Values of the coefficients were obtained by fitting data from the literature (5, 7-9) or, in the case of B_{12}, from estimates by the method of Hayden and O'Connell (10). The coefficients for eq 9 are also listed in Table II.

Values of the parameters Δg_{21}, Δg_{12}, and α_{12} were selected to minimize the object function

$$\Phi = \sum_{j=1}^{21} \{ W_y [y_1(\text{exptl}) - y_1(\text{calcd})]^2 + W_t [t(\text{exptl}) - t(\text{calcd})]_j^2 \} \quad (10)$$

where the sum was taken over the 21 mixture compositions. The relative weights W_y and W_t were assigned proportional to the inverse squares of the error estimates $\epsilon(y_1)$ and $\epsilon(t)$. In order to obtain a reasonable fit of the results, it was necessary to consider Δg_{21} and Δg_{12} to be functions of t. A quadratic form in t was assumed for each of these. Minimization of Φ with respect to the seven parameters yielded

$$\Delta g_{21}/(\text{J·mol}^{-1}) = 2959.18 - 25.462(t/^\circ\text{C}) + 0.00517(t/^\circ\text{C})^2 \quad (11)$$

$$\Delta g_{12}/(\text{J·mol}^{-1}) = -1197.45 + 90.471(t/^\circ\text{C}) + 1.9536(t/^\circ\text{C})^2 \quad (12)$$

$$\alpha_{12} = 1.3213 \quad (13)$$

Deviations of the calculated values of y_1 and t from the experimental results are listed in Table I. The corresponding standard deviations are $\sigma_y = 0.0067$ and $\sigma_t = 0.05\,^\circ\text{C}$. Curves of $t(\text{calcd})$ against x_1 and against $y_1(\text{calcd})$ are plotted in Figure 1. These show that the NRTL theory with the parameters given by eqs 11-13 provides a good correlation of the experimental data.

Glossary

A,B,C	coefficients in Antoine and quadratic forms, eqs 8 and 9
B_{ii}	molar second virial coefficient of pure component i, cm^3/mol
B_{12}	cross molar second virial coefficient, cm^3/mol
P_i°	vapor pressure of pure component i, Torr
Q	quadratic function, eq 9
R	molar gas constant, 8.314 51 J K^{-1} mol^{-1}
T	thermodynamic temperature, K
t	Celsius temperature, $^\circ$C
V_i°	molar volume of pure liquid i, cm^3/mol
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapor
$\alpha_{12}, \Delta g_{21}, \Delta g_{12}$	NRTL parameters, eqs 3, 4, and 11-13
γ_i	activity coefficient of component i in liquid
ϵ	estimated experimental uncertainty
σ_q	standard deviation of q, defined by $\sigma_q = \{\sum [q(\text{calcd}) - q(\text{exptl})]^2/m\}^{1/2}$ where the sum is taken over the set of m experimental measurements

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Excess Volumes for Binary Mixtures of n-Butyl Methyl Ether with n-Alkanes at 298.15 K

Luo Wang, George C. Benson,* and Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Excess volumes, obtained from density measurements at 298.15 K, are reported for binary mixtures of n-butyl methyl ether ($C_4H_9OCH_3$) with the n-alkanes (C_nH_{2n+2}, n = 6, 7, 8, 10, 12, and 16). The results are compared with values calculated from the Flory theory with use of interchange-energy parameters derived from a previous analysis of excess enthalpy data.

Introduction

A recent paper (1) from our laboratory reported measurements of excess enthalpies for mixtures of n-butyl methyl ether (BME) with each of the alkanes: n-hexane, n-heptane, n-octane, n-decane, n-dodecane, and n-hexadecane. As an extension of that investigation, we have determined excess volumes for the same set of binary mixtures.

Experimental Section

Sources of the component liquids and their densities measured at 298.15 K in an Anton Paar densimeter (Model DMA 02C) are listed in Table I, where densities from the literature (2-4) are given for comparison. In all cases, the manufacturers' specifications indicated purities of at least 99 mol %. Apart from storing the BME over Type 4A molecular-sieve beads, the component liquids were used without further purification.

Mixtures were prepared by weighing in onion cells (5), specially designed to minimize evaporation effects. The error in the mole fraction is estimated to be less than 1×10^{-4}. Excess molar volumes, V^E, were calculated from densities measured

Table I. Sources and Densities, ρ, of the Component Liquids at 298.15 K

		$\rho/(\text{kg m}^{-3})$		
component	source	obsd	lit.	
BME	Aldrich Chemical Co.	742.20	739.3[a]	744.1[b]
C_6H_{14}	Phillips Petroleum Co. (Research Grade)	655.11	654.84[c]	
C_7H_{16}	Phillips Petroleum Co. (Pure Grade)	679.77	679.46[c]	
C_8H_{18}	Phillips Petroleum Co. (Pure Grade)	699.41	698.62[c]	
$C_{10}H_{22}$	Phillips Petroleum Co. (Pure Grade)	726.25	726.35[c]	
$C_{12}H_{26}$	Phillips Petroleum Co. (Pure Grade)	745.42	745.18[c]	
$C_{16}H_{34}$	Aldrich Chemical Co.	770.14	769.94[c]	

[a] Reference 2. [b] Reference 3. [c] Reference 4.

Table II. Experimental Results for the Molar Excess Volumes, V^E, of n-Butyl Methyl Ether + n-Alkane (C_nH_{2n+2}) Mixtures as a Function of the Mole Fraction, x, of Ether

| x	$V^E/(\text{cm}^3 \text{mol}^{-1})$	x	$V^E/(\text{cm}^3 \text{mol}^{-1})$	x	$V^E/(\text{cm}^3 \text{mol}^{-1})$
		$n = 6$			
0.0500	0.0645	0.2990	0.2619	0.6990	0.2420
0.0991	0.1184	0.3995	0.2955	0.7995	0.1830
0.1495	0.1653	0.5020	0.3031	0.8997	0.0991
0.1995	0.2045	0.6001	0.2855	0.9494	0.0495
		$n = 7$			
0.1002	0.1421	0.4043	0.3370	0.6996	0.2844
0.1500	0.1906	0.5013	0.3453	0.8493	0.1670
0.2036	0.2358	0.5992	0.3287	0.8989	0.1115
0.3003	0.2977				
		$n = 8$			
0.0498	0.0566	0.3998	0.3051	0.7999	0.2145
0.0997	0.1076	0.4995	0.3239	0.8966	0.1205
0.1500	0.1571	0.5999	0.3160	0.9470	0.0616
0.2995	0.2625	0.6990	0.2808		
		$n = 10$			
0.0500	0.0441	0.3009	0.2330	0.6992	0.2655
0.0997	0.0893	0.4007	0.2725	0.7991	0.2112
0.1499	0.1280	0.4991	0.2927	0.8992	0.1227
0.1995	0.1688	0.6000	0.2907		
		$n = 12$			
0.0519	0.0349	0.2995	0.1874	0.6999	0.2315
0.1002	0.0722	0.3993	0.2257	0.7994	0.1908
0.1502	0.1048	0.4992	0.2463	0.8991	0.1154
0.2001	0.1349	0.6008	0.2509	0.9493	0.0624
		$n = 16$			
0.0510	0.0254	0.3066	0.1191	0.6991	0.1252
0.0998	0.0449	0.3993	0.1372	0.7996	0.0999
0.1490	0.0678	0.5000	0.1468	0.8992	0.0617
0.1992	0.0877	0.6002	0.1404	0.9504	0.0354

at 298.150 ± 0.003 K in a Sodev vibrating-tube densimeter (Model 02D) operated in a static mode (5). For each system, the calibration of the densimeter was based on measurements using the pure liquids, together with their densities, as given in Table I. The error in V^E is estimated to be less than 5×10^{-4} $\text{cm}^3 \text{mol}^{-1}$.

Results and Discussion

The experimental values of V^E are listed in Table II and plotted in Figure 1. In all cases, x is the mole fraction of BME. The smoothing equation

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x(1 - x)\sum_{j=1}^{m} v_j(1 - 2x)^{j-1} \qquad (1)$$

was fitted to each set of results by the method of least squares
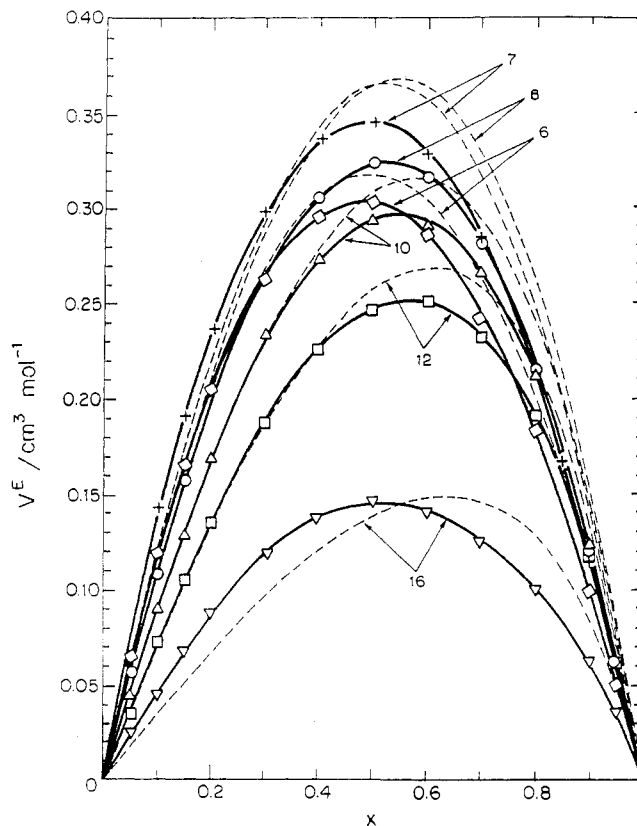
Figure 1. Molar excess volumes, V^E, of n-butyl methyl ether + n-alkane (C_nH_{2n+2}) mixtures as a function of the mole fraction, x, of ether at 298.15 K. Points, experimental results: ($\Diamond$) $n = 6$; (+) $n = 7$; (O) $n = 8$; ($\triangle$) $n = 10$; ($\square$) $n = 12$; (∇) $n = 16$. Curves: (—) calculated from eq 1 with coefficients from Table III; (- -) calculated from the Flory theory with X_{12} from eq 3 (curves labeled with values of n).

Table III. Coefficients v_j, Equation 1, and Standard Deviations s, Equations 2, for Least-Squares Representations of V^E for n-Butyl Methyl Ether + n-Alkane (C_nH_{2n+2}) Mixtures at 298.15 K

n	v_1	v_2	v_3	v_4	v_5	s
6	1.2089	0.1023	-0.0061	0.0675		0.0014
7	1.3817	0.0407	0.0267	0.2338		0.0019
8	1.2929	-0.1225	0.0476	0.1117	-0.1791	0.0009
10	1.1765	-0.2162				0.0021
12	0.9892	-0.2541	0.0648	-0.0766		0.0013
16	0.5825	-0.0213	-0.0405	-0.1292	0.1132	0.0011

with all points weighted equally. For these representations, Table III lists values of the coefficients, v_j, and the standard deviations, s, defined by

$$s/(\text{cm}^3 \text{mol}^{-1}) = \left\{\sum_{i=1}^{p} [V^E(\text{expt}) - V^E(\text{eq 1})]_i^2/(p - m)\right\}^{1/2} \qquad (2)$$

where p is the number of experimental points in the particular set. Curves calculated from eq 1 are shown in Figure 1.

V^E is positive at all mole fractions. Some of the curves in Figure 1 cross, having maxima that increase and then decrease in the order

n-hexane < n-heptane > n-octane > n-decane > n-dodecane > n-hexadecane
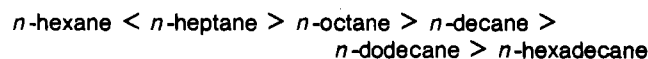
This is in contrast to the molar excess enthalpies (1), which increase successively with increasing size of the n-alkane. Similar behavior has been reported for the molar excess volumes (6) and enthalpies (7) of binary mixtures of di-n-propyl ether with n-alkanes, but the change from increasing to decreasing maxima occurred at a point higher in the n-alkane series.

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

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

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.

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Solubility of Naphthalene in Water + Alcohol Solutions at Various Temperatures

Pilar Pérez-Tejeda, Cayetano Yanes, and Alfredo Maestre*

Departamento de Quimica Fisica, Facultad de Farmacia, 41012 Sevilla, Spain

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, $\bar{G}_i^o$ in eq 1 and a_i in eq 2 are the standard molar

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

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

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,

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

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

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

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

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

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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