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Solubility in binary solvent systems. V. Monomer and dimer models for the solubility of *p*-tolylacetic acid in systems of non-specific interactions

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Summary

Solubilities are reported for *p*-tolylacetic acid in binary mixtures of cyclohexane with *n*-hexane, *n*-heptane, *n*-octane and isooctane at 25°C. The results are compared to the predictions of equations developed previously for solubility in systems of purely non-specific interactions, with the carboxylic acid considered as either monomeric or dimeric molecules in solution. The dimer model provided the more accurate predictions, with a maximum deviation of 5.6% between observed and predicted solubility in all systems studied.

Introduction

This work continues a systematic search (Acree and Bertrand, 1977, 1981, 1983; Acree and Rytting, 1982a and b; Acree et al., 1983; Acree, 1982, 1983) for mixing models and equations which will provide reasonable predictions for the thermochemical properties of a solute in binary solvent mixtures. In an earlier paper, Acree and Bertrand (1981) reported benzoic acid and *m*-toluic acid solubilities in solvent mixtures containing carbon tetrachloride. The experimental data were interpreted

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with solution models

$$RT \ln(a_{3,i}^{\text{solid}}/X_{3,i}^{\text{sat}}) = (1 - \phi_{3,i}^{\text{sat}})^2 \left[\phi_1^{\text{o}} (\Delta G_{3,i}^{\text{ex}})_{X_1^{\text{o}}=1} + \phi_2^{\text{o}} (\Delta G_{3,i}^{\text{ex}})_{X_2^{\text{o}}=1} - V_{3,i} (X_1^{\text{o}}V_1 + X_2^{\text{o}}V_2)^{-1} (\Delta G_{12}^{\text{ex}}) \right] \quad (1)$$

$$RT \left[\ln(a_{3,i}^{\text{solid}}/\phi_{3,i}^{\text{sat}}) - (1 - \phi_{3,i}^{\text{sat}}) \left(1 - \frac{V_{3,i}}{(X_1^{\text{o}}V_1 + X_2^{\text{o}}V_2)} \right) \right] = (1 - \phi_{3,i}^{\text{sat}})^2 \left[\phi_1^{\text{o}} (\Delta G_{3,i}^{\text{fh}})_{X_1^{\text{o}}=1} + \phi_2^{\text{o}} (\Delta G_{3,i}^{\text{fh}})_{X_2^{\text{o}}=1} - V_{3,i} (X_1^{\text{o}}V_1 + X_2^{\text{o}}V_2)^{-1} (\Delta G_{12}^{\text{fh}}) \right] \quad (2)$$

based on a monomeric treatment ($i = \text{mon}$) and a dimeric treatment ($i = \text{dim}$) of the carboxylic acid (component 3). In Eqns. 1 and 2 X_j and ϕ_j are mole and volume fractions of component j , V_j is the molar volume of component j , and $\Delta G_{12}^{\text{ex}}$ and $\Delta G_{12}^{\text{fh}}$ refer to the excess Gibbs free energies of the binary solvent mixture based on Raoult's law and the Flory-Huggins model, respectively. Remaining symbols are defined in the glossary appearing at the end of the paper. Deviations between observed and predicted values were on the order of 6–10% for the monomeric treatment and 2–4% for the dimeric treatment.

While this earlier study did suggest that a dimeric treatment is more applicable for describing the properties of benzoic acid and *m*-toluic acid, the model should be tested using other carboxylic acid solutes. For this reason, we have measured the solubility of *p*-tolylacetic acid in binary solvent systems containing cyclohexane with *n*-hexane, *n*-heptane, *n*-octane and isooctane. These systems were selected in anticipation of extending Eqns. 1 and 2 to mixtures saturated with respect to two carboxylic acid solutes. Mixtures having two carboxylic acids are interesting from a theoretical standpoint because the solutes may exist in 'mixed dimeric' form as well. For example, in a non-polar solvent mixture containing both benzoic acid and *p*-tolylacetic acid the three dimeric species are: benzoic acid dimers, *p*-tolylacetic acid dimers and mixed benzoic acid–*p*-tolylacetic acid dimers. Formation of the mixed dimer leads to an enhanced solubility for each carboxylic acid provided that solid solution does not form. Interpretation of solution nonideality in mixtures containing two carboxylic acid solutes does require a thorough understanding of the simpler systems having only a single carboxylic acid. A better understanding of the thermochemical behavior of carboxylic acid solute(s) in non-polar solvents will be useful in controlling the solubility and partitioning of molecules having –COOH functional groups.

Experimental

p-Tolylacetic acid (Aldrich 99%) was dried at 60°C for several hours before use. Cyclohexane (Fisher ACS Certified), *n*-heptane (Aldrich Gold Label), *n*-octane

(Aldrich Gold Label), *n*-hexane (Fisher 99 mol%) and isooctane (Phillips 99%) were stored over molecular sieves to remove trace amounts of water.

Solvent mixtures were prepared by weight with sufficient accuracy to allow calculation of compositions to 0.0001 mole fraction. Solvents and excess carboxylic acid were placed in amber glass containers and allowed to equilibrate in a constant temperature bath at $25.0 \pm 0.1^\circ\text{C}$ for several days. The attainment of equilibrium

TABLE I

COMPARISON BETWEEN THE CALCULATED AND OBSERVED SOLUBILITIES FOR *p*-TOLYLACETIC ACID IN BINARY SOLVENT MIXTURES AT 25.0°C

Solvent (1)+Solvent (2)	X_1^0	X_3^{sat}	Deviations (%) of calculated values ^a				$\Delta G_{12}^{\text{ex}}$ Ref.
			Monomer Model		Dimer Model		
			Eqn. 3	Eqn. 4	Eqn. 3	Eqn. 4	
$\text{C}_6\text{H}_{12} + \text{C}_6\text{H}_{14}$	0.0000	0.00780	-	-	-	-	b
	0.2325	0.00928	-4.1	-4.0	-1.5	-1.1	
	0.4147	0.01055	-6.5	-6.5	-2.6	-2.0	
	0.5496	0.01146	-7.1	-7.0	-2.7	-2.0	
	0.6943	0.01239	-7.1	-7.0	-2.8	-2.3	
	0.8244	0.01286	-4.1	-4.0	-0.9	-0.5	
	1.0000	0.01335	-	-	-	-	
$\text{C}_7\text{H}_{16} + \text{C}_6\text{H}_{12}$	0.0000	0.01355	-	-	-	-	c
	0.1553	0.01284	-3.6	-3.5	-1.8	-0.9	
	0.2788	0.01213	-3.8	-3.7	-1.1	+0.1	
	0.4249	0.01138	-4.3	-4.2	-1.2	+0.2	
	0.5737	0.01056	-3.7	-3.7	-0.8	+0.5	
	0.7436	0.00958	-1.8	-1.8	+0.4	+1.3	
	1.0000	0.00837	-	-	-	-	
<i>n</i> - $\text{C}_8\text{H}_{18} + \text{C}_6\text{H}_{12}$	0.0000	0.01335	-	-	-	-	d
	0.1413	0.01274	-2.7	-2.6	-1.5	0.0	
	0.2680	0.01211	-3.6	-3.5	-1.7	+0.4	
	0.3906	0.01143	-3.3	-3.3	-1.0	+1.3	
	0.5521	0.01078	-4.2	-4.2	-1.7	+0.4	
	0.7221	0.01006	-4.0	-4.0	-1.9	-0.5	
	1.0000	0.00867	-	-	-	-	
<i>i</i> - $\text{C}_8\text{H}_{18} + \text{C}_6\text{H}_{12}$	0.0000	0.01335	-	-	-	-	e
	0.1423	0.01253	-2.6	-2.5	-1.3	+0.3	
	0.2603	0.01215	-6.5	-6.5	-4.6	-2.5	
	0.3971	0.01139	-7.7	-7.6	-5.6	-3.2	
	0.6041	0.01018	-6.9	-6.9	-5.2	-3.2	
	0.7922	0.00915	-3.5	-4.7	-3.6	-2.4	
	1.0000	0.00801	-	-	-	-	

^a Deviation (%) = $100 \ln(X_3^{\text{sat}})_{\text{calc}} / (X_3^{\text{sat}})_{\text{obs}}$.

^b Li, Lu and Chen (1973).

^c Young et al. (1977).

^d Jain and Yadav (1971).

^e Battino (1966).

was verified by repetitive measurements after several additional days. Acid solubility was determined by transferring a weight aliquot into a flask containing blank methanol-toluene titration solvent. The solutions were titrated with freshly standardized sodium methoxide solution to the thymol blue end-point, giving solubilities reproducible to within 1%. The experimental solubilities are given in Table 1 as formal mole fractions, calculated as though the solute were monomeric, and solvent compositions (X_1^0) are calculated as if the solute were not present.

Results and Discussion

Comparison between experimental and predicted values are shown in the last four columns of Table 1. The predicted values were based on the infinite dilution approximations

$$\ln X_{3,i}^{\text{sat}} = \phi_1^0 \ln(X_{3,i}^{\text{sat}})_{X_1^0=1} + \phi_2^0 \ln(X_{3,i}^{\text{sat}})_{X_2^0=1} + V_{3,i}(X_1^0 V_1 + X_2^0 V_2)^{-1} (RT)^{-1} \Delta G_{12}^{\text{ex}} \quad (3)$$

$$\ln \phi_{3,i}^{\text{sat}} = \phi_1^0 \ln(\phi_{3,i}^{\text{sat}})_{X_1^0=1} + \phi_2^0 \ln(\phi_{3,i}^{\text{sat}})_{X_2^0=1} + V_{3,i}(X_1^0 V_1 + X_2^0 V_2)^{-1} (RT)^{-1} \Delta G_{12}^{\text{fh}} \quad (4)$$

of Eqns. 1 and 2 because the enthalpy of fusion for *p*-tolylacetic acid, needed to calculate $a_{3,i}^{\text{solid}}$, was not available in the chemical literature. Errors resulting from this approximation are negligible whenever the experimental solubility is sufficiently small so that one can assume the $1 - \phi_{3,i}^{\text{sat}}$ terms are unity. The molar volume of *p*-tolylacetic acid, $V_{3,\text{mon}} = 139.2 \text{ cm}^3/\text{mol}$, was obtained by adding twice the incremental 'CH₂' volume of 17.4 cm³/mol to the molar volume of benzoic acid ($V_{3,\text{mon}} = 104.4 \text{ cm}^3/\text{mol}$). For the systems studied in this investigation, a 10% error in estimating $V_{3,\text{mon}}$ affects the predicted solubilities by less than 1%. Solvent properties used in the calculations are listed in Table 2.

Inspection of Table 1 reveals that the dimer model of Eqn. 4 provides the more accurate predictions, with a maximum deviation of 3.2% between observed and predicted values for the four binary systems considered. The dimeric form of Eqn. 4 is slightly better in predictive ability than that of Eqn. 3, suggesting that the Flory-Huggins model may provide a better mathematical description of solution

TABLE 2
SOLVENT PROPERTIES USED IN CALCULATIONS

Solvent	V_j (cm ³ /mol)
Cyclohexane	108.76
<i>n</i> -Hexane	131.51
<i>n</i> -Heptane	147.48
<i>n</i> -Octane	163.46
Isooctane	166.09

ideality in systems having molecules of dissimilar sizes. Eqn. 3 is based on Raoult's law whereas Eqn. 4 is based on the Flory-Huggins model.

The dimer model gives very good predictions for the solubility of *p*-tolylacetic acid in simple binary solvent mixtures and should be equally applicable to solubilities of most monofunctional carboxylic acids in multicomponent systems of non-specific solvent-solvent and solvent-solute interactions. The solubility of solid phenol in systems of this type is expected to obey similar equations based on either a trimer model (Woolley et al., 1971) or a pentamer model (Anderson et al., 1979), but the solubility of gaseous phenol at high dilution (or if one prefers, the Henry's law constant) should be best described by a monomer model. Extraction equilibria present an interesting case in that the most adequate model may depend on the concentration range studied.

Abbreviations

a_3^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure supercooled liquid
(ΔG_3^{ex})	partial molar excess Gibbs free energy of the solute (Raoult's law), extrapolated back to infinite dilution
(ΔG_3^{fh})	partial molar excess Gibbs free energy of the solute (Flory-Huggins model), extrapolated back to infinite dilution
$\Delta G_{12}^{\text{ex}}$	excess Gibbs free energy of the binary solvent mixture based on Raoult's law
$\Delta G_{12}^{\text{fh}}$	excess Gibbs free energy of the binary solvent mixture based on the Flory-Huggins solution model
V_j	molar volume of component <i>j</i>
X_1^o, X_2^o	mole fraction composition of the solvent mixture, calculated as if the solute were not present
X_3^{sat}	mole fraction solubility of the solute
ϕ_1^o, ϕ_2^o	ideal volume fraction compositions of the solvent mixture, calculated as if the solute were not present
ϕ_3^{sat}	ideal volume fraction solubility of the solute

Subscripts

$X_j^o = 1$	value in pure solvent <i>j</i>
mon	denotes the value is calculated by assuming the solute exists entirely in monomeric form
dim	denotes the value is calculated by assuming the solute completely dimerizes in solution
1, 2	solvent components
3	solute

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