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EXCESS ENTHALPIES OF NONAN-1-OL AND UNDECAN-1-OL WITH OCTANE AT HIGH DILUTIONS AND AT 298.15 K

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ABSTRACT

Heats of mixing at high dilutions were determined for binary systems consisting of nonan-1-ol or undecan-1-ol and *n*-octane at 298.15 K. Partial molar heats of mixing at infinite dilution, giving approximate values of hydrogen bonding energies in alcohols, were determined by extrapolation of the experimental data to zero concentrations of the alcohols ($x_1 = 0$).

The results are correlated by means of polynomials, the UNIQUAC and the UNIQUAC associated-solution models. The ability of these equations to represent the thermodynamic functions of dilute mixtures of alkan-1-ols in *n*-alkanes at 298.15 K is discussed.

INTRODUCTION

The thermodynamic properties of alkan-1-ol + *n*-alkane mixtures have long attracted the attention of experimenters. Alcohols are known to form intermolecular H-bonds which are ruptured when the alcohols are mixed with inert solvents such as *n*-alkanes. This effect is particularly important in the dilute alcohol region of such binary mixtures. There have been a number of measurements of the excess volumes, excess enthalpies, excess Gibbs functions and excess isentropic compressibilities of alkan-1-ol + *n*-alkane mixtures [1–11]. Several association models as well as interesting correlations have also been reported [12–17]. From studies [3–6] performed at a constant temperature, it is apparent that for a fixed *n*-alkane the excess molar volume decreases with the increasing number of $-CH_2-$ groups in the homologous series of alkan-1-ols. On the other hand, for a fixed alkan-1-ol, the excess molar volume becomes more positive with the increasing number of $-CH_2-$ groups in successive members of the homologous series of *n*-alkanes. From the measurements of the excess molar enthalpies H_m^E of decan-1-ol + *n*-alkane at 298.15 K [7], a regular increase in the magnitude of

H_m^E was observed as the number of $-CH_2-$ groups in the n-alkanes progressively increased. In a previous work [18] we determined heats of mixing of dilute alcohol solutions of $\{x_1CH_3(CH_2)_nOH + (1 - x_1)CH_3(CH_2)_{h-2}CH_3\}$ at 298.15 K for $n = 8$ and 10 and $h = 6$, 7, 10 and 16.

In this paper, studies of the binary mixtures of the same alkanols in octane were made to add to the previous study, and to make a comparison between the correlated and experimental results of both studies with a well known theory of solutions.

In the calorimetric investigations of solute–solvent interactions, thermodynamic properties are usually discussed in the form of apparent molar values as functions of solution molalities, an unwieldy form for thermodynamic computation. In this paper the results of measurements are correlated by means of polynomials in which molalities are used as concentrated units, and by polynomials and two correlation equations that describe the Gibbs excess free energy of mixing G_m^E: the UNIQUAC [19] and UNIQUAC associated-solution models [20], in which mole fractions are used.

EXPERIMENTAL

Solvents were dried over type 4 Å molecular sieves (SERVA, Heidelberg, F.R.G.) and purified by distillation under lower pressure or by fractional distillation through a 50-plate laboratory column. Specifications of the component liquids are summarised in Table 1.

Calorimetric measurements were made using an LKB 8700 precision calorimetry system with a chart recorder output to which a Sargent recorder (model SRL, S-72180-57) was applied. A description of the system used is given in full detail in ref. 23. The volume of the reaction vessel was 100 cm^3. The measurements were carried out at 298.15 ± 0.05 K. The system was tested by measuring the heat of solution of potassium chloride in water up to 0.04 mol l^{-1} at the same temperature. The value of 17.358 ± 0.062 kJ

TABLE 1

Specifications and densities (ρ) of component liquids at 298.15 K

Component	Specification	ρ (kg m^{-3})	
		Obs.	Lit.
Nonan-1-ol	International Enzymes Ltd. (Windsor, Berkshire, Gt. Britain)	823.84	824.33 [a]
Undecan-1-ol	Fluka AG (Busch SG, Switzerland)	828.98	828.01 [a]
n-Octane	Fluka AG (Busch SG, Switzerland)	698.52	698.62 [b]

[a] Reference 21.

[b] Reference 22.

mol^{-1} determined is close to the value for the heat of solution of potassium chloride given in the work of Somsen et al. [24].

The heat of mixing was determined by the glass ampoule technique. A known amount of alcohol was sealed in a glass ampoule of 1 cm^3 volume. After thermostatting, the ampoule was broken and the alcohol dissolved in 100 cm^3 of pure *n*-octane. The heat absorbed was simultaneously recorded. The densities of the liquid measured at 298.15 K in an Anton–Paar digital densimeter are included in Table 1, along with literature values [21,22] for comparison.

RESULTS AND DISCUSSION

In alkan-1-ol + *n*-alkane mixtures, a number of factors may contribute to the values of the excess functions. Some of these factors are: self-association of the alkanol and the change in the extent and strength of hydrogen bonding with alkanol chain length, orientational order in the *n*-alkanes and its change with chain length, interstitial accommodation of the alkane within the alkanol structure, disruption of the alkanol structure by the alkane molecules, mixing of the alkanol and alkane chains, and the relative size of the component molecules. Each factor makes a positive or negative contribution to the resultant value of the excess function and the magnitude of the contribution is dependent on the mole-fraction range. All the processes investigated may be seen to be endothermic, which means that the predominant factor in the region of high dilution of the alkanol is the disruption of the associated molecules of the alkanol, and in the case of mixtures containing long alkanes, the orientational order in the alkane may also be contributary. Therefore, heats of mixing in the high dilution region are very useful in the interpretation of the thermodynamic properties of solutions [25,26].

The results of the determinations at 298.15 K at atmospheric pressure are shown in Tables 2 and 3 for nonan-1-ol and undecan-1-ol, respectively. The extrapolation of the individual curves of excess enthalpy, $H_{\mathrm{m}}^{\mathrm{E}}/x_1$, to infinite dilution ($x_1 \rightarrow 0$) gives the value of the heat of mixing of 1 mole of alcohol with an infinitely large amount of hydrocarbon: it is equal to the partial molar heat of mixing of the alcohol at infinite dilution. Molecules of an alkan-1-ol in the pure state are bound together by hydrogen bonds which are broken during the transition from the pure state to the infinitely dilute solution. Assuming that in the systems studied the contribution of non-specific interactions is small [27], the value of the partial molar heat of mixing at infinite dilution can be regarded as approximately equal to the hydrogen bond energy in the alcohol [1]. The value of $H_{\mathrm{m}}^{\mathrm{E}}/x_1$ corresponding to this point is 21.9 ± 0.4 kJ mol^{-1}. The hydrogen bond energy similarly evaluated by Savini et al. [28] is 21.8 kJ mol^{-1} for octan-1-ol, by Wóycicka and Rećko [1], 23.4 ± 0.4 kJ mol^{-1} for hexan-1-ol and by Klofutar et al.

TABLE 2

Experimental and UNIQUAC ASM calculated results of the excess molar enthalpies H_m^E of $\{x_1CH_3(CH_2)_8OH+(1-x_1)C_8H_{18}\}$ at 298.15 K

$x_1 \times 10^2$	m_1 (mol kg^{-1})	H_m^E(exp) (J mol^{-1})	H_m^E(cal) (J mol^{-1})
0.1583	0.01388	33.51	33.84
0.2805	0.02462	58.06	58.29
0.4527	0.03981	90.60	90.43
0.5731	0.05046	111.49	111.30
0.6731	0.05932	128.06	127.90
0.7482	0.06600	139.86	139.78
0.8640	0.07630	157.28	157.27
0.8770	0.07743	158.96	159.18

[18], 23.566 ± 154 kJ mol^{-1} for nonan-1-ol and undecan-1-ol. The values of hydrogen-bond formation enthalpy taken from the work of Brandani [29] for several *n*-alcohols at 323.15 K, extrapolated for nonan-1-ol and undecan-1-ol by means of the polynomial are 23.30 and 22.30 kJ mol^{-1}, respectively. The values presented by Brandani [29] are based on the homomorph concept with hydrocarbons as homomorphs.

The relation between the enthalpy of mixing and the concentration H_m^E (m_1), as is similar in the literature [30,31], is presented by

$$H_m^E(m_1) = B_1 m_1 + B_2 m_1^2 + \dots \qquad (1)$$

where m_1 is the molality of solution after dilution, and B_1 and B_2 are two adjustable parameters.

The H_m^E of each mixture can also be expressed as a function of the mole fraction, x_1, of alcohol by a quotient of polynomials

$$H_m^E(x_1) = C_1 x_1 + C_2 x_1^2 + \dots \qquad (2)$$

TABLE 3

Experimental and UNIQUAC ASM calculated results of the excess molar enthalpies H_m^E of $\{x_1CH_3(CH_2)_{10}OH+(1-x_1)C_8H_{18}\}$ at 298.15 K

$x_1 \times 10^2$	m_1 (mol kg^{-1})	H_m^E(exp) (J mol^{-1})	H_m^E(cal) (J mol^{-1})
0.1960	0.01719	41.56	41.45
0.3179	0.02792	64.37	65.33
0.3853	0.03386	78.33	77.95
0.4762	0.04189	94.41	94.34
0.5342	0.04701	104.93	104.42
0.6229	0.05487	119.08	119.30
0.7225	0.06371	135.59	135.25
0.7986	0.07048	146.57	146.92

TABLE 4

Values of the parameters obtained by polynomials, eqns. (1) and (2), and deviations of H_m^E of tested alkanols in octane

Solute	No. of data points	Parameters		Deviations			
		Eqn. (1)	Eqn. (2)	Eqn. (1)		Eqn. (2)	
		B_1 (J kg mol^{-2}) B_2 (J kg^2 mol^{-3})	C_1 (J mol^{-1}) C_2 (J mol^{-1})	σ (J mol^{-1})	σ_R	σ (J mol^{-1})	σ_R
Nonan-1-ol	8	2502.79 −5799.98	21944 −434088	0.09	0.16	0.11	0.19
Undecan-1-ol	8	2504.49 −5984.65	21950 −446827	0.49	0.70	0.49	0.69

where C_1 and C_2 are two adjustable parameters. The values of coefficients B_i and C_i in eqns. (1) and (2) are given in Table 4.

The non-ideality of the system at a given temperature T can be interpreted in terms of the excess thermodynamic functions, i.e. the excess Gibbs free energy G_m^E, the excess enthalpy H_m^E and the excess entropy S_m^E, following the well known UNIQUAC [19] or UNIQUAC ASM (Kretchmer–Wiebe model) [20] models and according to the Gibbs–Helmholtz relation

$$H_m^E = G_m^E - T\left(\partial G_m^E/\partial T\right) \tag{3}$$

The pure component structural parameters r (volume parameter) and q (surface parameter), in the UNIQUAC equations were obtained in accordance with the methods suggested by Vera et al. [32] by means of the following simple relationships taken from Hofman and Nagata [33]

$$r_i = 0.029281\, V_i \tag{4}$$

$$q_i = \left[(Z-2)r_i/Z\right] + \left[2(1-l_i)/Z\right] \tag{5}$$

where V_i is the molar volume of pure component i at 298.15 K, Z is the coordination number, assumed to be 10, and l_i is the bulk factor, accepted as 0.

The comparison was made between predicted and experimental results for nonan-1-ol and undecan-1-ol with n-octane, as well as with other n-hydrocarbons previously studied [18], using UNIQUAC and UNIQUAC ASM. In the calculations, the value of hydrogen-bond formation enthalpy, $h_2 = -23{,}2$ kJ mol^{-1}, was used, this being the average value of the C_1 constant of eqn. (2) in every system studied.

Two measures of the correlation are used: firstly, the root-mean-square deviation of the excess enthalpy, defined by

$$\sigma = \left[\sum_{i=1}^{n}\left(H_m^{E,cal} - H_m^E\right)^2 (n-k)^{-1}\right]^{1/2} \tag{6}$$

where $H_m^{E,cal}$ and H_m^E are the calculated and experimental excess enthalpies of the ith point, n is the number of experimental points and k is the number of adjustable parameters; and secondly, relative root-mean-square deviation, computed according to

$$\sigma_R = 100\left[\sum_{i=1}^{n}\frac{\left(H_m^{E,cal} - H_m^E\right)^2}{H_m^{E2}}(n-k)^{-1}\right]^{1/2} \tag{7}$$

The parameters in the tested relationships were fitted by an optimisation technique. As an objective function, the relative root-mean-square deviations were minimised. The values of the calculated excess enthalpies of alkanols in n-octane of the ith point, computed by UNIQUAC ASM, are shown in Tables 2 and 3.

TABLE 5

Values of the parameters obtained by UNIQUAC and UNIQUAC ASM, and of the root-mean-square deviation[a] of H_m^E and the relative root-mean-square deviation[b] of H_m^E

System	No. of data points	Parameters		K (298.15)	Deviations			
		UNIQUAC	UNIQUAC ASM		UNIQUAC		UNIQUAC ASM	
		Δu_{12} (J mol^{-1}) Δu_{21} (J mol^{-1})	Δu_{12} (J mol^{-1}) Δu_{21} (J mol^{-1})		σ (J mol^{-1})	σ_R	σ (J mol^{-1})	σ_R
Nonan-1-ol								
n-Hexane	9	−1253.31 7678.07	−2208.17 7172.03	7.92	0.31	0.34	0.33	0.36
n-Heptane	10	−1247.56 7595.58	−2203.00 7091.30	7.84	0.93	0.75	0.96	0.79
n-Octane	8	−1135.35 6922.05	−2104.46 6468.80	5.78	0.34	0.33	0.34	0.34
n-Decane	7	−1165.05 7162.25	−2135.70 6565.95	7.78	0.28	0.23	0.31	0.26
n-Hexadecane	10	−1167.20 7475.04	−2157.37 6983.59	7.59	2.46	1.26	2.56	1.31
Undecan-1-ol								
n-Hexane	8	−1353.61 7073.39	−2127.14 6658.60	6.38	0.64	0.63	0.69	0.68
n-Heptane	10	−1352.63 7026.91	−2124.99 6622.15	6.21	0.65	0.69	0.69	0.72
n-Octane	8	−1245.39 6414.60	−2026.55 6033.44	4.80	0.53	0.69	0.57	0.76
n-Decane	7	−1336.15 6910.91	−2111.02 6511.46	6.00	0.47	0.29	0.51	0.32
n-Hexadecane	9	−1464.02 7525.12	−2222.14 7092.36	8.08	1.72	0.75	1.80	0.79

[a] σ is given by eqn. (6).

[b] σ_R is given by eqn. (7).

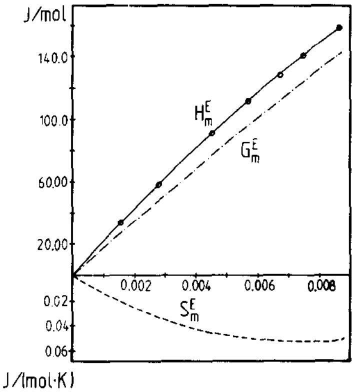

Fig. 1. Excess thermodynamic properties of diluted mixtures of nonan-1-ol with *n*-octane at 298.15 K. Lines are calculated by the UNIQUAC ASM; o, experimental points.

The comparison of the correlation by UNIQUAC equations with two and three adjustable parameters is given in Table 5 in the form of parameters of the equations and the corresponding root-mean-square deviations.

For the ten systems presented in Table 5, the results of the fit obtained by UNIQUAC are similar to those derived by the UNIQUAC ASM theory. All relative deviations are in the range of $\sigma_R = 0.23–1.31$. An association constant *K*(298.15 K), computed by UNIQUAC ASM (adjustable parameter), has values from 5.78 to 7.92 for nonan-1-ol and from 6.00 to 8.08 for undecan-1-ol. Association constants *K* (323.15 K) evaluated by Brandani [29] for several *n*-alcohols and extrapolated for nonan-1-ol and undecan-1-ol are 38.20 and 27.30, respectively. The values presented by Nagata [34] are 32.10 for nonan-1-ol and 19.50 for undecan-1-ol (extrapolated value).

In general, the UNIQUAC equations with two or three adjustable parameters simultaneously produce information regarding other thermodynamic

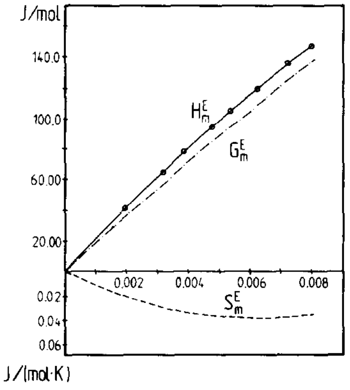

Fig. 2. Excess thermodynamic properties of diluted mixtures of undecan-1-ol with *n*-octane at 298.15 K. Lines are calculated by the UNIQUAC ASM; o, experimental points.

properties of the mixtures, such as G_m^E and S_m^E. The H_m^E, G_m^E and S_m^E values of the compounds investigated are presented in Figs. 1 and 2. As can be seen from the figures, all mixtures have positive values of H_m^E, G_m^E and S_m^E.

At high dilution, the results of the fit obtained by polynomials were found to be satisfactory, but the values of an alcohol association constant K can be computed using the UNIQUAC ASM equation.

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LIST OF SYMBOLS

B_1, B_2	parameters of polynomials of H_m^E versus molality
C_1, C_2	parameters of polynomials of H_m^E versus mole fraction
G_m^E	molar excess Gibbs free energy
H_m^E	molar excess enthalpy
$H_m^{E,cal}$	calculated molar excess enthalpy
h_2	enthalpy of hydrogen bond formation
K	association constant, $(\phi_{1i+1}/\phi_{1i}\phi_{1M})[i/(i+1)]$
k	number of adjustable parameters
l_i	bulk factor of pure component i as defined by $l_i = (Z/2)(r_i - q_i) - (r_1 - 1)$
q_i	surface parameter of pure component i
n	number of experimental points
r_1, r_2	size parameter of pure component 1 or 2
R	universal gas constant
S_m^E	molar excess entropy
T	temperature
ΔU_{12}, ΔU_{21}	binary interaction parameters
V	true molar volume of mixture of components 1 and 2
x_1	mole fraction of the solute
Z	lattice coordination number, a constant set to 10

Greek letters

σ	root-mean-square deviation of excess enthalpy
σ_R	relative root-mean-square deviation of excess enthalpy

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