that a wide range of redox metals inhibited silicones against oxidation, provided the ions were suitably dispersed or solubilized (*10*). Cerium was chosen for more intensive study because it is commercially available, highly effective, and its stabilizers remain soluble when stabilized silicones are heated in oxygen-poor environments.

The benzene-soluble cerium complex described earlier (*7*, *10*) had the disadvantage of passing into a colloidal precipitate when first added to the silicone. A long processing at 280° C. (with a resulting loss of material and increase in viscosity) is required to remove the volatiles and clarify the stabilized silicone. To obviate these difficulties, a more direct process for the preparation of silicone-soluble cerium compounds was therefore sought.

The discovery that the Si—H bond is involved in the formation of a stable inhibitor system (*9*) provided a rational approach to the development of improved methods and reactions for stabilizing silicones. The new process improves the