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EXCESS ENTHALPIES OF 1-OCTANOL WITH CYCLOHEXANE AT 298.15 K

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ABSTRACT

Heats of mixing at high dilutions were determined for the binary system 1-octanol + cyclohexane at 298.15 K. The standard molar enthalpy of H-bond formation of 1-octanol was evaluated. The values measured for 1-octanol + cyclohexane, and for other *n*-alcohol + cyclohexane systems, were correlated by polynomials and with the UNIQUAC associated-solution model.

INTRODUCTION

The binary mixtures 1-alcohol + cyclohexane have been studied many times, and all measurements [1–4], including those for 1-octanol in cyclohexane [3,4], were made over the whole concentration range. In the first part of this series [5] we have systematically measured the heats of mixing of dilute mixtures of 1-alkanols, $CH_3(CH_2)_nOH$ ($n = 8$, 9, 10) and cyclohexane at 298.15 K and 308.15 K. The objectives of this paper are two-fold. Firstly, to study the new system 1-octanol + cyclohexane, and secondly, to attempt a correlation of all the experimental results with established theories of solutions.

EXPERIMENTAL

Calorimetric measurements were made on an LKB 8700 precision calorimetry system using the method described in detail earlier [6]. Solvents were dried over type 4A molecular Sieves (SERVA, Heidelberg, F.R.G.). 1-Octanol (Fluka AG, Busch SG, Switzerland) was purified by distillation under reduced pressure ($n_D^{298.15\,K} = 1.4276$; $\rho^{298.15\,K} = 822.08$ kg m^{-3}) and cyclohexane (International Enzymes Ltd., Windsor, U.K.) by fractional distillation through a 50-plate laboratory column ($n_D^{298.15\,K} = 1.42361$; $\rho^{298.15\,K} = 773.53$ kg m^{-3}).

RESULTS AND DISCUSSION

The results of the measurements at 298.15 K and atmospheric pressure are shown in Table 1.

The relationship between the enthalpy of mixing and the concentration $H_m^E(m_1)$, is described by eqn. (1), similar to that given in ref. 7,

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

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

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

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

where C_1 and C_2 are adjustable parameters. The values of the coefficients B_i and C_i are given in Table 2.

The extrapolation of the individual values of excess enthalpy H_m^E/x_1 to infinite dilution ($x_1 \to 0$) gives the value of the heat of mixing of 1 mole of

TABLE 1

Experimental results of the excess molar enthalpies H_m^E of 1-octanol + cyclohexane binary system at 298.15 K

$x_1 \times 10^2$	m_1 (mol kg^{-1})	H_m^E (J mol^{-1})	H_m^{Ecal} [a] (J mol^{-1})
0.0873	0.01038	20.88	21.38
0.1221	0.01453	28.99	29.51
0.1883	0.02242	43.90	44.36
0.2912	0.03470	66.17	65.96
0.3389	0.04041	75.06	75.42
0.4126	0.04923	88.94	89.33
0.4250	0.05071	91.67	91.60
0.4899	0.05850	103.27	103.09
0.5611	0.06704	116.63	115.04
0.6075	0.07263	122.64	122.47
0.6663	0.07970	132.00	131.50
0.7054	0.08442	137.74	137.29
0.7253	0.08681	138.27	140.11

[a] Values calculated by UNIQUAC ASM KW.

TABLE 2

Values [a] of the adjustable parameters in eqns. (1) and (2) and of the deviations of H_m^E for the 1-octanol + cyclohexane binary system

Parameters		Deviations	
Eqn. (1) B_1/B_2 (J kg mol^{-2})/ (J kg mol^{-3})	Eqn. (2) C_1/C_2	Eqn. (1) σ/σ_R (J mol^{-1})	Eqn. (2) σ/σ_R (J mol^{-1})
2076.7	24697	0.76	0.75
−5332.7	−741191	0.65	0.65

[a] All calculated from 13 data points.

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 1-alkanols are bound together, in the pure state, by hydrogen bonds, and these are broken during the transition from the pure state to the infinitely dilute solution. Assuming that in the system studied the contribution of non-specific interactions is small, the standard molar enthalpy of H-bond formation is equal to the negative of parameter C_1 of eqn. (2). Thus, for 1-octanol in cyclohexane at 298.15 K, $\Delta H_m^\ominus = -24.7 \pm 0.2$ kJ mol^{-1}. The hydrogen-bond energy evaluated similarly by Savini et al. [8] is −21.8 kJ mol^{-1} for 1-octanol in *n*-hydrocarbons. The value given by Nagata [9] is −21.9 kJ mol^{-1}, but that calculated by Brandani [10], who applied the homomorph concept to hydrocarbons, is −24.90 kJ mol^{-1}.

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), excess enthalpy (H_m^E) and excess entropy (S_m^E), using expressions from the well-known UNIQUAC ASM [11] model of polar mixtures and the Gibbs–Helmholtz relation

$$H_m^E = G_m^E - T\frac{\partial G_m^E}{\partial T} \qquad (3)$$

The results of the present measurements, and those obtained earlier [5], were correlated by UNIQUAC ASM theory using two models of association, namely those of Mecke–Kempter (UNIQUAC ASM MK) and of Kretschmer–Wiebe (UNIQUAC ASM KW).

The pure component structural parameters r (volume parameter) and q (surface parameter) were obtained as suggested by Vera et al. [12] from the following simple relationships taken from Hofman and Nagata [13]

$$r_i = 0.029281 V_i \qquad (4)$$

$$q_i = (Z-2)r_i/Z + 2(1-l_i)/Z \qquad (5)$$

where V_i is the molar volume of pure component i at 298.15 K; Z is the

TABLE 3

Values of the parameters and of the root-mean square deviations obtained by UNIQUAC ASM for 1-alkanol + cyclohexane binary systems at 298.15 K and 308.15 K

Solute	No. of data points	Parameters				Deviations			
		MK		KW		MK		KW	
		Δu_{12} Δu_{21} (J mol^{-1})	$K^{298.15\,\mathrm{K}}$	Δu_{12} Δu_{21} (J mol^{-1})	$K^{298.15\,\mathrm{K}}$	σ (J mol^{-1})	σ_R	σ (J mol^{-1})	σ_R
$T = 298.15$ K									
1-octanol	13	−2287.4 6875.9	22.5	−2144.2 7138.8	8.6	0.86	1.17	0.88	1.21
1-nonanol [a]	10	−2211.9 6382.4	17.9	−2066.8 6630.0	6.6	1.25	1.43	1.25	1.45
1-decanol [a]	11	−2114.1 6050.8	15.4	−1968.2 6276.8	5.7	1.39	1.53	1.39	1.54
1-undecanol [a]	10	−2023.2 5735.1	13.3	−1876.5 5949.7	4.8	0.20	0.46	0.20	0.47
$T = 308.15$ K									
1-nonanol [a]	10	−1913.0 4844.4	23.2	−1718.3 6097.1	2.5	0.32	0.47	0.32	0.48
1-decanol [a]	11	−2004.4 5525.7	15.3	−1830.9 5751.6	5.5	0.67	0.85	0.68	0.86
1-undecanol [a]	10	−1825.6 4983.2	12.1	−1642.7 5193.9	4.2	0.49	0.54	0.49	0.54

[a] Data from ref. 5.

coordination number, assumed to be 10, and l_i is the bulk factor, taken as zero.

Two measures of the goodness-of-fit are used namely (1) the root-mean-square deviation of the excess enthalpy defined by eqn. (6)

$$\sigma = \left[\sum_{i=1}^{n} \left(H_{\mathrm{m}}^{\mathrm{Ecal}} - H_{\mathrm{m}}^{\mathrm{E}} \right)^2 (n-k)^{-1} \right]^{1/2} \tag{6}$$

and (2) the relative root-mean-square deviation computed according to eqn. (7)

$$\sigma_{\mathrm{R}} = 100 \left[\sum_{i=1}^{n} \frac{\left(H_{\mathrm{m}}^{\mathrm{Ecal}} - H_{\mathrm{m}}^{\mathrm{E}} \right)^2}{\left(H_{\mathrm{m}}^{\mathrm{E}} \right)^2} (n-k)^{-1} \right]^{1/2} \tag{7}$$

where $H_{\mathrm{m}}^{\mathrm{Ecal}}$ and $H_{\mathrm{m}}^{\mathrm{E}}$ 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. The parameters in the relationships tested were fitted by an optimization technique. As an objective function, the root-mean-square deviations were minimized. The values of calculated excess enthalpies of the 1-octanol + cyclohexane system of the ith point, computed by UNIQUAC ASM KW are shown in Table 1. The comparison of the correlation by the UNIQUAC method, with two different models of association, is given in Table 3 in the form of equation parameters and corresponding root-mean-square deviations. In the calculations, we have

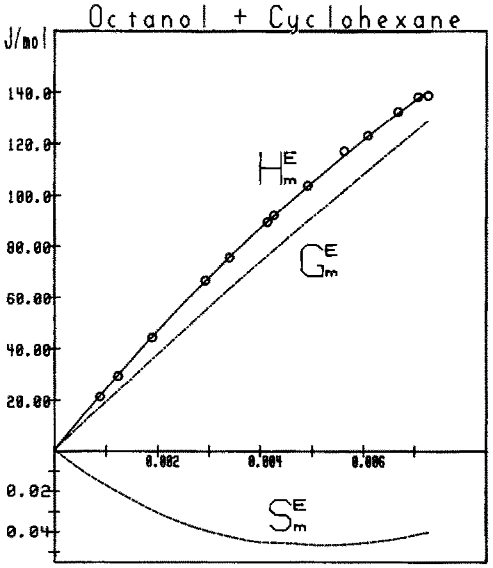

Fig. 1. Excess thermodynamic properties of diluted mixtures of 1-octanol with cyclohexane at 298.15 K. Lines are calculated by the UNIQUAC ASM KW; o are experimental points.

used the value of hydrogen-bond formation enthalpy, $h_2 = -24.33$ kJ mol^{-1}, this being the average value of C_1 for all systems studied previously [5] and the present system.

At high dilutions, the results of the fit obtained by polynomials, NRTL (not presented) and UNIQUAC (not presented), as well as UNIQUAC ASM for two different models of association (MK, KW) are similar to each other. All relative deviations are in the range σ_R from 0.46 to 1.54. The values of the alkanol association constant K (298.15 K) were 12.1–23.2 and 2.5–8.6 for the MK and KW models, respectively. Association constants reported by Brandani [10] and Nagata [11] for several *n*-alcohols have higher values.

In general, the UNIQUAC ASM MK and KW equations with three adjustable parameters also provide information about other thermodynamic 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 for the system investigated are presented in Fig. 1. As can be seen the mixture has positive values of all three excess properties.

At high dilution, the results of the fit obtained by polynomials were found to be satisfactory. The UNIQUAC ASM equation also allowed the value of an alcohol association constant (K) to be computed.

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LIST OF SYMBOLS

B_1, B_2	adjustable parameters in eqn. (1) molality
C_1, C_2	adjustable parameters in eqn. (2)
G_m^E	molar excess Gibbs free energy
H_m^E	molar excess enthalpy
H_m^{Ecal}	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; $l_i = (Z/2)(r_i - q_i) - (r_1 - 1)$
n	number of experimental points
q_i	surface parameter of pure component 1
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, set at 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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