Thermochemical Investigations of Nearly Ideal Binary Solvents VII: Monomer and Dimer Models for Solubility of Benzoic Acid in Simple Binary and Ternary Solvents

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Abstract □ Solubilities are reported for benzoic acid at 25.0° in binary mixtures of carbon tetrachloride with cyclohexane, *n*-hexane, or *n*-heptane and of cyclohexane with *n*-hexane or *n*-heptane and in ternary mixtures of carbon tetrachloride–cyclohexane–*n*-hexane and carbon tetrachloride–cyclohexane–*n*-heptane. Solubilities also are reported for benzoic acid in some binary solvents at 30.0° and for *m*-toluic acid in binary mixtures of cyclohexane and *n*-hexane at 25.0°. The results are compared to the predictions of equations developed previously for solubility in systems of purely nonspecific interactions, with the benzoic acids considered as either monomeric or dimeric molecules in solution. The dimer model gave more accurate predictions, with a maximum deviation of 4.4% between observed and predicted solubilities in all systems studied. Solubility maxima were predicted and observed for benzoic and *m*-toluic acids in cyclohexane–*n*-hexane and for benzoic acid in cyclohexane–*n*-heptane. The application of these solubility relationships to liquid–liquid partition coefficients is discussed.

Keyphrases □ Binary solvents—thermochemical study of monomer and dimer models for benzoic acid solubility □ Benzoic acid—thermochemical study, monomer and dimer models for solubility in simple binary and ternary solvents □ Solubility—benzoic acid in simple binary and ternary solvents, monomer and dimer models □ Thermochemistry—monomer and dimer models for solubility of benzoic acid in simple binary and ternary solvents

The use of mixed solvents for influencing solubility and multiphase partitioning has great potential application in pharmaceutical research. Maximum realization of this potential depends on the development of equations that predict solubilities or partition coefficients in mixed solvents from the properties of the individual components. This study continued the testing (1–4) of applications and limitations of the nearly ideal binary solvent (NIBS) model for predicting solution enthalpies (1, 2), solubilities (3), and gas–liquid partition coefficients (4) of solutes in binary solvent mixtures relative to their properties in pure solvents.

BACKGROUND

The NIBS model predicts that any partial molar thermodynamic excess property of a solute at infinite dilution in a binary solvent is a volume fraction average (a weighted mole fraction average gives somewhat better predictions for solution enthalpies) of its properties at infinite dilution in a pure solvent, with a correction for solvent "unmixing" by the presence of the solute. This model gives good predictions for solute properties in systems of nonspecific interactions, but it fails for systems with specific solvent–solvent or solvent–solute interactions. The solubility equations have been successfully applied to solubilities as high as 0.3 mole fraction (3) for solutes that do not self-associate or form solvent–solute complexes.

Benzoic acid presents an interesting test for these equations because of its very strong self-association in "inert" solvents, even at high dilution. Calculations with reported dimerization constants in cyclohexane (5), carbon tetrachloride (5, 6), and benzene (5, 7, 8) indicate that <4% of the benzoic acid molecules are monomers at saturation at 25°. Thus, this approach should give relatively poor predictions of the solubility of benzoic acid in terms of a monomer model, but it has a reasonable chance of success if a dimer model is used.

The dimer model may be an oversimplification, however, since Krishnan *et al.* (8) presented evidence for trimers of benzoic acid in benzene. The reported equilibrium constants for benzoic acid at saturation in benzene at 25° led to estimates that 2.5% of the benzoic acid molecules are monomers, 66% are dimers, and the remainder are trimers. To avoid the complications of trimeric forms, the present study was confined to solvents in which benzoic acid is considerably less soluble than in benzene.

During this work, the nearly ideal binary solvent model was found to predict maxima for benzoic acid solubility in mixtures of cyclohexane with *n*-hexane or *n*-heptane. Such maxima are usually explained with solubility parameter theory (9) in terms of the solubility parameter of the solute lying between the solubility parameters of the solvents. However, all estimates of the solubility parameters of benzoic acid monomers or dimers give values greater than any of the solvents studied, so these measurements provide a test of the more general applicability of the present approach. Similar predictions for maximum solubility of *m*-toluic acid also were tested.

The equations for solubility in binary solvents were expanded to include ternary solvents. Since these equations require excess free energy data (data that are often not available), an approximation was developed from the original nearly ideal binary solvent model for estimating the excess properties of a multicomponent system from the properties of the contributing binary systems. The resultant equations give good predictions for the solubility of benzoic acid in two simple ternary solvents.

EXPERIMENTAL

Benzoic acid (99%) was dried at 60° for several hours, mp 122.5 ± 0.5° [lit. (10) mp 122.4°]. *m*-Toluic acid (99%) was recrystallized twice from aqueous ethanol and dried at 80°, mp 109.5 ± 0.5° [lit. (10) mp 111–113°]. The recrystallized acid was titrated to a thymol blue end-point with freshly standardized sodium methoxide solution by the method of Fritz and Lisicki (11), except toluene was substituted for benzene. The purity of the *m*-toluic acid was calculated to be 100.1 ± 0.5%. Cyclohexane (99+%), *n*-heptane (99+%), and *n*-hexane (99%) were stored over molecular sieves (Type 4A) and distilled shortly before use. Carbon tetrachloride (99+%) was purified by the method of Scatchard *et al.* (12), stored in contact with mercury under an argon atmosphere, and distilled shortly before use.

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 brown glass containers and allowed to equilibrate in a constant-temperature bath at 25.00 ± 0.01 or 30.00 ± 0.01°, maintained constant to ±0.002°, for several days. The attainment of equilibrium was verified by repetitive measurements after several

Table I—Solubilities of Benzoic Acid and *m*-Toluic Acid in Pure Solvents

Solute(s)	Solvent	Temperature	$10^2 X_2^{sat}$
Benzoic acid	*c*-C_6H_{12}	25.0°	1.15
	c-C_6H_{12}	30.0°	1.46 (1.43[a])
Benzoic acid	*n*-C_6H_{14}	25.0°	1.00
	n-C_6H_{14}	30.0°	1.26
Benzoic acid	*n*-C_7H_{16}	25.0°	1.14
	n-C_7H_{16}	30.0°	1.47
Benzoic acid	CCl_4	25.0°	4.92 (4.99[b])
	CCl_4	30.0°	5.98
m-Toluic acid	*c*-C_6H_{12}	25.0°	1.27
	n-C_6H_{14}	25.0°	1.17

[a] Reference 15. [b] Reference 16.

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Table II—Solubility of Benzoic Acid in Binary Solvents at 25.0 and 30.0°: Comparison of the Predictions of Monomer and Dimer Models in Eqs. 1 and 2

Temperature	Solvent 1	Solvent 2	X_1^0	$10^2\ X_s^{sat}$ [a]	Percent Deviation (Monomer Model) [b], Eq. 1 or 2	Percent Deviation (Dimer Model) [b] Eq. 1	Eq. 2
25.0°	c-C_6H_{12}	CCl_4	0.1847	3.89	−4.3	−0.9	−0.9
			0.3681	3.07	−8.1	−3.5	−3.5
			0.5207	2.46	−8.2	−3.3	−3.3
			0.6226	2.12	−8.0	−4.0	−4.0
			0.8084	1.56	−4.2	−1.6	−1.6
25.0°	n-C_7H_{16}	CCl_4	0.1784	3.75	−6.5	−1.6	−1.2
			0.2303	3.47	−7.9	−2.1	−1.0
			0.3348	2.95	−8.9	−2.5	−0.5
			0.3930	2.70	−9.2	−2.7	−1.4
			0.3932	2.69	−9.0	−2.5	−1.2
			0.4708	2.40	−9.0	−2.8	−1.4
			0.5433	2.14	−7.8	−2.0	−0.6
			0.7013	1.70	−5.8	−1.4	−0.4
30.0°	n-C_7H_{16}	CCl_4	0.2421	4.23	−8.4	−2.5	−1.4
			0.4269	3.22	−9.6	−3.2	−1.8
			0.6237	2.41	−7.6	−2.6	−1.4
			0.7346	2.06	−5.3	−1.5	−0.8
25.0°	n-C_6H_{14}	CCl_4	0.1550	3.95	−6.4	−1.5	−1.1
			0.3419	2.97	−10.4	−3.1	−2.3
			0.4408	2.51	−10.4	−2.7	−1.9
			0.5951	1.95	−9.4	−2.7	−2.0
			0.8028	1.37	−4.9	−1.1	−0.7
30.0°	n-C_6H_{17}	CCl_4	0.2255	4.83	−9.6	−2.9	−2.4
			0.3078	3.91	−10.8	−3.5	−2.9
			0.4556	3.04	−11.0	−3.4	−2.7
			0.6438	2.26	−9.1	−2.2	−1.5
			0.7564	1.85	−6.5	−2.0	−1.5
25.0°	c-C_6H_{12}	n-C_6H_{14}	0.2573	1.08	−1.8	0.0	+0.3
			0.4699	1.13	−3.0	0.0	+0.5
			0.5342	1.15	−4.1	−0.9	−0.5
			0.6566	1.18	−4.9	−1.6	−1.3
			0.8044	1.17	−2.6	0.0	+0.2
30.0°	c-C_6H_{12}	n-C_6H_{14}	0.2341	1.36	−2.8	−0.9	−0.7
			0.2845	1.38	−3.2	−1.1	−0.9
			0.5059	1.46	−4.8	−1.8	−1.4
			0.6670	1.50	−5.1	−2.0	−1.7
			0.7821	1.51	−4.4	−1.8	−1.5
25.0°	c-C_6H_{12}	n-C_7H_{16}	0.2781	1.19	−2.1	−0.3	+0.2
			0.4602	1.21	−3.0	−0.6	+0.1
			0.5713	1.21	−3.2	−1.0	0.0
			0.6825	1.22	−4.0	−1.7	−1.0
			0.8142	1.19	−2.2	−0.6	−0.1

[a] X_s^{sat} is calculated as if the solute is monomeric. [b] Percent deviation = $100 \ln (X_s^{sat})_{calc}/(X_s^{sat})_{obs}$.

additional days. Acid solubility was determined by transferring a weight aliquot through a coarse filter into a flask containing blank nonaqueous titration solvent. The solutions were titrated with freshly standardized sodium methoxide solution to the thymol blue end-point, giving solubilities reproducible to within 1%.

Solubilities in pure solvents (Table I), in binary solvents (Tables II and III), and in ternary solvents (Table IV) are reported as formal mole fractions, calculated as though the solute were monomeric, and solvent compositions (X_i^0) are calculated as if the solute were not present. Table I results are in good agreement with previously reported values.

DISCUSSION

Monomer and Dimer Models for Solubility in Binary Solvents—The following two equations for solubility in systems of nonspecific interactions were developed from the general equation (3), depending on whether a regular solution model (Eq. 1) or Flory–Huggins model (Eq. 2) is used:

$$RT \ln(a_s^{solid}/X_s^{sat}) = (1 - \Phi_s^{sat})^2[\Phi_1^0(\Delta\overline{G}^e_{s\dot{X}_1^0=1} + \Phi_2^0(\Delta\overline{G}^e_s)_{\dot{X}_2^0=1} - \overline{V}_s(X_1^0\overline{V}_1 + X_2^0\overline{V}_2)^{-1}(\Delta\overline{G}^e_{12})] \quad \text{(Eq. 1)}$$

$$RT\left[\ln(a_s^{solid}/\Phi_s^{sat}) - (1 - \Phi_s^{sat})\left(1 - \frac{\overline{V}_s}{(X_1^0\overline{V}_1 + X_2^0\overline{V}_2)}\right)\right] = (1 - \Phi_s^{sat})^2[\Phi_1^0(\Delta\overline{G}^{f/h}_s)^*_{\dot{X}_1^0=1} + \Phi_2^0(\Delta\overline{G}^{f/h}_s)^*_{\dot{X}_2^0=1} - \overline{V}_s(X_1^0\overline{V}_1 + X_2^0\overline{V}_2)^{-1}(\Delta\overline{G}^{f/h}_{12})] \quad \text{(Eq. 2)}$$

in which $\overline{V}_i$ is the molar volume of a pure liquid, X_i is the mole fraction, Φ_i is the volume fraction, $\Delta\overline{G}^e_{12}$ is the molar excess Gibbs free energy of the mixed solvent, and:

$$\Delta\overline{G}^{f/h}_{12} = \Delta\overline{G}^e_{12} + RT[\ln(X_1^0\overline{V}_1 + X_2^0V_2) - X_1^0\ln(\overline{V}_1) - X_2^0\ln(\overline{V}_2)] \quad \text{(Eq. 3)}$$

The superscript (0) indicates that the solvent mole fraction or volume fraction is calculated as if the solute were not present. The activity of the solid solute (a_s^{solid}), relative to the supercooled liquid (also equal to the mole fraction solubility in an ideal solution), can be calculated from the melting point (T_m) and the molar enthalpy of fusion (ΔH_s^{fus}):

$$\ln(a_s^{solid}) = \int_{T_m}^{T} (\Delta H_s^{fus}/RT^2)\, dT \quad \text{(Eq. 4)}$$

The use of these equations for solubility predictions in mixed solvents is as follows. The quantities $(\Delta\overline{G}^e_s)^*_{\dot{X}_i^0=1}$ or $(\Delta\overline{G}^{f/h}_s)^*_{\dot{X}_i^0=1}$ are calculated from the mole fraction or volume fraction solubility of the solute in the pure solvents (the asterisk indicates that these are approximations of infinite dilution properties). Then these properties are used in the appropriate equation to calculate the solubility as X_s^{sat} or Φ_s^{sat} in a solvent mixture, using a reiterative process. The quantity $(1 - \Phi_s^{sat})$ is taken as unity in

Table III—Solubility of *m*-Toluic Acid in Cyclohexane (1) + *n*-Hexane at 25°

X_1^0	$10^2\ X_s^{sat}$	Percent Deviation (Monomer Model), Eq. 1 or 2	Percent Deviation (Dimer Model) Eq. 1	Eq. 2
0.2380	1.27	−4.3	−2.0	−1.7
0.4028	1.33	−6.4	−3.0	−2.6
0.6121	1.37	−7.2	−3.3	−2.8
0.8239	1.36	−5.6	−2.8	−2.5

Table IV—Solubility of Benzoic Acid in Ternary Solvents at 25.0°: Comparison of Predictions of the Dimer Model in Eqs. 13 and 14

Solvent 1	Solvent 2	Solvent 3	X_1^0	X_2^0	$10^2 X_s^{sat}$	Percent Deviation (Dimer Model) Eq. 13	Eq. 14
CCl_4	c-C_6H_{12}	n-C_6H_{14}	0.1109	0.4951	1.37	−1.5	−1.2
			0.2099	0.1836	1.50	−2.5	−2.0
			0.1903	0.6665	1.58	−2.2	−1.9
			0.3084	0.3713	1.86	−1.2	−3.3
			0.4225	0.4807	2.27	−4.4	−4.3
			0.5273	0.1011	2.49	−4.0	−3.2
			0.6766	0.1774	3.20	−2.9	−1.6
CCl_4	c-C_6H_{12}	n-C_7H_{16}	0.1144	0.5450	1.41	−1.3	+0.8
			0.1891	0.2337	1.54	−2.1	−1.1
			0.1795	0.6927	1.56	−2.6	−2.1
			0.2216	0.1952	1.60	−1.8	−0.8
			0.3205	0.3927	1.90	−2.8	−1.8
			0.4754	0.4457	2.43	−3.6	−3.2
			0.5426	0.0991	2.55	−4.1	−2.8
			0.6973	0.1740	3.26	−2.6	−1.9

the first approximation, and convergence is rapid unless the solubility is quite large.

Applications of the monomer and dimer models to these equations are straightforward, taking the molecular weight, molar volume, and molar enthalpy of fusion of the dimer to be exactly twice the values for the monomer[1], and lead to the relationships:

$$(a_{ss}^{solid}) = (a_s^{solid})^2, \; ss = \text{dimer} \qquad \text{(Eq. 5)}$$

$$X_{ss}^{sat} = X_s^{sat}/(2 - X_s^{sat}) \qquad \text{(Eq. 6)}$$

$$\bar{V}_{ss} = 2\bar{V}_s \qquad \text{(Eq. 7)}$$

$$\Phi_{ss}^{sat} = \Phi_s^{sat} \qquad \text{(Eq. 8)}$$

Activities and molar volumes used in these calculations are given in Table V. The same molar volumes are used for calculations at 25 and 30° since, in the original equations, molar volumes are used as approximations of temperature-independent parameters. The major difference between the monomer and dimer models appears to be due to the different values calculated for the activity of the solid; while important for absolute predictions of solubilities, this effect is relatively unimportant for predictions of solubility in mixed solvents from values in pure solvents. For example, the predictions of Eqs. 1 and 2 are completely independent of the value assigned to the activity of the solid for solutes of very low solubility. The important difference between these models is in the ratio of the molar volume of the solute to that of the solvent, operating on the excess free energy of solvent mixing.

The results of calculations with monomer and dimer models in Eqs. 1 and 2 are given in Tables II and III as percentage deviations between calculated and observed values. The dimer model is definitely superior to the monomer model, and Eq. 2 is slightly more accurate than Eq. 1 for benzoic acid and *m*-toluic acid in these systems. While none of these models gives predictions within experimental uncertainty for these solutes, the accuracy of the dimer model is comparable to that of the monomer model for solutes such as iodine, naphthalene, and benzil, which are not considered to be capable of self-association. The limitation here appears to be due to the very simple solution model on which the equations are based rather than on the exact description of the chemical species in solution. The monomer model, however, is such a poor description of the real condition of carboxylic acid solutions that predictions are limited by the accuracy of the description.

Solubility in Multicomponent Solvents—Rigorous development of the multicomponent forms of Eqs. 1 and 2 from the original model (3) leads to equations containing the excess free energy ($\Delta\bar{G}_1^e \ldots N$) of the multicomponent system. Since data of this type are available for very few ternary systems and fewer systems of higher order, an approximation is necessary. The following equations, based on the original model, give very good predictions for simple multicomponent systems (13):

$$(\Delta\bar{G}_1^e \ldots N) = \sum_{i=1}^{N-1} \sum_{j>i}^{N} (X_i^0 + X_j^0)(\Phi_i^0 + \Phi_j^0)(\Delta\bar{G}_{ij}^e)^* \qquad \text{(Eq. 9)}$$

$$(\Delta\bar{G}_1^{fh} \ldots N) = \sum_{i=1}^{N-1} \sum_{ji}^{N} (X_i^0 + X_j^0)(\Phi_i^0 + \Phi_j^0)(\Delta\bar{G}_{ij}^{fh})^* \qquad \text{(Eq. 10)}$$

with:

$$X_i^* = X_i^0/(X_i^0 + X_j^0) \, . \qquad \text{(Eq. 11)}$$

$$(\Delta\bar{G}_{ij}^{fh})^* = (\Delta\bar{G}_{ij}^e)^* + RT[\ln(X_i^*\bar{V}_i + X_j^*\bar{V}_j) - X_i^*\ln(\bar{V}_i) - X_j^*\ln(\bar{V}_j)] \qquad \text{(Eq. 12)}$$

and $(\Delta\bar{G}_{ij}^e)^*$ is the excess Gibbs free energy of the binary solvent mixture at composition X_i^*. The solubility equations for a solid solute then become:

$$RT\ln(a_s^{solid}/X_s^{sat}) = (1 - \Phi_s^{sat})^2 \left[\sum_{i=1}^{N} \Phi_i^0(\Delta\bar{G}_s^e)_{\dot{X}_i^0=1} - (\bar{V}_s/\bar{V}_m)(\Delta\bar{G}_1^e \ldots N)\right] \qquad \text{(Eq. 13)}$$

and:

$$RT\left[\ln(a_s^{solid}/\Phi_s^{sat}) - (1 - \Phi_s^{sat})\left(1 - \frac{V_s}{\bar{V}_m}\right)\right] = (1 - \Phi_s^{sat})^2 \times \left[\sum_{i=1}^{N} \Phi_i^0(\Delta\bar{G}_s^{fh})_{X_i^0=1} - (\bar{V}_s/\bar{V}_m)(\Delta\bar{G}_1^{fh} \ldots N)\right] \qquad \text{(Eq. 14)}$$

with:

$$\bar{V}_m = \sum_{i=1}^{N} X_i^0\bar{V}_i \qquad \text{(Eq. 15)}$$

These equations, while unfortunately rather complex, are rigorous within the model and are easily adaptable to computerized calculations. An important feature of Eqs. 9 and 10 is the ability to use binary data in any form, independent of the form of the equation by which the binary data may be represented. As previously noted (4), the contribution of the binary or multicomponent mixing term may be negligible if the system is nearly ideal and the molar volume of the solute is small in comparison

Table V—Solvent and Solute Properties Used in Calculations

	Temperature	a_i^{solid}	$\bar{V}_i$, cm³/mole
Solute			
Benzoic acid (monomer)	25°	0.2275[a]	104.38[a]
	30°	0.2468[a]	104.38
Benzoic acid (dimer)	25°	0.0518	208.76
	30°	0.0609	208.76
m-Toluic acid (monomer)	25°	0.2489[b]	121.8[c]
m-Toluic acid (dimer)	25°	0.0620	243.6
Solvent			
Carbon tetrachloride	—	—	97.08
Cyclohexane	—	—	108.76
n-Hexane	—	—	131.57
n-Heptane	—	—	147.48
Solvent Mixture		$(\Delta\bar{G}_{12}^e)^d$	
c-C_6H_{12} + CCl_4		Ref. 17	
n-C_6H_{14} + CCl_4		Ref. 18	
n-C_7H_{16} + CCl_4		Ref. 19	
c-C_6H_{12} + n-C_6H_{14}		Ref. 20	
c-C_6H_{12} + n-C_7H_{16}		Ref. 21	

[a] Reference 22. [b] Estimated from data in Ref. 10. [c] Estimated by approximating the difference between the molar volumes of *m*-toluic acid and benzoic acid as the difference between toluene and benzene. [d] The excess Gibbs free energy was assumed to be the same at 25 and 30°.

[1] The enthalpy of fusion is actually for the transition of the solid to a mixture of monomers and dimers; but for consistency in these calculations, the melt is considered to be completely monomeric for the monomer model and completely dimeric for the dimer model.

to the solvents. Large solute molecules magnify the contribution of the unmixing term and, in the application to multicomponent solvents, also magnify the errors in the approximations of Eqs. 9 and 10. Thus, Eqs. 13 and 14 can be expected to become increasingly less accurate with increasing complexity of the solvent mixture. For the simple ternary solvents studied, the dimer model predicts solubilities of benzoic acid as accurately as in binary solvents. The results of calculations with the monomer model are not shown since they were very similar to results for binary systems and considerably less accurate than those of the dimer model.

The authors have serious doubts about the applicability of these equations to the solubility of benzoic acids in mixtures of aromatic and aliphatic solvents, partly because of the possible existence of trimers in aromatic solvents. Of more concern, however, is the possibility of specific $\pi-\pi$ interactions between the solvent and solute, which would violate the basic assumptions of the NIBS model.

CONCLUSIONS

The dimer model of the nearly ideal binary solvent equation gives very good predictions for the solubility of benzoic and *m*-toluic acids in these simple solvent mixtures and should be equally applicable to solubilities of most monofunctional carboxylic acids in multicomponent systems of nonspecific solvent–solvent and solvent–solute interactions. The solubility of solid phenol in systems of this type is expected to obey similar equations based on a trimer model (14), but the solubility of gaseous phenol at high dilution (or the Henry's law constant) should be best described by a monomer model. Extraction equilibria present an interesting case in that the appropriate model may depend on the concentration range studied.

The nearly ideal binary solvent equations cannot be rigorously developed for liquid–liquid extraction in systems of practical importance because of the thermodynamic complexity of these systems, but equations developed for idealized systems may have some practical applicability. The simplest system of this type involves the distribution of a solute between two completely immiscible liquid phases, one phase consisting of a mixture of solvents and a reference phase in which the activity coefficient of the solute may be expected to remain fairly constant over the concentration range studied. For solutions sufficiently dilute to allow approximation of $(1 - \Phi_s)$ as unity, Eq. 2 becomes:

$$\ln(K_s)_m = \sum_{i=1}^{N} \Phi_i^0 \ln(K_s)_{X_i^0=1} + (\overline{V}_s/\overline{V}_m)(RT)^{-1}(\Delta\overline{G}_1^{fh} \ldots N) \qquad \text{(Eq. 16)}$$

with the distribution coefficient (K_s) based on molar (moles per liter) concentrations (C_s):

$$(K_s)_m = (C_s)_m/(C_s)_{\text{reference}} \qquad \text{(Eq. 17)}$$

The distribution of benzoic acid between water (reference) and mixtures of inert solvents should be best described by a dimer model ($\overline{V}$ = 209 cm^3/mole) at high concentrations and by a monomer model ($\overline{V}_s$ = 104 cm^3/mole) in very dilute solutions. Experiments are being conducted to determine whether the presence of water in the organic phase interferes with these predictions.

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