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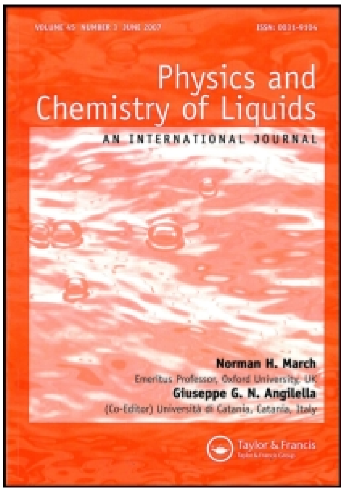

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Solubility in Binary Solvent Systems. Part 9. Estimation of the Carbazole-Tetrahydropyran Association Constant Based Upon Mobile Order Theory

William E. Acree Jr.[a]; Sheryl A. Tucker[a]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA

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SOLUBILITY IN BINARY SOLVENT SYSTEMS. PART 9. ESTIMATION OF THE CARBAZOLE-TETRAHYDROPYRAN ASSOCIATION CONSTANT BASED UPON MOBILE ORDER THEORY

WILLIAM E. ACREE, JR.* and SHERYL A. TUCKER

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068, USA

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A relatively simple equation is derived from Mobile Order theory for calculating solute-solvent association constants from measured solubility data in binary solvent mixtures. The newly-derived expression was found to describe carbazole solubilities in five binary tetrahydropyran + alkane solvent mixtures to within an overall average absolute deviation of 2.5% using a single association constant. For four of the five systems studied, the calculated association constant was found to vary only slightly with inert hydrocarbon cosolvent, with the numerical values ranging from a lower limit of $K_{AC} = 5{,}090$ for *n*-hexadecane to an upper value of $K_{AC} = 5{,}976$ for 2,2,4-trimethylpentane. A much larger value of $K_{AC} = 11{,}290$ was obtained in the *n*-hexane + tetrahydropyran system.

KEY WORDS: Carbazole solubilities, binary solvents, molecular complexation, Mobile Order theory.

INTRODUCTION

Investigations into molecular complexation provide a fertile testing ground for theoretical descriptions of condensed matter, phase transitions, "lock-key" molecular recognition and solvation. Molecular complexation is predicated upon a delicate balance between long-range and short-range intermolecular forces. At one extreme are weakly bonded van der Waals complexes, characterized by loose, nonspecific physical interactions and primarily stabilized by long-range dispersion forces. At the far opposite extreme are the hydrogen-bonded complexes that exhibit relatively strong, specific and highly directional binding of a primarily electrostatic nature. So-called "donor – acceptor" complexes possess intermediate strengths, and are stabilized by both charge transfer interactions, as well as electrostatic and/or dispersion effects. From a thermodynamic standpoint, molecular complexation is generally treated by

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* To whom correspondence should be addressed.

invoking a dynamic equilibria between the presumed association species (A_iC_j) and the uncomplexed monomers (A_1 and C_1)

$$iA_1 + jC_1 \leftrightharpoons A_iC_j \quad K^x_{A_iC_j} = \hat{x}_{A_iC_j}\hat{\gamma}_{A_iC_j}/(\hat{x}_{A_1}\hat{\gamma}_{A_1})^i(\hat{X}_{C_1}\hat{\gamma}_{C_1})^j$$

$$K^\phi_{A_iC_j} = \hat{\phi}_{A_iC_j}\hat{\gamma}_{A_iC_j}/(\hat{\phi}_{A_1}\hat{\gamma}_{A_1})^i(\hat{\phi}_{C_1}\hat{\gamma}_{C_1})^j$$

with the equilibrium constant being expressed in either mole fraction ($K^x_{A_iC_j}$) or volume fraction ($K^\phi_{A_iC_j}$) concentration units. Chemical effects are contained in the concentration ratio while the much weaker physical interactions are incorporated into the activity coefficients. Neglect of nonspecific physical interactions can lead to an appreciable error in the calculated equilibrium constant, particularly in the case of weak molecular complexes.[1,2]

Our earlier studies have been primarily devoted to the development of simple mixing models for describing thermodynamic excess properties of ternary associated solutions containing AB, AC, and/or AC_2 molecular complexes. Expressions have been derived for the calculation of volume-fraction based[2-5]

$$A_1 + C_1 \rightleftharpoons AC \quad K^\phi_{AC} = \hat{\phi}_{AC}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

$$\ln \phi_A^{\mathrm{sat}} = \phi_B^0 \ln(\phi_A^{\mathrm{sat}})_B + \phi_C^0 \ln(\phi_A^{\mathrm{sat}})_C + \ln[1 + K^\phi_{AC}V_A\phi_C^0/(V_A + V_C)] \tag{1}$$
$$- \phi_C^0 \ln[1 + K^\phi_{AC}V_A/(V_A + V_C)] + V_A\Delta G^{fh}_{BC}(RT)^{-1}(x_B^0V_B + x_C^0V_C)^{-1}$$

and mole-fraction based[6]

$$A_1 + C_1 \rightleftharpoons AC \quad K^x_{AC} = \hat{x}_{AC}/(\hat{x}_{A_1}\hat{x}_{C_1})$$

$$\ln x_A^{\mathrm{sat}} = \phi_B^0 \ln(x_A^{\mathrm{sat}})_B + \phi_C^0 \ln(x_A^{\mathrm{sat}})_C + \ln[1 + K^x_{AC}x_C^0] \tag{2}$$
$$- \phi_C^0 \ln[1 + K^x_{AC}] + V_A\Delta G^{ex}_{BC}(RT)^{-1}(x_B^0V_B + x_C^0V_C)^{-1}$$

solute-solvent association from experimental solute solubility using the infinite dilution form of the Extended Nearly Ideal Binary Solvent (NIBS) model. Activity coefficients are absent from the equilibrium constant expressions as the Extended NIBS model requires that the $\hat{\gamma}_{AC}/(\hat{\gamma}_{A_1}\hat{\gamma}_{C_1})$ ratio be independent of mixture composition. This constant does not necessarily equal unity, however, and it is incorporated into the calculated K^ϕ_{AC} and K^x_{AC} values. Excess molar Gibbs free energies of the binary solvent mixture, relative to Raoult's law (ΔG^{ex}_{BC}) and to the Flory-Huggins model (ΔG^{fh}_{BC}), can be calculated from published vapor pressure data or can be estimated using

$$\Delta G^{ex}_{BC} = (x_B^0V_B + x_C^0V_C)\phi_B^0\phi_C^0(\delta_B - \delta_C)^2 \tag{3}$$

$$\Delta G^{fh}_{BC} = \Delta G^{ex}_{BC} + RT[\ln(x_B^0V_B + x_C^0V_C) - x_B^0 \ln V_B - x_C^0 \ln V_C] \tag{4}$$

the Scatchard-Hildebrand solubility parameter theory, where δ_i refers to the solubility parameter of component i. The superscript (^) denotes the "true equilibrium" compositions of the various species in the associated solution, rather than the stoichiometric concentrations. Other symbols used in Eqs. (1)–(4) are defined in the Appendix. To date, we have calculated association constants for *presumed* carbazole-dibutyl ether ($K^{\phi}_{AC} = 25.3 \pm 2.7$),[2,5,6] pyrene-dichlorobutane ($K^{\phi}_{AC} = 14.2 \pm 2.4$),[7] anthracene-chlorobutane ($K^{\phi}_{AC} = 3.9 \pm 1.3$),[8] anthracene-dichlorobutane ($K^{\phi}_{AC} = 9.6 \pm 1.8$),[9] and anthracene-butyl acetate ($K^{\phi}_{AC} = 6.2 \pm 1.4$)[10] from measured solute solubilities.

Ruelle, Huyskens and coworkers[11–14] recently suggested an alternative thermodynamic treatment for complexing systems which is based upon the theory of mobile disorder in fluid solution. It is assumed that all molecular groups perpetually move, and that neighbors of a given external atom in a molecule constantly change identity. All molecules of a given kind dispose of the same volume, equal to the total volume V of the solution divided by the number of N_A molecules of the same kind, i.e., Dom $A = V/N_A$. The center of this domain perpetually moves. Highest mobile disorder is achieved whenever groups visit all parts of their domain without preference. Preferential contacts lead to deviations with respect to this "random" visiting. This is especially true in the case of hydrogen-bonding as specific interactions result in a specific orientation of the "donor" molecule with respect to an adjacent "acceptor" molecule.

In the case of complexation between a crystalline solute and a non-self-associating solvent, Mobile Order theory expresses the volume fraction saturation solubility (ϕ_A^{sat}) as:

$$\begin{aligned}\ln \phi_A^{\text{sat}} = {} & \ln a_A^{\text{solid}} - 0.5(1 - V_A/V_{\text{solvent}})\phi_{\text{solvent}} \\ & + 0.5 \ln[\phi_A^{\text{sat}} + \phi_{\text{solvent}}(V_A/V_{\text{solvent}})] - \phi^2_{\text{solvent}} V_A(\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1} \\ & + \ln[1 + K_{A\text{solvent}}\phi_{\text{solvent}}/V_{\text{solvent}}]\end{aligned} \tag{5}$$

where δ'_A and δ'_{solvent} denote the modified solubility parameters of the solute and solvent, respectively, and a_A^{solid} is the activity of the solid solute. This latter quantity is defined as the ratio of the fugacity of the solid to the fugacity of the pure hypothetical subcooled liquid. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{mp} - T)/(RTT_{mp}) \tag{6}$$

the molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature, T_{mp}. Contributions from nonspecific interactions, and their effect on activity coefficients are incorporated into Mobile Order theory through the $\phi^2_{\text{solvent}} V_A (\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1}$ term.

The authors presented a very impressive set of comparisons between experimental and predicted solubilities for anthracene, naphthalene, phenanthrene and methylparaben in a wide range of neat organic complexing and noncomplexing solvents. Conspicuously absent from the author's comparisons were binary solvent mixtures, which would have provided a more demanding test of the predictive ability of Eq. (5). Comparisons between predicted and experimental values in pure solvents are often misleading if solute-solvent complexation occurs since differences in $\phi_A^{\text{sat,exp}}$ and $\phi_A^{\text{sat,calc}}$ are used to calculate the association constant. Binary solvent mixtures overcome this particular limitation. The composition of the complexing cosolvent is varied so as to give several solutions having a common solute-solvent complex. To provide greater insight into the applications and limitations of Eq. (5), we report in this communication results of using Mobile Order theory to describe published carbazole solubilities in five binary alkane + tetrahydropyran solvent mixtures.[15] This particular set of systems should provide a very demanding test of the applications and limitations of Mobile Order theory as the experimental solubilities cover upto a 340-fold range in mole fraction.

RESULTS AND DISCUSSION

Published applications using Mobile Order theory have been limited, for the most part, to solubility predictions in pure solvents. Extension of the basic model to binary solvents containing an AC solute-solvent molecular complex requires that one assume a mathematical form for how δ'_{solvent} varies with mixture composition. The function assumed must reduce to $\delta'_{\text{solvent}} = \delta'_B$ and $\delta'_{\text{solvent}} = \delta'_C$ at $x_B^0 = 1.0$ and $x_C^0 = 1.0$, respectively, in order to give a correct thermodynamic description of solubilities in both pure solvents. Noting that the $(\delta'_A - \delta'_{\text{solvent}})^2$ term in Eq. (5) accounts for nonspecific physical interactions, and because of similarities between δ'_i and δ_i solubility parameters, we approximate δ'_{solvent} as a volume fraction average of the modified solubility parameters of the two pure solvents, i.e., $\delta'_{\text{solvent}} = \phi_B^0 \delta'_B + \phi_C^0 \delta'_C$. Gordon and Scott[16] invoked a similar approximation, $\delta_{\text{solvent}} = \phi_B^0 \delta_B + \phi_C^0 \delta_C$, in using the Scatchard-Hildebrand solubility parameter theory to explain the solubility maximum observed in the phenanthrene-cyclohexane-methylene iodide system. The molar volume of the mixed solvent is given by $V_{\text{solvent}} = x_B^0 V_B + x_C^0 V_C$ and all ϕ_{solvent} terms in Eq. (5) are replaced by $1 - \phi_A^{\text{sat}}$, except inside the logarithm term containing the equilibrium constant. Here $\phi_{\text{solvent}}/V_{\text{solvent}}$ should be replaced by the volume fraction of the complexing solvent divided by its molar volume.[14] The reduction of the free energy of the system caused by specific solute-solvent interactions depends upon the molar concentration of the "active" sites in the solvent, which in the present case would be the lone electron pairs on the oxygen atom of tetrahydropyran.

The computation procedure can be simplified further by noting that carbazole has a fairly low mole fraction solubility in tetrahydropyran and in the six alkane cosolvents (see Table 1 for experimental values of x_A^{sat}). Within this limitation, one can approximate $1 - \phi_A^{\text{sat}}$ as equal to unity with little loss in predictive accuracy. Performing the aforementioned substitution, Eq. (5) is rewritten as follows:

$$\begin{aligned} \ln \phi_A^{\text{sat}} = {} & \ln a_A^{\text{solid}} - 0.5(1 - V_A/V_{\text{solvent}}) + 0.5 \ln[V_A/(x_B^0 V_B + x_C^0 V_C)] \\ & - V_A(\delta'_A - \phi_B^0 \delta'_B - \phi_C^0 \delta'_C)^2 (RT)^{-1} + \ln[1 + K_{AC} \phi_C^0/V_C] \end{aligned} \tag{7}$$

Utilization of Eq. (7) requires *a prior* knowledge of the modified solubility parameters of the solute and both solvent components. In the case of a crystalline solid, the numerical value is not readily available. To eliminate δ'_A from the final predictive expression, the term $(\delta'_A - \phi_B^0 \delta'_B - \phi_C^0 \delta'_C)^2$ is expanded to give

$$\begin{aligned} & RT\{\ln(a_A^{\text{solid}}/\phi_A^{\text{sat}}) - 0.5\,[1 - V_A/(x_B^0 V_B + x_C^0 V_C)] + 0.5 \ln[V_A/(x_B^0 V_B + x_C^0 V_C)] \\ & + \ln[1 + K_{AC} \phi_C^0/V_C]\} = V_A[\phi_B^0(\delta'_A - \delta'_B)^2 + \phi_C^0(\delta'_A - \delta'_C)^2 - \phi_B^0 \phi_C^0 (\delta'_B - \delta'_C)^2] \end{aligned} \tag{8}$$

It must be borne in mind that the maximal number of complexes formed is determined by the number of sites that are in the minority. In the present case, carbazole is the limiting reagent. Equations (7) and (8) thus hold for small values of ϕ_A^{sat}. At higher volume fraction solubilities, a more elaborate expression which reportedly does not contain new parameters must be used.[17,18]

Careful examination of Eq. (8) reveals that, for model systems obeying Mobile Order theory, the $(\delta'_A - \delta'_B)^2$ and $(\delta'_A - \delta'_C)^2$ terms can be eliminated from the basic model *via*

$$RT\{\ln[a_A^{\text{solid}}/(\phi_A^{\text{sat}})_B] - 0.5(1 - V_A/V_B) + 0.5\ln(V_A/V_B)\} = V_A(\delta'_A - \delta'_B)^2 \tag{9}$$

and

$$\begin{aligned} &RT\{\ln[a_A^{\text{solid}}/(\phi_A^{\text{sat}})_C] - 0.5(1 - V_A/V_C) + 0.5\ln(V_A/V_C) + \ln[1 + K_{AC}/V_C]\} \\ &\quad = V_A(\delta'_A - \delta'_C)^2 \end{aligned} \tag{10}$$

where $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$ denote the solubilities in the two pure solvents. Performing these substitutions one obtains a relatively simple mathematical expression for how the solubility varies with binary solvent composition

$$\begin{aligned} \ln\phi_A^{\text{sat}} = {} & \phi_B^0\ln(\phi_A^{\text{sat}})_B + \phi_C^0\ln(\phi_A^{\text{sat}})_C + \ln[1 + K_{AC}\phi_C^0/V_C] \\ & - \phi_C^0\ln[1 + K_{AC}/V_C] - 0.5[\ln(x_B^0V_B + x_C^0V_C) \\ & - \phi_B^0\ln V_B - \phi_C^0\ln V_C] + V_A\phi_B^0\phi_C^0(\delta'_B - \delta'_C)^2(RT)^{-1} \end{aligned} \tag{11}$$

which does not require *a prior* knowledge of the solute's enthalpy of fusion and melting point temperature. More-over, the derived expression correctly describes the solubility in the pure complexing and noncomplexing solvents, and if one desires, Eq. (11) can be used to calculate the "optimum value" of the solute-solvent association constant from measured solubility data.

Despite the complex appearance of Eq. (11) its application to solubilities in mixed solvents is relatively straightforward and is similar in concept to numerical examples presented previously (for example see McCargar and Acree[2]). The quantities $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$ are calculated from the measured mole fraction solubility of the solute in the pure solvents assuming that the excess molar volume (or alternatively the volume change upon mixing) is zero. These quantities, along with the molar volumes, modified solubility parameters, and an assumed value for the equilibrium constant, are then used in Eq. (11) to calculate ϕ_A^{sat} at each binary solvent composition. The entire procedure is repeated until the numerical value of K_{AC} that "best" describes the experimental solubility in a particular binary solvent system is obtained.

Large solubility enhancements, like those observed in Table 1 for carbazole dissolved in binary alkane + tetrahydropyran mixtures, often indicate complex formation. Spectroscopic studies of carbazole with two similar ethers, tetrahydrofuran[19,20] and dipropylether,[21] also suggest complexation between carbazole and tetrahydropyran. Table 1 compares published experimental carbazole solubilities to values calculated from Eq. (11) for five different binary alkane (B) + tetrahydropyran (C) solvent systems.

Predictions for a sixth system, *t*-butylcyclohexane + tetrahydropyran, were not performed by $\delta'_{t\text{-butylcyclohexane}}$ was not in the tabulation given by Ruelle *et al.*[13] Readers are reminded that several of the δ'_i values contained in this compilation, which are also listed in Table 2 along with the solvent molar volumes, were deduced by regressing solubility data of solid *n*-alkanes in accordance to Huyskens and Haulait-Pirson model.[22] Any errors or uncertainties in the measured data would naturally affect the calculated values of δ'_i, as would any shortcomings of the Huyskens and Haulait-Pirson model to back-calculate the observed mole fraction solubilities.

Careful examination of Table 1 reveals that Mobile Order did provide very reasonable predictions of the observed carbazole solubility data, which in most cases cover at least a 150-fold range (or more) in mole fraction. Inert cosolvents included both small

Table 1 Comparison Between Experimental Carbazole Solubilities and Calculated Values Based Upon Mobile Order theory [Eq. (7)].

x_C^0	$x_A^{\text{sat,exp}}$	$x_A^{\text{sat,calc}}$	% *Dev*[a]
	n-Hexane (B) + Tetrahydropyran (C); $K_{AC} = 11{,}200$		
0.0000	0.000139		
0.1442	0.002243	0.002365	5.3
0.2555	0.005188	0.004879	−6.1
0.3674	0.008676	0.008269	−4.8
0.4701	0.01259	0.01225	−2.7
0.5741	0.01761	0.01718	−2.5
0.6684	0.02257	0.02240	−0.8
0.8405	0.03180	0.03318	4.2
0.9262	0.03763	0.03860	2.5
1.0000	0.04284		
	n-Heptane (B) + Tetrahydropyran (C); $K_{AC} = 5{,}627$		
0.0000	0.000173		
0.0480	0.000496	0.000535	7.6
0.1188	0.001142	0.001199	4.9
0.2475	0.002993	0.002918	−2.5
0.3656	0.005155	0.005286	2.5
0.5020	0.009344	0.009344	0.0
0.5988	0.01381	0.01335	−3.4
0.7161	0.02081	0.01977	−5.1
0.8172	0.02821	0.02684	−5.0
0.9119	0.03608	0.03473	−3.8
1.0000	0.04284		
	n-Hexadecane (B) + Tetrahydropyran (C); $K_{AC} = 5{,}090$		
0.0000	0.000414		
0.0745	0.000985	0.000998	1.3
0.1539	0.001723	0.001723	0.0
0.2686	0.003019	0.003021	0.1
0.3531	0.004235	0.004235	0.0
0.4315	0.005579	0.005633	1.0
0.5332	0.007994	0.007991	0.0
0.6369	0.01215	0.01134	−6.9
0.7495	0.01812	0.01671	−8.1
0.8487	0.02473	0.02391	−3.4
0.9411	0.03439	0.03402	−1.1
1.0000	0.04284		

Table 1 (*Continued.*)

x_C^0	$x_A^{\mathrm{sat,exp}}$	$x_A^{\mathrm{sat,calc}}$	% Dev[a]
	Cyclohexane (B) + Tetrahydropyran (C); $K_{AC} = 5{,}255$		
0.0000	0.000183		
0.1192	0.001509	0.001603	6.0
0.2183	0.003271	0.003355	2.5
0.3270	0.006033	0.006014	−0.3
0.3861	0.007828	0.007830	0.0
0.5230	0.01325	0.01315	−0.7
0.6259	0.01832	0.01823	−0.5
0.7204	0.02339	0.02368	1.2
0.8172	0.03082	0.02994	−2.9
0.9079	0.03761	0.03625	−3.7
1.0000	0.04284		
	2,2,4-Trimethylpentane (B) + Tetrahydropyran (C); $K_{AC} = 5{,}976$		
0.0000	0.000126		
0.1394	0.001041	0.001010	−3.0
0.2076	0.001652	0.001651	−0.1
0.3032	0.002863	0.002878	0.5
0.3949	0.004538	0.004541	0.1
0.5021	0.007441	0.007327	−1.5
0.6073	0.01138	0.01128	−1.0
0.6992	0.01602	0.01604	0.2
0.8007	0.02297	0.02310	0.6
0.9032	0.03210	0.03236	0.8
1.0000	0.04284		

[a] Deviations (%) = 100 ln ($x_A^{\mathrm{sat,calc}}/x_A^{\mathrm{sat,exp}}$).

(cyclohexane, *n*-hexane) and fairly large (*n*-hexadecane) saturated hydrocarbons. For four of the five systems considered, Mobile Order theory returned nearly identical values of the "optimized" association constant, which varied from a lower limit of $K_{AC} = 5{,}090$ for *n*-hexadecane to an upper of $K_{AC} = 5{,}976$ for 2,2,4-trimethylpentane. In the case of binary *n*-hexane + tetrahydropyran mixtures, the optimized association constant was $K_{AC} = 11{,}200$, roughly twice the calculated values for cyclohexane,

Table 2 Solvent and Solute Properties Used in Mobile Order Predictions.

Component (*i*)	$V_i/(\mathrm{cm^3\ mole^{-1}})$	$\delta_i'/(\mathrm{MPa^{1/2}})$[a]
n-Hexane	131.51	14.56
n-Heptane	147.48	14.66
n-Hexadecane	294.12	15.61
Cyclohexane	108.76	14.82
2,2,4-Trimethylpentane	166.09	14.30
Tetrahydropyran	97.97	18.78[b]
Carbazole	150.0	

[a] Unless otherwise noted, tabulated values are taken from a compilation given in Ruelle *et al.*[13]

[b] Numerical value estimated by authors.

n-heptane, 2,2,4-trimethylpentane and *n*-hexadecane. We are unable at the present time to explain this abnormally large K_{AC} value.

In fairness, we state that these five carbazole systems were judiciously selected from the published chemical literature in order to provide the most demanding test of the limitations and applications of Mobile Order theory hither-to-fore attempted. It is very easy to mathematically describe solution nonideality in systems where the solute has a comparable mole fraction solubility in both pure solvents. Most solution models, and Mobile Order theory is no different, do break down as molecular interactions become more complex and as the observed solubility enhancement increases. Failure of Mobile Order theory to return a constant K_{AC} for all five systems suggests that there may be more than a single solute-solvent complex present, or that the Scatchard-Hildebrand solubility parameter approach [the $(\delta'_A - \phi^0_B\delta'_B - \phi^0_C\delta'_C)^2$ term in Eq. (7)] provides a poor approximation of nonspecific, physical interactions in this particular set of systems, or perhaps even the breakdown of the infinite dilution approximation that $1 - \phi^{\text{sat}}_A$ equals unity and that $\phi_C = \phi^0_C$ inside the logarithm term. Here, seemingly small changes in the equilibrium concentration of the complexing solvent can have a rather pronounced effect on the predicted solubility. A recently published study[23] involving carbazole dissolved in nine different binary alkane + dibutyl ether solvent systems showed that Mobile Order returned nearly identical values of $K_{AC} = 1710 \pm 190$ for the *presumed* carbazole-dibutyl ether equilibrium constant. These latter nine nonelectrolyte systems covered a much smaller 25-fold range in mole fraction solubilities, and which in all honesty, represent the ones that researchers are more likely to encounter. Mole fraction solubility ranges of 340-fold are rare. Despite the one failure noted, we still believe that Mobile Order theory and the Extended NIBS model [Eqs. (1) and (2)] are two of the better (though by no means perfect) association models at the present time.

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References

1. G. L. Bertrand, *J. Phys. Chem.*, **79**, 48 (1975).
2. J. W. McCargar and W. E. Acree, Jr., *Phys. Chem. Liq.*, **17**, 123 (1987).
3. W. E. Acree, Jr., D. R. McHan and J. H. Rytting, *J. Pharm. Sci.*, **72**, 929 (1983).
4. W. E. Acree, Jr., *Int. J. Pharm.*, **15**, 159 (1983).
5. J. W. McCargar and W. E. Acree, Jr., *J. Pharm. Sci.*, **76**, 572 (1987).
6. J. W. McCargar and W. E. Acree, Jr., *J. Solution Chem.*, **17**, 1081 (1988).
7. W. E. Acree, Jr., S. A. Tucker and A. I. Zvaigzne, *J. Chem. Soc., Faraday Trans.*, **86**, 2197 (1990).
8. W. E. Acree, Jr., *J. Solution Chem.*, **20**, 307 (1991).
9. W. E. Acree, Jr. and A. I. Zvaigzne, *Phys. Chem. Liq.*, **23**, 225 (1991).
10. W. E. Acree, Jr., *J. Chem. Soc., Faraday Trans.*, **87**, 461 (1991).
11. P. L. Huyskens, and G. G. Siegel, *Bull. Soc. Chim. Belg.*, **97**, 821 (1988).
12. G. G. Siegel, P. L. Huyskens and G. Vanderheyden, *Ber. Bunsen-Ges. Phys. Chem.*, **94**, 549 (1990).
13. P. Ruelle, M. Buchmann, H. Nam-Tran and U. W. Kesselring, *Int. J. Pharm.*, **87**, 47 (1992).
14. P. Ruelle, M. Buchmann, H. Nam-Tran and U. W. Kesselring, *Pharm. Res.*, **9**, 788 (1992).
15. W. E. Acree, Jr., J. W. McCargar, A. I. Zvaigzne and I.-L. Teng, *Phys. Chem. Liq.*, **23**, 27 (1991).

16. L. J. Gordon and R. L. Scott, *J. Am. Chem. Soc.*, **74**, 4138 (1952).
17. P. L. Huyskens, M. C. Haulait-Pirson, L. D. Brandts Buys and X. M. Van der Borght, *J. Coat. Technol.*, **57**, 57 (1985).
18. P. L. Huyskens, M. C. Haulait-Pirson, G. G. Siegel and F. Kapuku, *J. Phys. Chem.*, **92**, 6841 (1988).
19. G. Thyagarajan and D. S. R. Rao, *Z. Phys. Chem. Leipzig*, **255**, 97 (1974).
20. T. G. Meister, E. L. Trubina and V. P. Klindukhov, *Opt. Spektrosk.*, **52**, 961 (1982).
21. A. L. Campillo and M. Martinaud, *Chem. Phys. Letters*, **33**, 126 (1975).
22. P. L. Huyskens and M. C. Haulait-Pirson, *J. Mol. Liq.*, **31**, 135 (1985).
23. W. E. Acree, Jr. and S. A. Tucker, *Int. J. Pharm.*, in press.

APPENDIX: GLOSSARY OF SYMBOLS

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid.
ΔG_{BC}^{ex}	excess Gibbs free energy of the binary solvent mixture based upon Raoult's law.
ΔG_{BC}^{fh}	excess Gibbs free energy of the binary solvent mixture based upon the Flory-Huggins model.
ΔH_A^{fus}	molar enthalpy of fusion of the solute at its normal melting point temperature.
K_{AC}^{x}	mole fraction based equilibrium constant for the formation of the AC molecular complex.
K_{AC}^{ϕ}	volume fraction based equilibrium constant for the formation of the AC molecular complex.
K_{AC}	equilibrium constant for the formation of the AC molecular complex based upon Mobile Order theory.
T_{mp}	normal melting point temperature of the solute.
V_i	molar volume of component i.
x_B^0, x_C^0	mole fraction compositions of the binary solvent mixture, calculated as if the solute were not present.
x_A^{sat}	mole fraction solubility of the solute.
γ_i	activity coefficient of component i.
δ_i'	modified solubility parameter of component i.
ϕ_B^0, ϕ_C^0	ideal volume fraction compositions of the binary solvent mixture, calculated as if the solute were not present.
ϕ_A^{sat}	ideal volume fraction solubility of the solute.