HEATS OF SOLUTION OF 1-NONANOL, 1-DECANOL AND 1-UNDECANOL IN CYCLOHEXANE AT 298.15 K AND 308.15 K

ŠPELA PALJK and CVETO KLOFUTAR *

J. Stefan Institute, E. Kardelj University of Ljubljana, 61111 Ljubljana (Yugoslavia)

URSZULA DOMAŃSKA

Department of Physical Chemistry, Warsaw Technical University, 00-664 Warsaw (Poland)

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ABSTRACT

The enthalpies of solution of 1-nonanol, 1-decanol and 1-undecanol in cyclohexane were measured at 298.15 K and 308.15 K. The experimental values of enthalpy changes per mole of solution as a function of solute mole fraction are given in the form of a second-degree polynomial. The hydrogen bond enthalpies of 1-alkanol molecules in the systems studied were obtained from the enthalpy changes per mole of solute at infinite dilution. In addition, the values of the relative molar enthalpy of the pure solutes, the relative partial molar enthalpy of the solutes and solvent, and the relative apparent molar enthalpy of the solutes were determined at 298.15 K and 308.15 K. On the basis of a semi-ideal model of associated solution, the practical molal osmotic coefficients and the molal activity coefficient of the solutes were calculated from the thermochemical data. The non-ideal behaviour of these systems was described by the excess thermodynamic functions of solution, as well as by the partial excess thermodynamic functions of solutes and solvent. The enthalpic pair interaction coefficients were determined in the sense of the McMillan–Mayer theory. The non-ideality of the investigated systems was also described on the basis of an association model with an extended series of multimers, assuming that each addition of monomer to the progressively growing oligomeric species is more difficult.

INTRODUCTION

The heat of solution is one of the most accurate thermochemical parameters which characterise a solution, giving valuable indirect information about the structure of the solution as well as the intermolecular interactions between its components. In the past a number of investigations of thermochemical properties have dealt with the systems of alkanol and hydrocarbon mixtures, e.g. ref. 1. But among the investigated solutes, only 1-decanol has

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* Author to whom correspondence should be addressed.

so far been studied in cyclohexane. Most of the studies of higher alcohols in cyclohexane have been made over the whole concentration range [2–4]. To explain the thermodynamic, spectroscopic and dielectric properties of diluted solutions of ethanol in cyclohexane, Stokes [5] used a model based on mole fraction statistics. This model assumes the presence of open chain and closed cyclic hydrogen-bonded oligomers with allowance for a non-polar interaction term.

In the first part of this series [6] we measured the heat of solution of 1-nonanol and 1-undecanol in n-hexane, n-heptane, n-decane and n-hexadecane at 298.15 K, to determine some thermodynamic parameters which describe the non-ideal behaviour of these systems in which the presence of linear oligomeric species only was assumed. As was mentioned previously [7], the predominant factor in the region of high dilution is the disruption of the 1-alkanol associated molecules. In the present investigation some thermodynamic properties of 1-nonanol, 1-decanol and 1-undecanol in cyclohexane at 298.15 K and 308.15 K were obtained on the basis of thermochemical data, with the aim of elucidating the effects of solvent and temperature on association processes and on the hydrogen bond enthalpy, as well as on the van der Waals interactions among solute molecules of different chain lengths.

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. The 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. A Sargent recorder (model SRL, S-72180-57) was applied. A description of the system used is given in full detail in ref. 10. The volume of the reaction vessel was 100 cm^3. The

TABLE 1

Specification and densities of component liquids at 298.15 K

Component	Specification	d (kg m^{-3})	
		Experimental	Literature
1-Nonanol	International Enzymes Ltd. (Windsor, Berkshire, Gt. Britain)	823.84	824.33 [8]
1-Decanol	Fluka AG (Bush SG, Switzerland)	826.90	826.09 [8]
1-Undecanol	Fluka AG (Bush SG, Switzerland)	828.98	828.01 [8]
Cyclohexane	Fluka AG (Bush SG, Switzerland)	773.53	773.89 [9]

measurements were carried out at 298.15 ± 0.05 K and 308.15 ± 0.05 K. The heat of mixing was determined by the glass-ampoule technique. A known amount of solute was sealed in a glass ampoule of 1 cm^3 volume. After thermostating, the ampoule was broken and the solute dissolved in 100 cm^3 of pure solvent. The heat absorbed was recorded simultaneously. The system was tested by measuring the heat of solution of potassium chloride in water up to 0.04 mol dm^{-3} at both temperatures. The determined values of 17.36 ± 0.06 and 15.62 ± 0.06 kJ mol^{-1} at 298.15 K and 308.15 K, respectively, for the heat of solution of potassium chloride are close to the values given in the work of Somsen et al. [11] and Sanahuja [8].

The densities of the liquids, measured at 298.15 K with an Anton–Paar digital densimeter (model DMA 10), are included in Table 1 along with values from the literature [9,12].

RESULTS AND DISCUSSION

For a process

$$n_2 B + n_1 S = n_2 B[(n_1/n_2)S] \tag{1}$$

where n_2 moles of solute B and n_1 moles of solvent S are mixed, the accompanying enthalpy change is given by [13]

$$\Delta H = n_2 \Delta_{sol} H_{int}[(n_1/n_2)S] \tag{2}$$

where $\Delta_{sol} H_{int}[(n_1/n_2)S]$ (J mol^{-1}) is the integral heat of solution per mole of solute. For the systems investigated, where n_2 moles of 1-alkanol are mixed with n_1 moles of cyclohexane as solvent, the values of enthalpy change per mole of solution, $\Delta H/(n_1 + n_2)$ (J mol^{-1}), at 298.15 and 308.15 K are given in Tables 2 and 3, respectively.

The enthalpy change for process (1) may also be given by [14]

$$\Delta H = n_1 \bar{L}_1 + n_2 (\bar{L}_2 - L_2^\cdot) = L - n_2 L_2^\cdot \tag{3}$$

where $\bar{L}_1$ and $\bar{L}_2$ (J mol^{-1}) are the relative partial molar enthalpies of solvent and solute, respectively, $L_2^\cdot$ (J mol^{-1}) is the relative molar enthalpy of pure solute and L (J) is the relative enthalpy of solution.

The experimental data of $\Delta H/(n_1 + n_2)$ against mole fraction of solute, X_2, are shown in Figs. 1 and 2. The smoothed curves in Figs. 1 and 2 were used in an analytical form

$$\Delta H/(n_1 + n_2) = C_1 x_2 + C_2 x_2^2 \tag{4}$$

where C_i is an empirical constant which depends on solute, solvent and temperature. The values of the constant C_i, obtained by the method of least-squares, are given in Table 4.

From the limit values of the derivative $(\partial \Delta H/\partial n_2)_{n_1}$ of eqns. (3) and (4), as $n_2 \to 0$, it follows that $-L_2^\cdot = C_1$.

TABLE 2

Values of enthalpy changes per mole of solution of $x_2CH_3(CH_2)_nOH + (1 - x_2)C_6H_{12}$ mixtures at 298.15 K; $h = 8$, 9 or 10

$x_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})	$x_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})
1-Nonanol			
0.1010	23.42	0.4718	98.93
0.1740	40.02	0.5437	111.47
0.2010	45.39	0.6030	121.24
0.3287	72.39	0.6279	121.66
0.4090	87.74	0.6874	134.56
1-Decanol			
0.0595	14.41	0.3906	85.27
0.1323	31.29	0.4740	102.73
0.1758	41.33	0.5338	115.12
0.2298	52.46	0.5466	114.10
0.2973	68.41	0.5959	121.00
0.3369	75.34		
1-Undecanol			
0.0707	17.34	0.3501	79.64
0.1108	27.02	0.3857	86.88
0.1548	37.35	0.4497	99.17
0.2355	55.41	0.4964	108.42
0.3124	72.14	0.5464	117.01

TABLE 3

Values of enthalpy changes per mole of solution of $x_2CH_3(CH_2)_nOH + (1 - x_2)C_6H_{12}$ mixtures at 308.15 K; $h = 8$, 9 or 10

| $x_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})	$x_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})
1-Nonanol			
0.0402	9.37	0.4251	92.09
0.0909	20.91	0.5030	107.05
0.1651	37.60	0.5453	115.23
0.2560	57.60	0.6148	127.62
0.3624	79.54	0.6306	131.59
1-Decanol			
0.0576	13.63	0.4280	94.78
0.1395	32.39	0.4881	106.28
0.1652	38.23	0.5305	114.05
0.2356	54.11	0.5629	120.49
0.2799	63.17	0.5691	119.67
0.3565	79.69		
1-Undecanol			
0.0433	10.53	0.3375	76.90
0.0780	18.74	0.4101	92.44
0.1277	30.22	0.4576	102.15
0.1926	45.36	0.4942	110.60
0.2717	63.07	0.5058	111.17
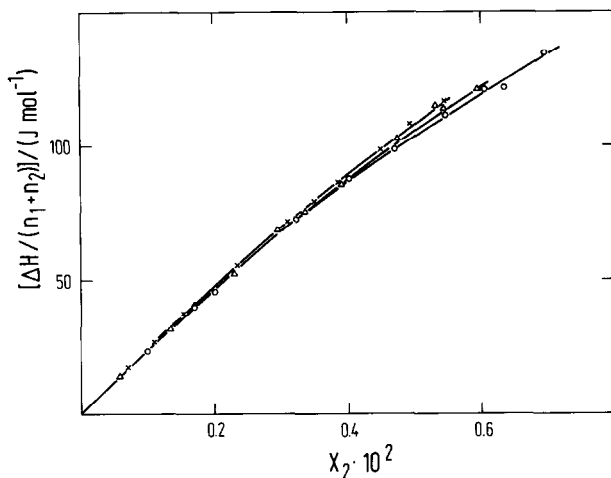
Fig. 1. Concentration dependence of $\Delta H/(n_1 + n_2)$ for solutions of 1-alkanol + cyclohexane at 298.15 K: $\circ$, 1-nonanol; $\triangle$, 1-decanol; $\times$, 1-undecanol.

Assuming that the contributions of non-specific interactions at infinite dilution are negligible, the integral heat of solution per mole of solute at infinite dilution, $\Delta_{sol} H_{int}^{\ominus}[(n_1/n_2)S]$, equal to the regression coefficient C_1 (see relation (4)), can be considered as the hydrogen bond enthalpy of 1-alkanol molecules in these systems.

From Table 4, it can be seen that the average values of regression coefficient C_1 are 24745 ± 355 J mol^{-1} at 298.15 K and 24067 ± 254 J mol^{-1} at 308.15 K. The above values of hydrogen bond enthalpy are close to those determined previously for similar systems [15–17]. From the values of
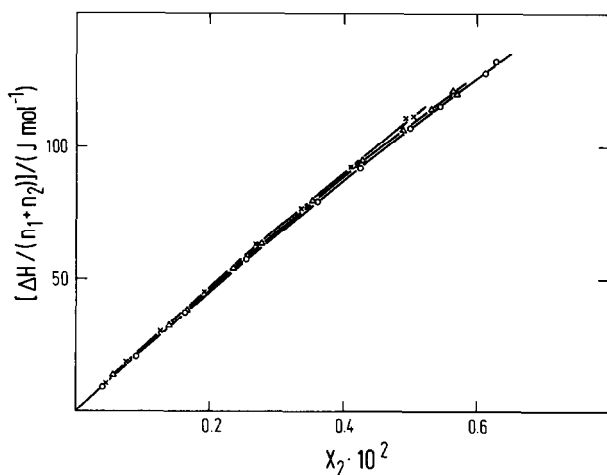

Fig. 2. Concentration dependence of $\Delta H/(n_1 + n_2)$ for solutions of 1-alkanol + cyclohexane at 308.15 K: $\circ$, 1-nonanol; $\triangle$, 1-decanol; $\times$, 1-undecanol.

TABLE 4

Values of regression coefficients of eqn. (4) and the standard estimation error s for the investigated systems at 298.15 and 308.15 K

System	T (K)	No. of points	C_1	$-C_2$	s
Cyclohexane +	298.15				
1-nonanol		10	24182	700000	1.09
1-decanol		11	24652	720348	1.64
1-undecanol		10	25402	754430	0.45
Cyclohexane +	308.15				
1-nonanol		10	23603	443690	0.37
1-decanol		11	24120	479610	0.75
1-undecanol		10	24477	507586	0.82

regression coefficient C_2, it may be concluded that with increasing concentration of solute the intermolecular interactions are stronger in solutes with longer alkyl chain lengths.

Following eqns. (3) and (4), the relative enthalpy of solution may be given by

$$L = C_2 n_2^2 / (n_1 + n_2) \tag{5}$$

and the relative apparent molar enthalpy of solute $\Phi L_2 = L/n_2$ (J mol^{-1})

$$\Phi L_2 = C_2 x_2 \tag{6}$$

Thus, the relative partial molar enthalpy of solute $\bar{L}_2$ (J mol^{-1}) is given by

$$\bar{L}_2 = C_2 x_2 (2 - x_2) \tag{7}$$

and the relative partial molar enthalpy of solvent $\bar{L}_1$ (J mol^{-1}) can be expressed as

$$\bar{L}_1 = - C_2 x_2^2 \tag{8}$$

For the investigated systems, the values of ΦL_2 and $\bar{L}_2$ are negative and large, while those of $\bar{L}_1$ are positive and close to zero at the temperatures studied. As an example, the concentration dependence of $\mathscr{Y}$ (J mol^{-1}) $\equiv$ $(\Phi L_2, \bar{L}_2, \bar{L}_1)$ for solutions of 1-decanol in cyclohexane at 298.15 and 308.15 K are shown in Fig. 3. From Fig. 3, it is evident that the investigated systems behave non-ideally, even at the lowest concentration studied.

From the values of the integral heat of solution per mole of solute at infinite dilution and the temperatures studied, a rough estimate of the heat capacity, $\Delta C_p^{\ominus} = - 67.8$ J mol^{-1} K^{-1}, for the dissolution process (1) at infinite dilution was obtained. The negative value of $\Delta C_p^{\ominus}$ may be ascribed to changes in the self-association of alkanol molecules in the dissolution processes.

On the basis of the McMillan–Mayer theory [18] some valuable information about the intermolecular interactions among solute molecules may be
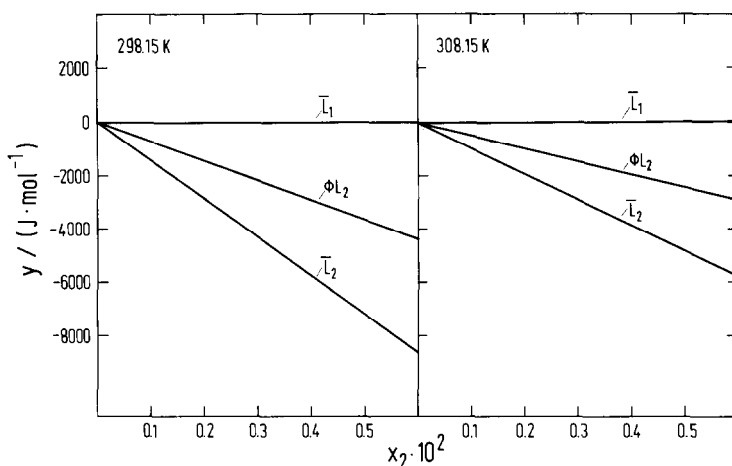
Fig. 3. Concentration dependence of relative apparent molar enthalpy, and relative partial molar enthalpies of the solute and the solvent for solutions of 1-decanol in cyclohexane at 298.15 K and 308.15 K.

obtained from the respective interaction coefficients. For example, the total enthalpy $H(m)$ (J) per kg of solvent for a binary mixture is given by

$$H(m) = H_s^* + \overline{H_2^\infty}m + h_{22}m^2 + h_{222}m^3 + \ldots \tag{9}$$

where H_s^* is the enthalpy of 1 kg of pure solvent, $\overline{H_2^\infty}$ (J mol^{-1}) is the standard partial molar enthalpy of the solute, and h_{22}, h_{222}, etc., are the virial coefficients which characterise pair, triplet and higher interactions among solute molecules.

On the other hand, the relation for the excess enthalpy H^{ex} (J kg^{-1})

$$H^{ex} = h_{22}m^2 + h_{222}m^3 + \ldots \equiv m\Phi L_2 \tag{10}$$

due to the high dilution of the systems investigated was used in the form

$$H^{ex} = C_2 M_1 10^{-3} m^2 \tag{11}$$

From eqns. (10) and (11), it is evident that the pair enthalpic interaction coefficient h_{22} (J mol^{-2} kg) is identical to $C_2 M_1 10^{-3}$. For the systems

TABLE 5

Values of the enthalpic pair interaction coefficient h_{22} for 1-alkanols in cyclohexane at 298.15 and 308.15 K

Solute	$-h_{22}$ (J mol^{-2} kg)	
	298.15 K	308.15 K
1-Nonanol	58 913	37 341
1-Decanol	60 625	40 364
1-Undecanol	63 493	42 719

investigated the enthalpic pair interaction coefficient may be related to hydrogen bonding between the OH groups of 1-alkanol molecules, as well as to non-specific interactions due to the van der Waals intermolecular forces between solute and solvent molecules. The calculated h_{22} values are given in Table 5. From these values it may be concluded that intermolecular interactions of 1-alkanol molecules in cyclohexane increase with increasing molecular weight of the solutes and decrease with increasing temperature.

If the systems investigated contain linear hydrogen-bonded oligomers formed by successive association reactions

$$B_1 + B_{l-1} \rightleftharpoons B_l; \qquad l \geq 2 \tag{12}$$

with a step-wise equilibrium constant K_l

$$K_l = [B_l]/[B_1][B_{l-1}] \tag{13}$$

where $[B_i]$ in mol kg^{-1} is the concentration of the species B_i, then the heat of dilution may be assumed to be mainly due to the dissociation of various oligomeric species.

In the case when the values of the enthalpy $\Delta H^{\ominus}$ of the step-wise association reaction (12) are equal, the relative apparent molar enthalpy ΦL_2 may be given by [19]

$$\Phi L_2 = (1 - \phi)\Delta H^{\ominus} \tag{14}$$

where ϕ is the practical molal osmotic coefficient, defined as $\phi = m_r/m$, where m_r (mol kg^{-1}) is the sum of the concentrations of species present.

Using relations (6) and (14), the practical osmotic coefficient is given by

$$\phi = 1 - (C_2/\Delta H^{\ominus})x_2 \tag{15}$$

but owing to the extremely dilute solution it was calculated from

$$\phi = 1 - (C_2 M_1 10^{-3}/\Delta H^{\ominus})m \tag{16}$$

Figure 4 shows the concentration dependence of ϕ for cyclohexane solutions of 1-nonanol, 1-decanol and 1-undecanol at 298.15 K and 308.15 K. From Fig. 4 it can be seen that the non-ideal behaviour is more pronounced the longer the alkyl chain in the alkanol molecule and the lower the temperature.

For the systems investigated, the molal activity coefficient of the solute, γ_2, defined by asymmetric normalisation, was obtained via Bjerrum's relation [20] and given in the form

$$\ln \gamma_2 = -(2C_2 M_1 10^{-3}/\Delta H^{\ominus})m \tag{17}$$

The concentration dependence of the activity coefficients for the solutes investigated in cyclohexane at 298.15 K and 308.15 K are presented in Fig. 5.

In addition, the non-ideal behaviour of the systems is elucidated by the excess thermodynamic functions $Y_{1,2}^{ex}$, i.e. excess Gibbs free energy $G_{1,2}^{ex}$ (J kg^{-1}), excess enthalpy $H_{1,2}^{ex}$ (J kg^{-1}) and excess entropy $TS_{1,2}^{ex}$ (J kg^{-1}) [21].
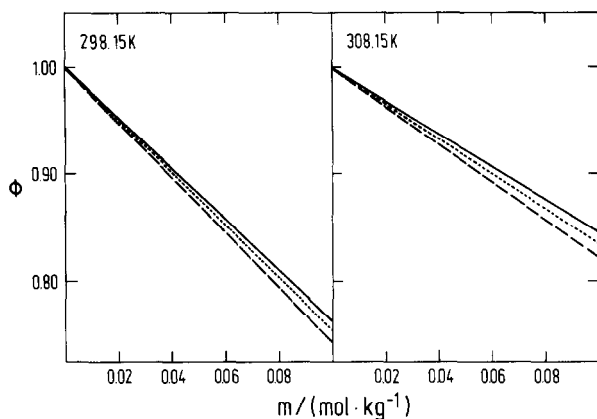
Fig. 4. Concentration dependence of practical osmotic coefficients for solutions of 1-alkanol + cyclohexane at 298.15 K and 308.15 K: ———, 1-nonanol; - - - - - -, 1-decanol; — — —, 1-undecanol.

The excess thermodynamic functions were calculated from the following relations

$$G_{1,2}^{ex} = -\left(RTC_2M_110^{-3}/\Delta H^{\ominus}\right)m^2 \tag{18}$$

$$H_{1,2}^{ex} = C_2M_110^{-3}m^2 \tag{19}$$

and

$$TS_{1,2}^{ex} = C_2M_110^{-3}\left[1 + \left(RT/\Delta H^{\ominus}\right)\right]m^2 \tag{20}$$

As an example, Fig. 6 shows the concentration dependence of the excess thermodynamic functions $Y_{1,2}^{ex} \equiv G_{1,2}^{ex}$ or $H_{1,2}^{ex}$ or $TS_{1,2}^{ex}$ for the system
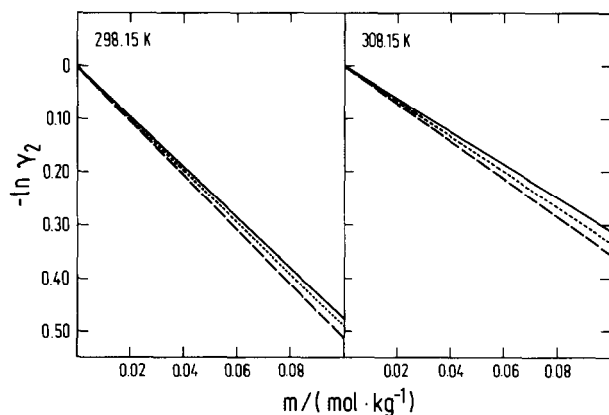

Fig. 5. Concentration dependence of activity coefficients of investigated solutes in cyclohexane at 298.15 K and 308.15 K: ———, 1-nonanol; - - - - - -, 1-decanol; — — —, 1-undecanol.
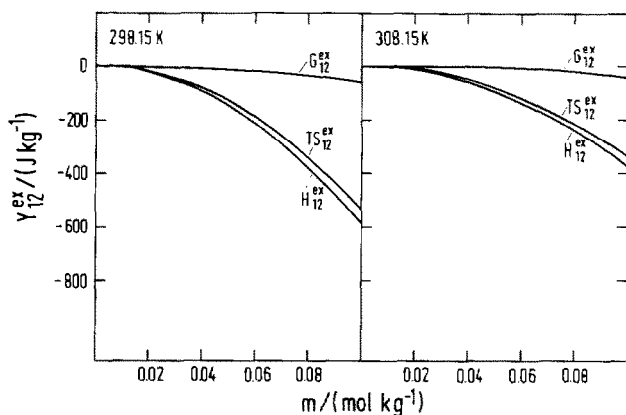
Fig. 6. Concentration dependence of excess thermodynamic functions of solutions of 1-nonanol + cyclohexane at 298.15 K and 308.15 K.

1-nonanol + cyclohexane at 298.15 and 308.15 K. From Fig. 6 it may be observed that the excess thermodynamic functions are negative. Thereby, $H_{1,2}^{ex}$ and $TS_{1,2}^{ex}$ are almost compensated in $G_{1,2}^{ex}$. The negative values of $H_{1,2}^{ex}$ can be attributed to hydrogen bonding between alkanol molecules. The negative values of $S_{1,2}^{ex}$ can also be considered to be a consequence of hydrogen bonding, as there is more order in such a mixture than for an ideal system.

The partial molar excess thermodynamic functions of solute and solvent $\overline{Y_i^{ex}}$ can be obtained from [22]

$$Y_{1,2}^{ex} = n_1\overline{Y_1^{ex}} + n_2\overline{Y_2^{ex}} \tag{21}$$

where $\overline{Y_i^{ex}}$ is the derivative of $(\partial Y_{1,2}^{ex}/\partial n_i)_{n_j}$.

So the partial molar excess thermodynamic functions of solute and solvent for the systems investigated are calculated from

$$\overline{G_2^{ex}} = RT \ln \gamma_2 = -\left(2RTC_2M_110^{-3}/\Delta H^\ominus\right)m \tag{22}$$

$$\overline{H_2^{ex}} \equiv \overline{L_2} = 2C_2M_110^{-3}m \tag{23}$$

$$\overline{TS_2^{ex}} = 2C_2M_110^{-3}\left[1 + \left(RT/\Delta H^\ominus\right)\right]m \tag{24}$$

and

$$\overline{G_1^{ex}} = (m/n_1)RT(1 - \phi) = \left(RTC_2M_1^2 10^{-6}/\Delta H^\ominus\right)m^2 \tag{25}$$

$$\overline{H_1^{ex}} \equiv \overline{L_1} = -C_2M_1^2 10^{-6}m^2 \tag{26}$$

$$\overline{TS_1^{ex}} = -C_2M_1^2 10^{-6}\left[1 + \left(RT/\Delta H^\ominus\right)\right]m^2 \tag{27}$$

As an example, Figs. 7 and 8 show the concentration dependence of the partial molar excess thermodynamic functions of solvent and solute, respectively, for solutions of 1-decanol + cyclohexane at 298.15 K. From the figures, it may be observed that the values of $\overline{Y_1^{ex}}$ are small and positive while those of $\overline{Y_2^{ex}}$ are larger and negative.
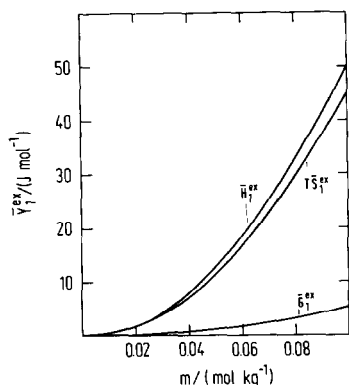
Fig. 7. Concentration dependence of partial molar excess thermodynamic functions of the solvent for solutions of 1-decanol + cyclohexane at 298.15 K.

The non-ideality of the systems investigated is described by an association model with an extended series of oligomers, the formation of which is determined by two independent parameters, i.e. the dimerisation constant, β_2, and a constant, κ [23]. The step-wise association constant K_l of reaction (12) is correlated with constant κ through

$$K_l = \kappa/(l-1); \qquad l \geq 3 \tag{28}$$

where $K_l \to 0$ as $l \to \infty$, which means that each addition of monomer to the progressively growing oligomeric species is more difficult. For the adopted
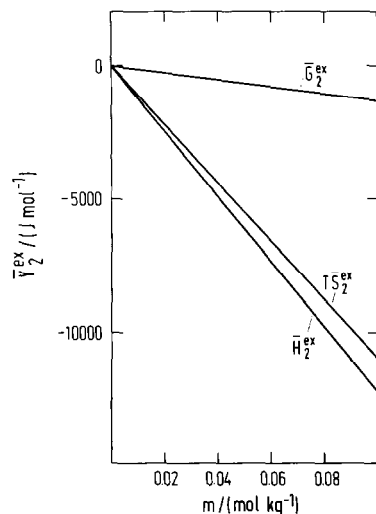

Fig. 8. Concentration dependence of partial molar excess thermodynamic functions of the solute for solutions of 1-decanol + cyclohexane at 298.15 K.

model, the self-association constant β_l of the self-association reaction

$$lB_1 \rightleftharpoons B_l; \qquad l \geq 2 \tag{29}$$

defined as

$$\beta_l = [B_l]/[B_1]^l \tag{30}$$

is correlated with the dimerisation constant β_2 and constant κ through

$$\beta_l = \beta_2 \kappa^{l-2}/(l-1)!; \qquad l \geq 2 \tag{31}$$

In calculation of the parameters needed, the concentration of free mono-mer, b, is obtained via Bjerrum's relation [24]

$$\log(b/b_1) = \int_{m_{r_1}}^{m_r} \phi \; d \log m_r \tag{32}$$

where m_{r_1} is the value of m_r corresponding to a known value b_1 of the free monomer concentration. Bjerrum's integral was calculated by Simpson's rule. In this calculation an assumption was made that the free monomer concentration at the lowest concentration studied was equal to the stoichio-metric concentration of solute.

Both parameters β_2 and constant κ were obtained by the curve-fitting method. The experimental data of $\log T = \log[(m - b)/b]$ and $\log \Theta = \log[(m_r - b)/b]$ against $\log b$ were superimposed on a unique pair of normalised curves of $\log \mathbf{T}(\log \mathbf{b})$ and $\log \Theta(\log \mathbf{b})$. The normalised varia-bles were calculated from

$$\mathbf{T} = \sum_2^\infty \frac{l\mathbf{b}^{l-1}}{(l-1)!} = l^\mathbf{b}(1 + \mathbf{b}) - 1 \tag{33}$$

and

$$\Theta = \sum_2^\infty \frac{\mathbf{b}^{l-1}}{(l-1)!} = l^\mathbf{b} - 1 \tag{34}$$

The values of parameters β_2 and constant κ were determined from the differences of coordinate values of normalised and experimental plots super-imposed in the position of the best fit, following relations

$$\log \mathbf{T} - \log T = \log \kappa - \log \beta_2 \tag{35}$$

$$\log \Theta - \log \Theta = \log \kappa - \log \beta_2 \tag{36}$$

and

$$\log \mathbf{b} - \log b = \log \kappa \tag{37}$$

The values of dimerisation constant, β_2, and constant κ for the systems investigated are given in Table 6. As an example, the normalised curves of $\log \mathbf{T}(\log \mathbf{b})$ and $\log \Theta(\log \mathbf{b})$ superimposed on the experimental data of

TABLE 6

Values of dimerisation constant, β_2, and constant κ for extensive self-association reactions according to eqns. (36)–(38) for the investigated systems at 298.15 K and 308.15 K

Solute	β_2		κ	
	298.15 K	308.15 K	298.15 K	308.15 K
1-Nonanol	0.84	0.73	31.5	19.4
1-Decanol	0.88	0.74	31.0	20.3
1-Undecanol	0.98	0.81	29.0	20.7

log $T(\log b)$ and log $\Theta(\log b)$ for the 1-decanol and cyclohexane system at 298.15 K are shown in Fig. 9.

From these data it can be seen that the dimerisation constant at a definite temperature increases with increasing chain length in the 1-alkanol molecule, and, for the same solute, decreases with increasing temperature. In contrast, the values of the constant κ at a definite temperature seem, within experimental error, to be independent of solute chain length and are lower at higher temperatures. On the basis of the adopted model, the non-ideal behaviour of the investigated systems may be ascribed to the different
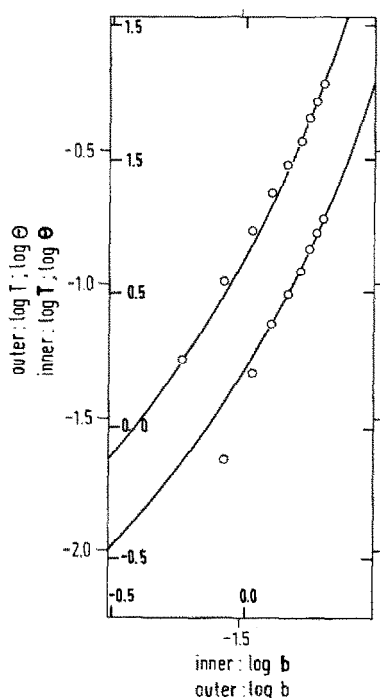

Fig. 9. Normalised curves, log $T(\log b)$ and log $\Theta(\log b)$, superimposed on the experimental data, log $T(\log b)$ and log $\Theta(\log b)$, for the 1-decanol + cyclohexane system at 298.15 K.
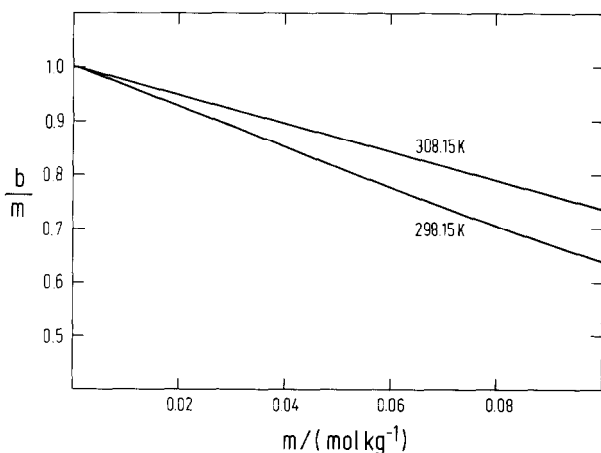
Fig. 10. Distribution of the monomeric species of 1-decanol in cyclohexane at 298.15 K and 308.15 K.

degrees of association of the solutes, which increase from 1-nonanol to 1-undecanol. Consequently, the self-association reactions of solute molecules affect the values of the practical osmotic coefficients, activity coefficients and excess thermodynamic functions of the systems. The relevance of the adopted model at both temperatures studied was confirmed by recalculating the primary data of m and m_r, using the corresponding parameters from Table 6, postulating oligomeric species up to heptamers. The experimental and recalculated values agree to within better than 1×10^{-3} mol kg^{-1}. Figure 10 shows the distribution of fractions of monomeric species for 1-decanol in cyclohexane at 298.15 K and 308.15 K.

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