Previously (*1*) we found that the molar excess enthalpies of the present systems could be correlated satisfactorily by the Flory theory (*8*, *9*) using values of the interchange-energy parameter, X_{12}, given by the equation

$$X_{12}/(\mathrm{J\ cm^{-3}}) = 8.700 + 0.3487n - 0.02089n^2 \qquad (3)$$

where n is the number of carbon atoms in the alkane molecule. The broken curves in Figure 1 were calculated from the Flory theory with these same values of X_{12}. The necessary values of the characteristic pressures, volumes, and temperatures (p^*, V_m^*, and T^*) for the pure components, along with the ratios s_{12} of ether-to-alkane molecular surface areas of contact per segment, were taken from ref 1 (see Table 4).

As shown in Figure 1, the Flory curves are more skewed toward $x = 1$ than those found experimentally. The theory predicts increasing maxima of V^E followed by successive decreases, although the latter do not occur until after *n*-octane instead of after *n*-heptane as observed. Despite these discrepancies, it appears that the theory provides a reasonable description of the volume behavior of the present systems, bearing in mind that the V^E data were not used in adjusting the parameters.

Literature Cited

(1) Wang, L; Benson, G. C.; Lu, B. C.-Y. *J. Chem. Thermodyn.* **1990**, *22*, 173.
(2) TRC Thermodynamic Tables—Non-Hydrocarbons; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1988; 1963, p a-6040 (loose-leaf data sheet).
(3) Villamañan, M. A.; Casanova, C.; Roux, A. H.; Grolier, J.-P. E. *J. Chem. Thermodyn.* **1982**, *14*, 251.
(4) TRC Thermodynamic Tables—Hydrocarbons; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1988; 1976, p a-1011; 1977, p a-1010 (loose-leaf data sheets).
(5) Takenaka, M.; Tanaka, R.; Murakami, S. *J. Chem. Thermodyn.* **1980**, *12*, 849.
(6) Wang, L.; Benson, G. C.; Lu, B. C.-Y. *J. Chem. Thermodyn.* **1989**, *21*, 147.
(7) Wang, L.; Benson, G. C.; Lu, B. C.-Y. *J. Chem. Thermodyn.* **1988**, *20*, 975.
(8) Flory, P. J. *J. Am. Chem .Soc.* **1965**, *87*, 1833.
(9) Abe, A.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1838.

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Solubility of Naphthalene in Water + Alcohol Solutions at Various Temperatures

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Solubility measurements of naphthalene in water and water + alcohol solutions (methanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol), ranging from 278.15 to 313.15 K, are reported. Thermodynamic functions of transfer and pair Gibbs free energy interaction parameters, g_{NA}, at 298.15 K have been obtained. The solubilities increase with the amount of alcohol in the mixtures. The entropy of transfer governs the sign of the Gibbs free energy of transfer.

Introduction

Solubility measurements of hydrophobic nonelectrolytes in water and aqueous mixed solvents are of interest from a theoretical and practical point of view. This paper continues a study of hydrophobic nonelectrolytes solubilities in aqueous mixed solvents (*1*).

The determination of thermodynamic transfer functions (G, H, and S) of nonelectrolytes from a reference solvent, like water (w), to aqueous mixed solvents (s) can be obtained from solubility measurements (*2*). The standard molar partial Gibbs free energy of transfer for a nonelectrolyte can be determined from eq 2, $\bar{G}_i°$ in eq 1 and a_i in eq 2 are the standard molar partial Gibbs free energy and the activity of the nonelectrolyte i, respectively. If one assumes that the solubilities are low enough to consider the concentrations instead of the activities,

$$\Delta\bar{G}_t°(i) = {}^{s}\bar{G}_i° - {}^{w}\bar{G}_i° \qquad (1)$$

$$\Delta\bar{G}_t°(i) = 2.303RT \log \left(\frac{{}^{w}a_{i(\mathrm{sat.})}}{{}^{s}a_{i(\mathrm{sat.})}}\right) \qquad (2)$$

$$\Delta\bar{G}_t°(i) = 2.303RT \log ({}^{w}c_{i(\mathrm{sat.})}/{}^{s}c_{i(\mathrm{sat.})}) \qquad (3)$$

Entropies of transfer, $\Delta\bar{S}_t°(i)$, are derived from the temperature dependence of the solubility, S, with the equation

$$\Delta\bar{S}_t°(i) = -\left(\frac{\partial\Delta\bar{G}_t°(i)/T}{\partial T}\right)_{P,N} \qquad (4)$$

Enthalpies of transfer, $\Delta\bar{H}_t°(i)$, are obtained by the difference in the equation

$$\Delta\bar{G}_t°(i) = \Delta\bar{H}_t°(i) - T\Delta S_t(i) \qquad (5)$$

In the present paper, we report solubility measurements of naphthalene in water and aqueous solutions of alcohol (methanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol) at various temperatures. From the experimental results, thermodynamic functions of transfer have been obtained.

Experimental Section

Materials. All alcohols used in this work were analysis grade from Merck. Their purity was determined by GC, was better than 99.7 mol % for methanol, 1-propanol, and 2-propanol, and was better than 99.5 mol % for 2-methyl-2-propanol. Naphthalene (Fluka, grade puriss., >99 mol %) was recrystallized from ethanol before use. Water was distilled twice in an all-glass apparatus. The solvents were prepared by mixing weighed quantities of water and alcohol.

Solubility Measurements. In order to obtain saturated solutions of naphthalene in water and mixed solvents, we have used the method described by Canady et al. (*3*). The measurements were made at temperatures ranging between 278.15 and 313.15 K (±0.05 K), except for water + 2-propanol solutions, which were only made at 298.15 K. Samples were analyzed by a spectrophotometric technique using a Perkin-Elmer

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Table I. Solubilities (10^4S/(mol•dm^{-3})) of Naphthalene in Water and Water + Alcohol Solutions at Different Temperatures

$m_{alcohol}$/(mol·kg^{-1})	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Water								
0	1.35	1.58	1.90	2.24	2.63	3.24	3.71	4.36
Water + MeOH								
1.3193	1.62	1.93	2.36	2.96	3.44	4.07	4.62	
2.5165	1.85	2.20	2.82	3.36	3.98	4.92	5.47	
3.8190	2.12	2.68	3.28	3.92	4.95	5.88	6.97	
4.9828	2.63	3.23	4.26	5.25	6.31	7.85	8.71	
6.2146	3.24	4.17	5.46	6.68	8.41	10.85	13.06	
Water + 1-PrOH								
0.9216	1.65	2.04	2.63	3.16	3.98	4.97	5.82	
1.3455	1.99	2.43	3.22	3.89	4.77	5.96	7.02	
1.8501	2.37	3.13	3.70	4.84	6.16	7.49	9.16	
2.3816	3.05	4.21	5.31	6.62	8.28	10.36	12.65	
2.9590	4.57	6.03	7.41	8.32	12.02	14.80	18.62	
Water + 1-BuOH								
0.1631		1.64	2.06	2.44	2.95	3.65	4.26	5.01
0.3478		1.74	2.24	2.79	3.45	4.15	5.03	5.83
0.5507		2.19	2.85	3.45	4.03	4.72	5.71	6.66
0.7166		2.45	3.01	3.53	4.47	5.32	6.12	7.43
Water + *t*-BuOH								
0.3109	1.51	1.82	2.24	2.63	3.16	3.72	4.37	
0.7036	1.80	2.15	2.62	2.97	3.49	4.38	4.98	
1.0122	1.93	2.33	2.95	3.38	4.07	4.95	5.63	
1.3549	2.24	2.69	3.31	3.79	4.67	5.67	6.67	
1.6883	2.50	3.02	3.80	4.47	5.24	6.63	7.63	

Table II. Coefficients and Standard Deviations of log *S* from Equation 1 and Thermodynamic Functions for Transfer of Naphthalene from Water to Water + Alcohol Solutions at 298.15 K

$m_{alcohol}$/(mol·kg^{-1})	A	B/K	C	$10^3\sigma$	$-\Delta\bar{G}_t°(i)$/(kJ·mol^{-1})	$\Delta\bar{H}_t°(i)$/(kJ·mol^{-1})	$\Delta\bar{S}_t°(i)$/(J·K^{-1}·mol^{-1})
Water + MeOH							
1.3193	62.76	4042.0	-9.245	3.1	0.63	0.12	2.5
2.5165	60.83	3996.5	-8.920	3.5	1.03	1.12	7.2
3.8190	21.16	2334.2	-2.922	2.1	1.50	3.51	16.8
4.9828	133.03	7261.5	-19.636	2.7	2.15	2.42	15.4
6.2146	8.81	2002.8	-0.907	2.3	2.89	8.68	38.8
Water + 1-PrOH							
0.9216	4.40	1698.4	-0.369	2.5	0.99	5.93	23.2
1.3455	35.49	3054.5	-5.514	2.9	1.47	5.36	22.9
1.8501	-4.97	1356.3	1.107	3.6	2.03	7.81	33.0
2.3816	77.95	5030.1	-11.261	2.8	2.85	7.53	34.8
2.9590	8.43	1982.5	-0.825	1.4	3.73	8.76	41.9
Water + 1-BuOH							
0.1631	30.53	2735.9	-4.366	2.1	0.30	2.98	11.0
0.3478	117.01	6677.5	-17.214	0.9	0.65	5.10	19.3
0.5507	75.23	4676.2	-11.046	3.3	1.06	1.98	10.2
0.7166	6.08	1628.8	-0.698	2.8	1.24	2.69	13.2
Water + *t*-BuOH							
0.3109	25.81	2405.6	-3.728	1.5	0.43	0.28	2.4
0.7036	-41.05	-563.0	6.269	3.6	0.75	0.50	4.2
1.0122	37.95	2957.0	-5.514	2.8	1.08	0.65	5.8
1.3549	-56.31	-1160.7	8.614	2.4	1.40	2.45	12.9
1.6883	-21.23	377.6	3.374	3.1	1.72	2.01	12.5
Water							
	-31.24	-143.5	4.772	1.1			

Lambda 5 spectrophotometer. In order to restrict the absorbance values within the range of Beer's law, the aliquots were removed and diluted at 82% alcohol by volume prior to their quantification. In the case of water + 1-butanol, the dilution was made with ethanol because of the low solubility of 1-butanol in water. Readings were made at 275.0 nm (ϵ = 4680/(dm^3·mol^{-1}·cm^{-1})), 275.4 nm (ϵ = 5320/(dm^3·mol^{-1}·cm^{-1})), 274.2 nm (ϵ = 5386/(dm^3·mol^{-1}·cm^{-1})), 275.3 nm (ϵ = 5189/(dm^3·mol^{-1}·cm^{-1})), 274.8 nm (ϵ = 5304/(dm^3·mol^{-1}·cm^{-1})), and 275.0 nm (ϵ = 5562/(dm^3·mol^{-1}·cm^{-1})) for water, water + methanol, water + 1-propanol, water + 2-propanol, water + 2-methyl-2-propanol, and water + 1-butanol, respectively. The maximum uncertainties in the solubility measurements were ±2%. At 298.15 K, the solubility of naphthalene in water was 2.63 × 10^{-4} mol·dm^{-3}. This value is in agreement with the findings of Bohon and Claussen (*4*), 2.68 × 10^{-4} mol·dm^{-3}, and Gordon and Thorne (*5*), 2.61 × 10^{-4} mol·dm^{-3}. However, Canady (*3*) and Schwarz (*6*) obtained lower values, 2.43 × 10^{-4} and 2.36 × 10^{-4} mol·dm^{-3}, respectively.

Results and Discussion

The solubilities of naphthalene (molar concentration scale) in pure water and aqueous solutions of alcohols at the tempera-

Table III. Pair Gibbs Free Energy Interaction Parameters between Naphthalene and Alcohol in Water at 298.15 K

	MeOH	1-PrOH	2-PrOH	1-BuOH	*t*-BuOH
g_{NA}/(J·kg·mol^{-2})	-176	-483	-314	-900	-558

tures of the experiment are given in Table I.

The variation of the solubility, *S*, with the temperature, *T*, was fitted by a nonlinear regression analysis (*7*) to an equation of this form

$$\log (S/(\text{mol·dm}^{-3})) = A - B/T + C \ln T \qquad (6)$$

where *T* is the Kelvin temperature and *A*, *B*, and *C* are adjustable parameters listed in Table II along with the standard deviation, σ, of the fit.

The standard thermodynamic functions, accompanying the transfer of naphthalene from the standard state in water, w, to the standard state in the water + alcohol solutions, s, were obtained at 298.15 K with the following equations:

$$\Delta\bar{G}_t^\circ(i) = -2.303RT \log ({}^{s}s_i/{}^{w}s_i) = -2.303R[(A_s - A_w)T + (B_w - B_s) + (C_s - C_w)T \ln T] \qquad (7)$$

$$\Delta\bar{S}_t^\circ(i) = 2.303R[(A_s - A_w)T + (C_s - C_w) + (C_s - C_w) \ln T] \qquad (8)$$

$$\Delta\bar{H}_t^\circ(i) = 2.303R[(B_s - B_w) + (C_s - C_w)T] \qquad (9)$$

Table II is devoted to the corresponding values of $\Delta\bar{G}_t^\circ(i)$, $\Delta\bar{H}_t^\circ(i)$, and $\Delta\bar{S}_t^\circ(i)$.

The solubility of naphthalene increases with the proporation of the organic compound in the solvent mixture. Such behavior has already been observed for other nonelectrolytes in aquo-organic mixtures (*2*, *8*–*12*).

The favorable increase of $\Delta\bar{G}_t^\circ(i)$ from methanol to 1-butanol may be explained by taking into consideration the combined action of two factors, van der Waals dispersive forces and hydrophobic interactions between naphthalene and the alkyl group of alcohol. Both interactions are expected to grow stronger as the size of the alkyl group of alcohol increases. On the other hand, enthalpic terms, $\Delta\bar{H}_t^\circ(i)$, are compensated by a still larger contribution from entropic terms, $T\Delta\bar{S}_t^\circ(i)$. This pattern is characteristic when hydrophobic interactions are involved, i.e., the entropy-controlled nature of the process.

During recent years, a great number of papers have focused on the molecular pair interaction parameters according to the McMillan–Mayer approach (*13*–*18*). We have calculated the corresponding pair Gibbs free energy interaction parameter for naphthalene (N) and alcohol (A) in water, g_{NA}, using Gibbs free energies of transfer. Following Perron and Desnoyers (*19*), for a ternary system, the equation to obtain g_{NA} is

$$\Delta\bar{G}_t^\circ(i)/m = 2g_{NA} + 3g_{NA}m + \ldots \qquad (10)$$

From plots of $\Delta\bar{G}_t^\circ(i)/m$ against *m*, where *m* is the variable molality of alcohol, g_{NA} can be obtained. Such plots are shown in Figure 1, and the corresponding values of g_{NA} are summarized in Table III. The g_{NA} shows itself related to alcohol size, and the differences between pairs are therefore significant. The marked difference in g_{NA} between 1-butanol and 2-methyl-2-propanol could be explained by the stereochemistry of 2-methyl-2-propanol compared to that of 1-butanol. The former has a lack of conformational freedom to interact optimally with naphthalene (*20*). To confirm the above fact, we have determined the solubilities of naphthalene in aqueous solutions of 2-propanol, and then they were calculated to the corresponding $\Delta\bar{G}_t^\circ(i)$ (Table IV). From Table III, it can be seen that the difference in g_{NA} between 1-propanol and 2-propanol is significant as in the case of the two butanols although it is not great.

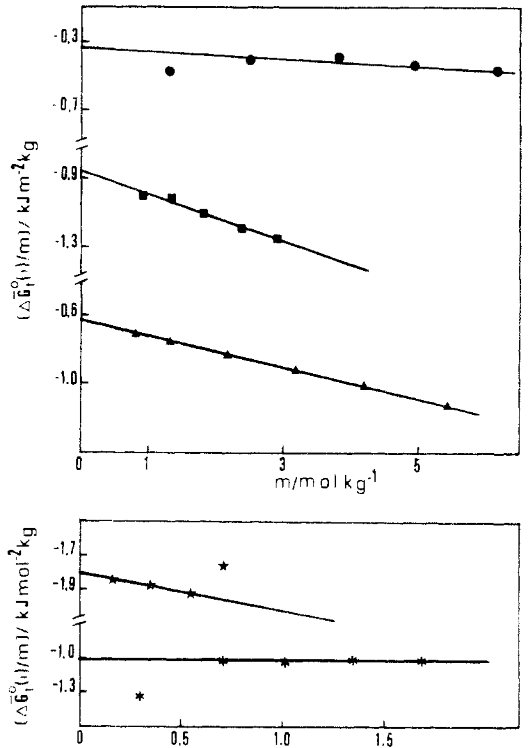

Figure 1. Plots of $\Delta\bar{G}_t^\circ(i)/m$ against alcohol molality, *m*, for water + MeOH (●), water + 1-PrOH (■), water + 2-PrOH (▲), water + 1-BuOH (★), and water + *t*-BuOH (*) solutions at 298.15 K.

Table IV. Solubilities and Standard Gibbs Free Energies of Transfer of Naphthalene from Water to Water + 2-Propanol Solutions at 298.15 K

m/(mol·kg^{-1})	0.8048	1.3426	2.2018	3.1835	4.1928	5.4363
10^4S/(mol·dm^{-3})	3.31	3.93	5.48	8.51	14.50	30.60
$-\Delta\bar{G}_t^\circ(i)$/(kJ·mol^{-1})	0.57	0.99	1.82	2.91	4.23	6.08

Registry No. MeOH, 67-56-1; 1-PrOH, 71-23-8; 2-PrOH, 67-63-0; 1-BuOH, 71-36-3; *t*-BuOH, 75-65-0; naphthalene, 91-20-3.

Literature Cited

(1) Pérez Camino, M. C.; Sánchez, E.; Balón, M.; Maestre, A. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1555.
(2) Popovych, O.; Tomkins, R. P. T. *Nonaqueous Solution Chemistry*; Wiley: New York, 1981; Chapter 5.
(3) Bennet, D.; Canady, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 910.
(4) Bohon, R. L.; Claussen, W. J. *J. Chem. Soc.* **1951**, *73*, 1571.
(5) Gordon, J. E.; Thorne, R. L. *J. Phys. Chem.* **1967**, *71*, 4390.
(6) Schwarz, F. P. *J. Chem. Eng. Data* **1977**, *22*, 273.
(7) Johnson, K. J. *Numerical Methods in Chemistry*; Dekker: New York, 1980; Chapter 5.
(8) Bose, K.; Kundu, K. K. *Can. J. Chem.* **1977**, *55*, 3961.
(9) Das, K.; Das, A. K.; Bose, K.; Kundu, K. K. *J. Phys. Chem.* **1976**, *82*, 1242.
(10) Veda, M.; Katayama, A.; Urahata, T.; Kuroki, N. *Kagaku to Kogyo (Osaka)* **1980**, *54*, 252.
(11) Chebib, H.; Jambon, C.; Merlin, J. C. *J. Chim. Phys.* **1982**, *79*, 259.
(12) Brisset, J. L. *J. Chem. Eng. Data* **1985**, *30*, 381.
(13) de Visser, C.; Perron, G.; Desnoyers, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 5894.
(14) McMillan, W.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 176.
(15) Kozak, J. J.; Knight, W. S.; Kauzmann, W. *J. Chem. Phys.* **1968**, *48*, 675.
(16) Clark, A. H.; Franks, F.; Pedley, M.; Reid, D. S. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 290.
(17) Perron, G.; Joly, D.; Desnoyers, J. E.; Avedikian, L.; Morel, J. P. *Can. J. Chem.* **1978**, *56*, 552.
(18) Desnoyers, J. E.; Perron, G.; Avedikian, L.; Morel, J. P. *J. Solution Chem.* **1976**, *5*, 631.
(19) Perron, G.; Desnoyers, J. E. *J. Chem. Thermodyn.* **1981**, *13*, 1105.
(20) Franks, F.; Pedley, M.; Reid, S. D. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 359.

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