International Journal of Pharmaceutics, 101 (1994) 199–207

IJP 03316

Thermochemical investigations of associated solutions: 16. Comparison of the extended NIBS model and mobile order theory for solubility in systems containing solute-solvent complexation

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(Received 9 February 1993)
(Modified version received 18 May 1993)
(Accepted 24 May 1993)

Key words: Mobile order theory; Association constant; Solute-solvent complexation; Solubility

Summary

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 nine binary dibutyl ether + alkane solvent mixtures to within an average absolute deviation of 2.5% using a single association constant. The association constant varied slightly with inert hydrocarbon cosolvent, with the numerical values ranging from a lower limit of $K_{AC} = 1400$ for *n*-heptane to an upper value of $K_{AC} = 1955$ for isooctane.

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

$$iA_1 + jC_1 \rightleftharpoons A_iC_j$$

$$K^{x}_{A_iC_j} = \hat{X}_{A_iC_j}\hat{\gamma}_{A_iC_j}/\left(\hat{X}_{A_1}\hat{\gamma}_{A_1}\right)^{i}\left(\hat{X}_{C_1}\hat{\gamma}_{C_1}\right)^{j}$$

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

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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.

Our earlier studies (Acree, 1983, 1991; Acree et al., 1983; McCargar and Acree, 1987a,b, 1988; Acree and Zvaigzne, 1991) 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:

$$A_1 + C_1 \rightleftharpoons AC \qquad K^{\phi}_{AC} = \hat{\phi}_{AC}/\left(\hat{\phi}_{A_1}\hat{\phi}_{C_1}\right)$$

$$\begin{aligned}\ln \phi^{sat}_{A} = {} & \phi^{o}_{B} \ln\left(\phi^{sat}_{A}\right)_{B} + \phi^{o}_{C} \ln\left(\phi^{sat}_{A}\right)_{C} \\ & + \ln\left[1 + K^{\phi}_{AC} V_A \phi^{o}_{C}/(V_A + V_C)\right] \\ & - \phi^{o}_{C} \ln\left[1 + K^{\phi}_{AC} V_A/(V_A + V_C)\right] \\ & + V_A \Delta G^{fh}_{BC} (RT)^{-1} (X^{o}_{B} V_B + X^{o}_{C} V_C)^{-1}\end{aligned} \tag{1}$$

and mole-fraction-based

$$A_1 + C_1 \rightleftharpoons AC \qquad K^{x}_{AC} = \hat{X}_{AC}/\left(\hat{X}_{A_1}\hat{X}_{C_1}\right)$$

$$\begin{aligned}\ln X^{sat}_{A} = {} & \phi^{o}_{B} \ln\left(X^{sat}_{A}\right)_{B} + \phi^{o}_{C} \ln\left(X^{sat}_{A}\right)_{C} \\ & + \ln\left[1 + K^{x}_{AC} X^{o}_{C}\right] - \phi^{o}_{C} \ln\left[1 + K^{x}_{AC}\right] \\ & + V_A \Delta G^{ex}_{BC} (RT)^{-1} (X^{o}_{B} V_B + X^{o}_{C} V_C)^{-1}\end{aligned} \tag{2}$$

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 mixtures, 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:

$$\Delta G^{ex}_{BC} = (X^{o}_{B} V^{o}_{B} + X^{o}_{C} V^{o}_{C})\ \phi^{o}_{B} \phi^{o}_{C} (\delta_B - \delta_C)^2 \tag{3}$$

$$\begin{aligned}\Delta G^{fh}_{BC} = {} & \Delta G^{ex}_{BC} + RT\left[\ln(X^{o}_{B} V_B + X^{o}_{C} V_C)\right. \\ & \left. - X^{o}_{B} \ln V_B - X^{o}_{C} \ln V_C\right]\end{aligned} \tag{4}$$

the Scatchard-Hildebrand solubility parameter theory (see Acree, 1984), where δ_i refers to the solubility parameter of component i. The symbol $\hat{}$ in Eqns 1 and 2 denotes the 'true equilibrium' compositions of the various species in the associated solution, rather than the stoichiometric concentrations. Other symbols used are defined in the Appendix.

McCargar and Acree (1987a,b, 1988) compared values for the carbazole-dibutyl ether association constant from carbazole solubilities in 10 binary dibutyl ether + alkane solvent mixtures. Eqns 1 and 2 described the experimental solubilities to within an average deviation of about 2% using a single association constant. Variation of the calculated equilibrium constant with inert cosolvent was less in the case of K^{ϕ}_{AC}, the numerical values ranging from $K^{\phi}_{AC} = 22$ for *n*-heptane to $K^{\phi}_{AC} = 30$ for both isooctane and *t*-butylcyclohexane. The success of Eqns 1 and 2 is even more remarkable if one realizes that the carbazole mole fraction solubilities covered a 25-fold range, and the inert cosolvents included both small (cyclohexane, *n*-hexane) and large (squalane, *n*-hexadecane) saturated hydrocarbons.

Ruelle, Huyskens and co-workers (Huyskens and Siegel, 1988; Siegel et al., 1990; Ruelle et al., 1991, 1992a,b) 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 liquid divided by the number 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:

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

where δ'_A and $\delta'_{solvent}$ 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:

$$\ln a_A^{solid} = -\Delta H_A^{fus}(T_{mp} - T)/\,(R \cdot T \cdot T_{mp}) \qquad (6)$$

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 $\phi_{solvent}^2 V_A$ $(\delta'_A - \delta'_{solvent})^2(RT)^{-1}$ 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 authors' comparisons were binary solvent mixtures, which would have provided a more demanding test of the predictive ability of Eqn 5. Comparisons between predicted and experimental values in pure solvents are often misleading if solute-solvent complexation occurs since differences in $\phi_A^{sat,exp}$ and $\phi_A^{sat,calc}$ are used to evaluate 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 Eqn 5, we report in this communication results of using mobile order theory to describe published carbazole solubilities in 10 binary alkane + dibutyl ether solvent mixtures (McCargar and Acree, 1987a,b, 1988).

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 $\delta'_{solvent}$ varies with mixture composition. The function assumed must reduce to $\delta'_{solvent} = \delta'_B$ and $\delta'_{solvent} = \delta'_C$ at $X_B^o = 1.0$ and $X_C^o = 1.0$, respectively, in order to give a correct thermodynamic description of solubilities in both pure solvents. Noting that the $(\delta'_A - \delta'_{solvent})^2$ term in Eqn 5 accounts for nonspecific physical interactions, and because of similarities between δ'_i and δ_i solubility parameters, we approximate $\delta'_{solvent}$ as a volume fraction average of the modified solubility parameters of the two pure solvents, i.e., $\delta'_{solvent} = \phi_B^o\ \delta'_B + \phi_C^o \delta'_C$. Gordon and Scott (1952) invoked a similar approximation, $\delta_{solvent} = \phi_B^o \delta_B + \phi_C^o \delta_C$, 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 $V_{\text{solvent}} = X_B^o V_B + X_C^o V_C$ and all ϕ_{solvent} terms in Eqn 5 are replaced by $1 - \phi_A^{\text{sat}}$, except inside the logarithmic 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 (see Ruelle et al., 1992b). 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 dibutyl ether.

The computational procedure can be simplified further by noting that carbazole has only a very limited mole fraction solubility in dibutyl ether and in the ten alkane cosolvents (see Table 1 for representative experimental values of X_A^{sat}). For all practical purposes, one can approximate $1 - \phi_A^{\text{sat}}$ as equal to unity with no loss in predictive accuracy. Performing the aforementioned substitutions, Eqn 5 is rewritten as follows:

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

It should 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. Eqn 7 thus holds 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 (see Husykens et al., 1985, 1988).

Table 1 compares experimental mole fraction solubilities to predicted values based upon Eqn 7 for carbazole dissolved in binary mixtures containing dibutyl ether with *n*-hexane, *n*-heptane and *n*-octane. The numerical value of $K_{AC} = 350.5$ used in these predictions was obtained by substituting the measured solubility of carbazole in pure dibutyl ether, $X_A^{\text{sat}} = 0.005011$, into Eqn 7 and then back-calculating the carbazole-dibutyl ether association constant. The remaining solute and solvent properties used in the computations are listed in Table 2. Examination of the last column in Table 1 reveals that Eqn 7 grossly underestimates the experimental solubilities by as much as 50%.

TABLE 1

Comparison between experimental carbazole solubilities and calculated values based upon Eqn 7

X_C^o	$X_A^{\text{sat,exp}}$	$X_A^{\text{sat,calc}}$	% dev. [a]
n-Hexane (B) + dibutyl ether (C); $K_{AC} = 350.5$			
0.0000	0.000139	0.000151	8.4
0.0789	0.000333	0.000242	−32.1
0.1602	0.000590	0.000369	−47.0
0.2498	0.000838	0.000557	−40.9
0.3404	0.001166	0.000806	−36.9
0.4368	0.001615	0.001145	−34.4
0.5382	0.002049	0.001595	−25.1
0.6435	0.002662	0.002170	−20.4
0.7581	0.003392	0.002929	−14.7
0.8748	0.003963	0.003851	−2.9
n-Heptane (B) + dibutyl ether (C); $K_{AC} = 350.5$			
0.0000	0.000173	0.000166	−4.0
0.0906	0.000392	0.000266	−38.6
0.1816	0.000642	0.000406	−45.8
0.2738	0.000943	0.000596	−45.8
0.3632	0.001301	0.000838	−44.0
0.4672	0.001771	0.001202	−38.7
0.5620	0.002275	0.001625	−33.7
0.6640	0.002761	0.002189	−23.2
0.7654	0.003263	0.002876	−12.6
0.8739	0.004012	0.003763	−6.4
n-Octane (B) + dibutyl ether (C); $K_{AC} = 350.5$			
0.0000	0.000198	0.000200	1.2
0.1028	0.000474	0.000318	−39.9
0.2030	0.000804	0.000477	−52.2
0.2963	0.001120	0.000675	−50.6
0.3835	0.001492	0.000913	−49.1
0.4902	0.001864	0.001290	−36.8
0.5949	0.002463	0.001767	−33.2
0.6907	0.002966	0.002316	−24.8
0.7885	0.003605	0.003002	−18.3
0.8873	0.004339	0.003843	−12.1

[a] Deviation (%) = 100 $\ln(X_A^{\text{sat,calc}}/X_A^{\text{sat,exp}})$.

The accuracy of the mobile order theory for predicting solubilities in mixed solvents can be improved significantly by eliminating the solute's modified solubility parameter from Eqn 5 in favor of the measured solubilities in the two pure sol-

TABLE 2

Solvent and solute properties used in mobile order and extended NIBS predictions

Component (i)	V_i (cm^3 mol^{-1})	δ_i (MPa$^{1/2}$) [a]	δ_i' (MPa$^{1/2}$) [b]
n-Hexane	131.51	14.87	14.56
n-Heptane	147.48	15.34	14.66
n-Octane	163.46	15.42	14.85
n-Hexadecane	294.12	16.34	15.61
Cyclohexane	108.76	16.75	14.82
Methylcyclohexane	128.32	16.02	15.00
Cyclooctane	134.88	17.41	15.40
Isooctane	166.09	14.03	14.30
t-Butylcyclohexane	173.93	16.00	
Squalane	525.30	16.16	16.25
Dibutyl ether	170.41	15.87	17.45
Carbazole [c]	150.00		22.82 [d]

[a] Tabulated values taken from a compilation given in McCargar and Acree (1988).

[b] Tabulated values taken from a compilation given in Ruelle et al. (1992a).

[c] The numerical value of $a_A^{solid} = 0.009354$ was calculated from the molar enthalpy of fusion, $\Delta H_A^{fus} = 27.20$ kJ/mol (Radomska and Radomska, 1980), at the normal melting point temperature of the solute, $T_{mp} = 519.2$ K.

[d] Numerical value was calculated using the measured carbazole mole fraction solubility in n-hexane, n-heptane and n-octane, in accordance with Eqn 5.

vents. The solubility parameter of the mixed solvent is again assumed to be a volume fraction average of values for the pure solvents. Substitution of $\delta'_{solvent} = \phi_B^o\ \delta'_B + \phi_C^o \delta'_C$ into Eqn 5, followed by suitable algebraic manipulations, gives:

$$RT\Big\{\ln\big(a_A^{solid}/\phi_A^{sat}\big) - 0.5\big[1 - V_A/(X_B^o V_B + X_C^o V_C)\big] + 0.5\ \ln\big[V_A/(X_B^o V_B + X_C^o V_C)\big] + \ln\big[1 + K_{AC}\phi_C^o/V_C\big]\Big\} = V_A\Big[\phi_B^o(\delta'_A - \delta'_B)^2 + \phi_C^o(\delta'_A - \delta'_C)^2 - \phi_B^o\phi_C^o(\delta'_B - \delta'_C)^2\Big] \qquad (8)$$

whenever the saturation solubility is sufficiently low so that $1 - \phi_A^{sat} \approx 1.0$.

Careful examination of Eqn 8 reveals that, for model systems obeying the mobile order theory, the $(\delta'_A - \delta'_B)^2$ and $(\delta'_A - \delta'_C)^2$ terms can be eliminated from the basic model via:

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

TABLE 3

Comparison between experimental carbazole solubilities and calculated values based upon Eqn 11

X_C^o	$X_A^{sat,exp}$	$X_A^{sat,calc}$	% dev. [a]
n-Hexane (B) + dibutyl ether (C); $K_{AC} = 1451$			
0.0789	0.000333	0.000308	−7.9
0.1602	0.000590	0.000527	−11.4
0.2498	0.000838	0.000822	−1.9
0.3404	0.001166	0.001178	1.0
0.4368	0.001615	0.001616	0.0
0.5382	0.002049	0.002135	4.1
0.6435	0.002662	0.002731	2.5
0.7581	0.003392	0.003430	1.1
0.8748	0.003963	0.004182	5.4
n-Octane (B) + dibutyl ether (C); $K_{AC} = 1676$			
0.1028	0.000474	0.000463	−2.4
0.2030	0.000804	0.000777	−3.5
0.2963	0.001120	0.001120	0.0
0.3835	0.001492	0.001486	−0.4
0.4902	0.001864	0.001989	6.5
0.5949	0.002463	0.002538	3.0
0.6907	0.002966	0.003081	3.8
0.7885	0.003605	0.003670	1.8
0.8873	0.004339	0.004290	−1.1
Methylcyclohexane (B) + dibutyl ether (C); $K_{AC} = 1827$			
0.0877	0.000500	0.000491	−1.7
0.1650	0.000797	0.000789	−1.0
0.2453	0.001123	0.001130	0.6
0.3347	0.001545	0.001542	−0.2
0.4294	0.001959	0.002008	2.5
0.5339	0.002450	0.002548	3.9
0.6885	0.003278	0.003371	2.8
0.7417	0.003656	0.003656	0.0
0.8568	0.004356	0.004270	−2.0
Cyclohexane (B) + dibutyl ether (C); $K_{AC} = 1612$			
0.0665	0.000442	0.000407	−8.2
0.1372	0.000687	0.000680	−1.0
0.2143	0.001013	0.001013	0.0
0.2975	0.001434	0.001404	−2.1
0.3876	0.001772	0.001853	4.4
0.4895	0.002296	0.002383	3.7
0.5996	0.002888	0.002966	2.7
0.7135	0.003406	0.003568	4.6
0.8510	0.004103	0.004278	4.2

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

and

$$RT\{\ln[a_{\mathrm{A}}^{\mathrm{solid}}/(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}}] - 0.5(1 - V_{\mathrm{A}}/V_{\mathrm{C}}) + 0.5\ln(V_{\mathrm{A}}/V_{\mathrm{C}}) + \ln[1 + K_{\mathrm{AC}}/V_{\mathrm{C}}]\} = V_{\mathrm{A}}(\delta'_{\mathrm{A}} - \delta'_{\mathrm{C}})^2 \qquad (10)$$

where $(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}}$ and $(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}}$ denote the solubilities in the two pure solvents. Performing these substitutions one obtains a relatively simple mathematical expression for the solubility in a binary solvent mixture:

$$\begin{aligned}\ln \phi_{\mathrm{A}}^{\mathrm{sat}} = {} & \phi_{\mathrm{B}}^{\mathrm{o}} \ln(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}} + \phi_{\mathrm{C}}^{\mathrm{o}} \ln(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}} \\ & + \ln[1 + K_{\mathrm{AC}}\phi_{\mathrm{C}}^{\mathrm{o}}/V_{\mathrm{C}}] \\ & - \phi_{\mathrm{C}}^{\mathrm{o}} \ln[1 + K_{\mathrm{AC}}/V_{\mathrm{C}}] \\ & - 0.5[\ln(X_{\mathrm{B}}^{\mathrm{o}}V_{\mathrm{B}} + X_{\mathrm{C}}^{\mathrm{o}}V_{\mathrm{C}}) \\ & - \phi_{\mathrm{B}}^{\mathrm{o}} \ln V_{\mathrm{B}} - \phi_{\mathrm{C}}^{\mathrm{o}} \ln V_{\mathrm{C}}] \\ & + V_{\mathrm{A}}\phi_{\mathrm{B}}^{\mathrm{o}}\phi_{\mathrm{C}}^{\mathrm{o}}(\delta'_{\mathrm{B}} - \delta'_{\mathrm{C}})^2(RT)^{-1} \qquad (11)\end{aligned}$$

which does not require a priori knowledge of the solute's enthalpy of fusion and melting point temperature. Moreover, the derived expression correctly describes the solubility in the pure complexing and noncomplexing solvents, and if one desires, Eqn 11 can be used to calculate the 'optimum value' of the solute-solvent association constant from measured solubility as a function of solvent composition.

This algebraic manipulation also permits one to directly compare the mathematical forms of the extended NIBS and mobile order theory. The two equations differ only in the last set of terms:

$$\begin{aligned}& V_{\mathrm{A}}(RT)^{-1}(X_{\mathrm{B}}^{\mathrm{o}}V_{\mathrm{B}} + X_{\mathrm{C}}^{\mathrm{o}}V_{\mathrm{C}})^{-1}\{(X_{\mathrm{B}}^{\mathrm{o}}V_{\mathrm{B}} + X_{\mathrm{C}}^{\mathrm{o}}V_{\mathrm{C}}) \\ & \times \phi_{\mathrm{B}}^{\mathrm{o}}\phi_{\mathrm{C}}^{\mathrm{o}}(\delta_{\mathrm{B}} - \delta_{\mathrm{C}})^2 + [\ln(X_{\mathrm{B}}^{\mathrm{o}}V_{\mathrm{B}} + X_{\mathrm{C}}^{\mathrm{o}}V_{\mathrm{C}}) \\ & - X_{\mathrm{B}}^{\mathrm{o}} \ln V_{\mathrm{B}} - X_{\mathrm{C}}^{\mathrm{o}} \ln V_{\mathrm{C}}]\} \qquad (12)\end{aligned}$$

for the extended NIBS model vs

$$\begin{aligned}& -0.5[\ln(X_{\mathrm{B}}^{\mathrm{o}}V_{\mathrm{B}} + X_{\mathrm{C}}^{\mathrm{o}}V_{\mathrm{C}}) - \phi_{\mathrm{B}}^{\mathrm{o}} \ln V_{\mathrm{B}} - \phi_{\mathrm{C}}^{\mathrm{o}} \ln V_{\mathrm{C}}] \\ & + V_{\mathrm{A}}\phi_{\mathrm{B}}^{\mathrm{o}}\phi_{\mathrm{C}}^{\mathrm{o}}(\delta'_{\mathrm{B}} - \delta'_{\mathrm{C}})^2(RT)^{-1} \qquad (13)\end{aligned}$$

for mobile order theory. Here $\Delta G_{\mathrm{BC}}^{\mathrm{fh}}$ has been approximated by Eqns 3 and 4. To date, all published applications involving the extended NIBS model have approximated the excess Gibbs free energies of the binary solvent mixtures using the Scatchard-Hildebrand solubility parameter theory as direct experimental values were not readily available in the chemical literature. Careful examination of Eqns 12 and 13 reveal that the extended NIBS and mobile order approaches become equivalent in systems having negligible molecular size disparity, provided that $(\delta_{\mathrm{B}} - \delta_{\mathrm{C}})^2 = (\delta'_{\mathrm{B}} - \delta'_{\mathrm{C}})^2$. Here, mole fractions and volume fractions are equal. Differences between the two models become magnified; however, as the $V_{\mathrm{B}}/V_{\mathrm{C}}$ (or $V_{\mathrm{C}}/V_{\mathrm{B}}$) molar volume ratio increases. The 10 carbazole systems should provide a very demanding test of the descriptive ability of Eqn 11 derived from mobile order theory since the cosolvents considered include both small (*n*-hexane, cyclohexane) and very large (*n*-hexadecane, squalane) saturated hydrocarbons.

One further notes that the extended NIBS model employs the total solubility parameter, δ_i, in solubility predictions whereas modified solubility parameters, δ'_i, are used in the case of mobile order theory. Intuitively, one would expect both sets of parameters to be nearly identical for the solvents considered in the present study. Most are saturated hydrocarbons whose only molecular interactions should involve very weak, nonspecific physical interactions. Examination of Table 2 indicates that the two sets are different, for example, a value of $\delta_i = 16.75$ MPa$^{1/2}$ vs $\delta'_i = 14.82$ MPa$^{1/2}$ for cyclohexane. Readers are reminded that several of the δ'_i values contained in the compilation of Ruelle et al. (1992a), which are also listed in Table 2, were deduced by regressing solubility data of solid *n*-alkanes in organic solvents in accordance with the model of Huyskens and Haulait-Pirson (1985). Any errors or uncertainties in the measured data would naturally affect the calculated numerical values of δ_i', as would any shortcomings of Huyskens and Haulait-Pirson model to back-calculate the observed mole fraction solubilities.

Despite the complex appearance of Eqn 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, 1987a). The quantities $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$ are calculated from the measured mole fraction solubility of the solid 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 Eqn 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.

Tables 3 and 4 compare experimental carbazole solubilities to values calculated from Eqn 11 for nine different binary dibutyl ether + alkane solvent systems. Predictions for the tenth system, dibutyl ether + *t*-butylcyclohexane, were not performed because $\delta'_{t\text{-butylcyclohexane}}$ was not included in the tabulation given by Ruelle, et al. (1992a). Also summarized in Table 4 are the corresponding predictions using the extended NIBS model. In all cases, only computations involving the 'optimized' association constant are reported. Inspection of Tables 3 and 4 reveals that our modifications have significantly improved the predictive ability of mobile order theory as the average absolute deviation is on the order of 2.5%. The derived expression is just slightly inferior to both extended NIBS expressions. Eqn 11 often underpredicted the observed carbazole solubilities by as much as 6–8% at low dibutyl ether mole fractions where the relative solubility enhancement is large.

Eqn 11 does give fairly consistent values for the carbazole-dibutyl ether association constant, which range from a low value of $K_{AC} = 1400$ for *n*-heptane to an upper limit of $K_{AC} = 1955$ for isooctane. When converted to a common scale for *n*-heptane:

$$K_{AC}/V_C = K_{AC}^{\phi} V_A/(V_A + V_C)$$

$$1400/150 \approx 22\ (150/320)$$

the association constants calculated from mobile order theory are comparable in magnitude to those obtained with the extended NIBS model. The present study shows that mobile order theory does provide a fairly reasonable (though by no means perfect) description of solute solubilities in

TABLE 4

Association constants for presumed carbazole-dibutyl ether complexes calculated from solubility data using the extended NIBS model and mobile order theory

Inert cosolvent	Eqn 1		Eqn 2		Eqn 11		
	K_{AC}^{ϕ}	% dev. [a]	K_{AC}^{x}	% dev.[a]	K_{AC}	K_{AC}^{ϕ} [b]	% dev. [a]
n-Hexane	24.0	2.0	15.2	2.0	1450	18.2	3.9
n-Heptane	22.0	1.8	12.0	1.8	1400	17.5	2.2
n-Octane	25.0	1.7	12.5	1.6	1675	21.0	2.5
n-Hexadecane	24.0	1.4	6.3	1.4	1775	22.2	1.7
Cyclohexane	24.0	2.2	18.5	1.8	1612	20.2	3.4
Methylcyclohexane	26.0	1.8	17.0	1.6	1827	22.9	1.7
Cyclooctane	25.0	2.1	15.5	2.1	1890	23.7	1.9
Isooctane	30.0	1.7	14.0	1.4	1955	24.5	2.7
t-Butylcyclohexane	30.0	1.5	14.0	1.7			
Squalane	23.0	1.7	3.5	1.6	1800	22.6	2.2

[a] Deviation (%) $= (100/N)\Sigma\,|\ln(X_A^{sat,calc}/X_A^{sat,exp})|$.

[b] Values were calculated as $K_{AC}^{\phi} = K_{AC}(V_A + V_C)/(V_C V_A)$.

binary solvent mixtures containing solute-solvent complexation. For the 10 carbazole systems considered here, the extended NIBS model was found to be just slightly superior to equations derived from mobile order theory.

Acknowledgements

This research was supported in part by a grant from the National Science Foundation (Grant No. CTS-8922485) and by a National Science Foundation Doctoral Research Fellowship awarded to S.A.T.

Appendix: Glossary of Symbols

Symbol	Meaning
$a_{\mathrm{A}}^{\mathrm{solid}}$	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
$\Delta G_{\mathrm{BC}}^{\mathrm{ex}}$	excess Gibbs free energy of the binary solvent mixture based upon Raoult's law
$\Delta G_{\mathrm{BC}}^{\mathrm{fh}}$	excess Gibbs free energy of the binary solvent mixture based upon the Flory-Huggins model
$\Delta H_{\mathrm{A}}^{\mathrm{fus}}$	molar enthalpy of fusion of the solute at its normal melting point temperature
K_{AC}	equilibrium constant for the formation of the AC molecular complex based upon mobile order theory
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
T_{mp}	normal melting point temperature of the solute
V_i	molar volume of component i
$X_{\mathrm{B}}^{\mathrm{o}}$, $X_{\mathrm{C}}^{\mathrm{o}}$	mole fraction compositions of the binary solvent mixture, calculated as if the solute were not present
$X_{\mathrm{A}}^{\mathrm{sat}}$	mole fraction solubility of the solute
γ_i	activity coefficient of component i
δ_i	Scatchard-Hildebrand solubility parameter of component i
δ_i'	modified solubility parameter of component i
$\phi_{\mathrm{B}}^{\mathrm{o}}$, $\phi_{\mathrm{C}}^{\mathrm{o}}$	ideal volume fraction compositions of the binary solvent mixture, calculated as if the solute were not present
$\phi_{\mathrm{A}}^{\mathrm{sat}}$	ideal volume fraction solubility of the solute

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