Thermochimica Acta, 158 (1990) 301–315
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HEATS OF SOLUTION OF 1-NONANOL AND 1-UNDECANOL IN *n*-HEXANE, *n*-HEPTANE, *n*-DECANE AND *n*-HEXADECANE AT 298.15 K

CVETO KLOFUTAR and ŠPELA PALJK

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

URSZULA DOMANSKA

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

(Received 25 July 1989)

ABSTRACT

The heats of mixing of 1-nonanol or 1-undecanol in *n*-hexane, *n*-heptane, *n*-decane and *n*-hexadecane were measured at 298.15 K. The enthalpy changes per mole of solution were expressed as a second degree polynomial in X, the mole fraction of solute in the concentration range studied. From the enthalpy changes per mole of solute at infinite dilution, the hydrogen-bond enthalpy of 1-alkanol molecules in the solvents investigated was determined. From thermochemical data the relative molar enthalpies of the pure solutes, the relative partial molar enthalpies of the solute and the solvent and the relative apparent molar enthalpies of the solutes were deduced. Assuming that the enthalpies of the stepwise associations are equal for both solutes in the solvents investigated, the practical osmotic coefficients were calculated from the apparent molar enthalpy of the solutes and the enthalpy of a stepwise association reaction on the basis of a semi-ideal model of associated solutions proposed by Prigogine. The molal activity coefficients of the solutes were determined via Bjerrum's relation. The non-ideal behaviour of these systems was described by the excess thermodynamic functions, i.e. the excess Gibbs free energy, excess enthalpy and excess entropy, as well as with partial molar excess Gibbs free energy of solute and solvent. Furthermore, the non-ideality of the investigated systems was treated on the basis of an association model with an extended series of multimers, supposing that the first stepwise associations occur more readily than the rest. In addition, the pair virial coefficients of the solutes were determined from the excess enthalpies of solutions according to McMillan–Mayer theory.

INTRODUCTION

It is well known that alcohol molecules are able to form strong intermolecular-hydrogen-bond associates, which dissociate when the alcohol is mixed with an inert solvent, such as a hydrocarbon. This effect is particularly important in the region of dilute alcohol. In the literature there are a number of determinations of the thermodynamic properties of such mix-

0040-6031/90/$03.50

tures, and several models of molecular association as well as some interesting correlations are proposed [1–17].

In a 1-alkanol + n-alkane mixture many factors contribute to the thermodynamic properties, e.g. the chain length of the 1-alkanol molecule, the orientational order in the n-alkane chain, interstitial accommodation of n-alkane molecules within the 1-alkanol structure, disruption of the 1-alkanol structure by n-alkane molecules, mixing of the 1-alkanol and n-alkane chains, the relative size of component molecules, the concentration of solute, temperature, etc. Each factor makes a positive or negative contribution to the resultant values of the thermodynamic functions. As was shown previously [18], in all these phenomena the predominant factor in the region of high dilution is the disruption of the associated 1-alkanol molecules. The heat of mixing in the high dilution region is thus very instructive in interpreting the thermodynamic properties of such solutions.

With this in view, the heats of mixing of diluted mixtures of a 1-alkanol, $CH_3(CH_2)_nOH$; $n = 8, 10$, and an n-alkane, $CH_3(CH_2)_{h-2}CH_3$; $h = 6, 7, 10, 16$, were determined at 298.15 K in the present investigation. The aim of this work was to describe the non-ideal behaviour of these systems and the elucidate the influence of the chain length of solute and solvent molecules on the hydrogen bonding of the OH group of 1-alkanol molecules and van der Waals intermolecular forces between 1-alkanol molecules and n-alkane molecules.

EXPERIMENTAL

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

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 [19,20].

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 used. A description of the system used is given in full detail in ref. 21. The volume of the reaction vessel was 100 cm^3. The measurements were carried out at 298.15 ± 0.05 K. The heat of mixing was determined using the glass ampoule technique. A known amount of solute was sealed in a glass ampoule of volume 1 cm^3. After thermostatting, the ampoule was broken and the solute dissolved in 100 cm^3 of pure solvent. Simultaneously the heat absorbed was recorded. The system was tested by measuring the heat of solution of potassium chloride in water up to 0.04 mol

TABLE 1

Specifications and densities of component liquids at 298.15 K

Component	Specification	d (kg m^{-3})	
		Experimental	Literature [a]
1-Nonanol	International Enzymes Ltd. (Windsor, Berkshire, Gt. Britain)	823.84	824.33 [19]
1-Undecanol	Fluka AG (Busch SG, Switzerland)	828.98	828.01 [19]
n-Hexane	REACHIM (VIO Sojuzchimexport, U.S.S.R.)	654.81	654.84 [20]
n-Heptane	VEB Jena Pharm. (Jena, G.D.R.)	679.51	679.46 [20]
n-Decane	BDH Chemicals Ltd. (Poole, Gt. Britain)	726.25	726.35 [20]
n-Hexadecane	International Enzymes Ltd. (Windsor, Berkshire, Gt. Britain)	769.86	769.94 [20]

[a] Reference given in square brackets.

l^{-3} at 298.15 K. The determined value of 17.358 ± 0.062 kJ mol^{-1} for the heat of solution of potassium chloride is close to the value given in the work of Somsen et al. [22].

RESULTS AND DISCUSSION

In a solution of n_2 mol of 1-alkanol, B, in n_1 mol of n-alkane, S, a mixture of composition $n_2\text{B}[(n_1/n_2)\text{S}]$ is obtained [23]

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

For such a process the enthalpy change ΔH is given by $n_2\ \Delta_{\text{sol}}H_{\text{int}}[(n_1/n_2)\text{S}]$ (J), where $\Delta_{\text{sol}}H_{\text{int}}[(n_1/n_2)\text{S}]$ (J mol^{-1}) is the integral heat of solution per mole of solute. Thus, the enthalpy change per mole of solution is $\Delta H/(n_1 + n_2)$ (J mol^{-1}). For the systems investigated, the experimental values of $\Delta H/(n_1 + n_2)$ are given in Tables 2 and 3. In Figs. 1 and 2 the smoothed curves are drawn through the experimental points of $\Delta H/(n_1 + n_2)$ versus mole fraction of solute X_2 and fitted into the following relation

$$\Delta H/(n_1 + n_2) = C_1X_2 + C_2X_2^2 \tag{2}$$

where C_i is an adjustable parameter. Rearrangement of eqn. (2) gives

$$\Delta H = C_1n_2 + C_2n_2^2/(n_1 + n_2) \tag{3}$$

The enthalpy change for process (1) may also be given by [24]

$$\Delta H = n_1\bar{L}_1 + n_2(\bar{L}_2 - L_2^{\circ}) = L - n_2L_2^{\circ} \tag{4}$$

where $\bar{L}_1$ (J mol^{-1}) and $\bar{L}_2$ (J mol^{-1}) are the relative partial molar enthalpies of the solvent and the solute, respectively, L_2° (J mol^{-1}) is the relative enthalpy of the pure solute and L (J) is the relative enthalpy of the solution. From the limiting values of the derivative $(\partial\,\Delta H/\partial n_2)_{n_1}$ of eqns.

TABLE 2

Values of enthalpy changes per mole of solution of $X_2CH_3(CH_2)_8OH + (1 - X_2)CH_3(CH_2)_{h-2}CH_3$ mixtures at 298.15 K; $h = 6, 7, 10$ or 16

$X_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})	$X_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})
n-Hexane			
0.2366	51.86	0.5855	113.62
0.3041	65.45	0.6863	128.51
0.3478	73.42	0.7555	137.89
0.4384	89.95	0.7888	142.16
0.5148	101.73		
n-Heptane			
0.2418	52.86	0.5721	113.37
0.3015	64.83	0.6898	131.89
0.3500	73.99	0.7359	138.70
0.4280	88.04	0.7987	147.06
0.5288	107.39	0.8383	150.63
n-Decane			
0.1935	42.45	1.0040	186.74
0.3417	72.35	1.1142	202.67
0.5277	107.47		
0.7338	143.55		
0.8362	160.13		
n-Hexadecane			
0.3181	72.33	1.0484	214.94
0.4772	105.93	1.2390	246.09
0.6142	133.69	1.4080	271.88
0.7688	163.92	1.5259	290.62
0.8915	193.07	1.6857	311.16

(3) and (4) as $n_2 \to 0$, it follows that $C_1 = -L_2^\circ$.

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

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

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

$$\Phi L_2 = C_2 X_2 \tag{6}$$

The relative partial molar enthalpy of the solute $\bar{L}_2$ (J mol^{-1}) obtained from the derivative of $[\partial(n_2 \Phi L_2)/\partial n_2]_{n_1}$ is given by

$$\bar{L}_2 = 2C_2 X_2 - C_2 X_2^2 \tag{7}$$

and the partial molar enthalpy of the solvent $\bar{L}_1$ (J mol^{-1}) obtained from the expression $-(n_2^2/n_1)(\partial \Phi L_2/\partial n_2)_{n_1}$ is given by

$$\bar{L}_1 = -C_2 X_2^2 \tag{8}$$

TABLE 3

Values of enthalpy changes per mole of solution of $X_2CH_3(CH_2)_{10}OH + (1 - X_2)CH_3(CH_2)_{h-2}CH_3$ mixtures at 298.15 K; $h = 6, 7, 10$ or 16

$X_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})	$X_2 \times 10^2$	$\Delta H/(n_1 + n_2)$ (J mol^{-1})
n-Hexane			
0.2051	45.67	0.5550	109.58
0.2807	60.36	0.6115	116.64
0.3946	82.05	0.6545	122.86
0.4384	88.80		
0.4893	98.29		
n-Heptane			
0.2160	47.77	0.5139	104.42
0.2841	61.72	0.5574	110.26
0.3055	64.90	0.6260	121.84
0.3767	79.39	0.6976	131.42
0.4185	86.84	0.7164	134.22
n-Decane			
0.3026	65.76	0.8539	163.44
0.4024	85.60	0.9386	174.93
0.5041	104.47		
0.6536	130.93		
0.7826	152.47		
n-Hexadecane			
0.4638	103.57	1.0302	206.67
0.5767	125.58	1.1462	222.72
0.7213	152.03	1.2516	238.02
0.8790	180.25	1.4265	256.89
1.0228	203.47		

Using eqns. (6), (7) and (8), it follows that for the systems investigated 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. As an example, the concentration dependence of $\mathcal{Y}$ (J mol^{-1}) $\equiv (\Phi L_2, \bar{L}_2, \bar{L}_1)$ for solutions of 1-nonanol and 1-undecanol, respectively, in *n*-hexadecane, is given in Fig. 3. From Fig. 3 it is evident that the systems investigated behave non-ideally even at the lowest concentration studied.

However, the regression coefficient C_1 may be considered to be the integral heat of solution per mole of solute at infinite dilution, $\Delta_{sol}H^0_{int}[(n_1/n_2)S]$. Assuming that in the systems investigated the contributions of non-specific interactions at infinite dilution are negligible, the integral heat of solution per mole of solute at infinite dilution can be considered to be equal to the hydrogen-bond enthalpy of the 1-alkanol molecules in these systems. The values of the regression coefficients of eqn. (2) are given in Table 4. As may be observed, the average values of

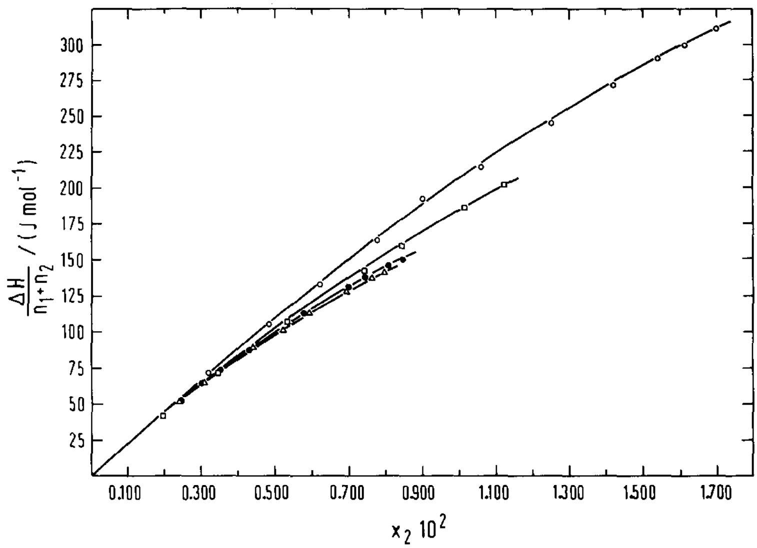

Fig. 1. Concentration dependence of $\Delta H/(n_1+n_2)$ for solutions of 1-nonanol + *n*-alkane at 298.15 K: △, *n*-hexane; ●, *n*-heptane; □, *n*-decane; ○, *n*-hexadecane.

$C_1 = 23391 \pm 238$ J mol^{-1} for 1-nonanol and $C_1 = 23740 \pm 182$ J mol^{-1} for 1-undecanol are equal within one standard deviation; the mean value of C_1 for the two solutes in the systems studied is 23566 ± 154 J mol^{-1}. The values for the hydrogen-bond enthalpy determined previously are: 21.8 kJ mol^{-1} for 1-octanol by Savini et al. [25] and 23.4 ± 0.4 kJ mol^{-1} for 1-hexanol by Wóycicka and Rećko [1]. From the values for the enthalpy of hydrogen-bond formation, given for several alcohols at 323.15 K by Brandani [26], the value of the hydrogen-bond enthalpy, obtained by extrapolation,

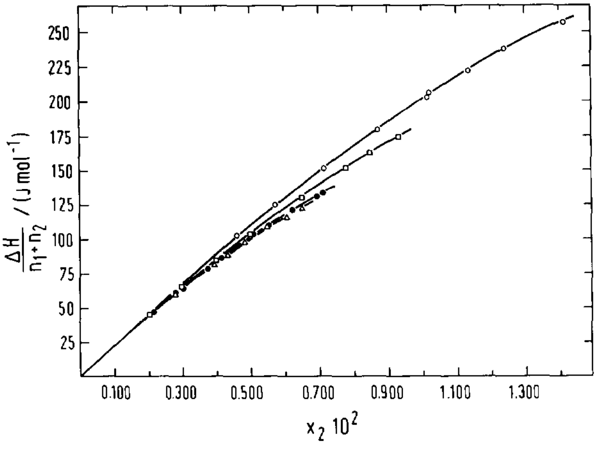

Fig. 2. Concentration dependence of $\Delta H/(n_1+n_2)$ for solutions of 1-undecanol + *n*-alkane at 298.15 K: △, *n*-hexane; ●, *n*-heptane; □, *n*-decane; ○, *n*-hexadecane.

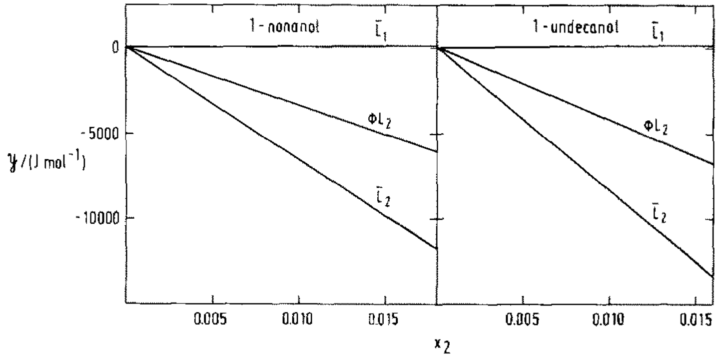

Fig. 3. Concentration dependence of relative apparent molar enthalpy, and relative partial molar enthalpies of the solute and the solvent for solutions of 1-nonanol and 1-undecanol in *n*-hexadecane at 298.15 K.

amounts to 23.3 kJ mol^{-1} for 1-nonanol and 22.3 kJ mol^{-1} for 1-undecanol, respectively. For the systems investigated, the values of the regression coefficient C_2 are negative. On the basis of the values of the regression coefficient C_2, however, it may be concluded that with increasing concentration the effects of non-specific interactions in 1-undecanol are slightly more intense than in 1-nonanol in the same *n*-alkane, and that in systems with the same 1-alkanol the non-specific interactions are the most pronounced in the *n*-alkane having the largest number of carbon atoms.

Assuming that the heat of dilution results from the dissociation of various oligomeric species in the form of linear hydrogen-bonded polymers, formed by successive reactions,

$$B_1 + B_{l-1} \rightleftharpoons B_l \qquad (9)$$

TABLE 4

Values of regression coefficients of eqn. (2) for the investigated systems at 298.15 K

System	No. of points	C_1	$-C_2$	s
1-Nonanol +				
n-hexane	9	23200 ± 162	667580 ± 21825	0.64
n-heptane	10	23245 ± 94	612906 ± 12709	0.38
n-decane	7	23028 ± 312	441780 ± 33387	1.68
n-hexadecane	10	24091 ± 97	331984 ± 6539	1.20
1-Undecanol +				
n-hexane	8	23668 ± 87	744809 ± 14552	0.25
n-heptane	10	23765 ± 98	701843 ± 14981	0.30
n-decane	7	23323 ± 64	501651 ± 7516	0.29
n-hexadecane	9	24206 ± 84	420768 ± 6644	0.80

with a stepwise equilibrium constant K_l given by

$$K_l = [B_l]/[B_1][B_{l-1}]; \qquad l \geq 2 \tag{10}$$

and with an enthalpy of stepwise association reaction ΔH^0, then the heat of infinite dilution for a solution of concentration m (mol kg^{-1}) may be expressed by $-m\Phi L_2$. This amount of heat reflects the effects of the dissociation of various oligomeric species and may be given by

$$m\Phi L_2 = [B_2]\ \Delta H_2^0 + [B_3][\Delta H_2^0 + \Delta H_3^0] + \ldots \tag{11}$$

where $[B_l]$ in mol kg^{-1} is the concentration of species B_l. If the enthalpies of stepwise association reactions are equal, i.e.

$$\Delta H_2^0 = \Delta H_3^0 = \ldots = \Delta H^0 \tag{12}$$

eqn. (11) reduces to

$$m\Phi L_2 = \Delta H^0([B_2] + 2[B_3] + 3[B_4] + \ldots) \tag{13}$$

or

$$m\Phi L_2 = \Delta H^0\left(K_2[B_1]^2 + 2K_2K_3[B_1]^3 + 3K_2K_3K_4[B_1]^4 + \ldots\right) \tag{14}$$

Taking into account the expression for the practical osmotic coefficient ϕ for the ideal associated solution

$$\phi = m_r/m = \sum_{i=1}^{L} [B_l] / \sum_{i=1}^{L} l[B_l] \tag{15}$$

where m_r (mol kg^{-1}) is the sum of the concentrations of species present, the relative apparent molar enthalpy ΦL_2 may be given by [27]

$$\Phi L_2 = (1 - \phi)\ \Delta H^0 \tag{16}$$

Using eqns. (6) and (16), the practical osmotic coefficient can be calculated from

$$\phi = 1 - \left(C_2/\Delta H^0\right) X_2 \tag{17}$$

and for extremely dilute solutions by

$$\phi = 1 - \left(C_2 M_1 10^{-3}/\Delta H^0\right) m \tag{18}$$

where M_1 (g mol^{-1}) is the molar mass of the solvent. The linear concentration dependence of practical osmotic coefficients is characteristic of non-electrolyte solutions at low concentration. As an example, in Fig. 4 the concentration dependence of practical osmotic coefficients for some systems is given. From Fig. 4 it may be observed that the non-ideal behaviour is more pronounced for systems with 1-undecanol than with 1-nonanol as solute in the same solvent, while for each 1-alkanol investigated the non-ideal behaviour is the more pronounced the longer is the n-alkane chain.

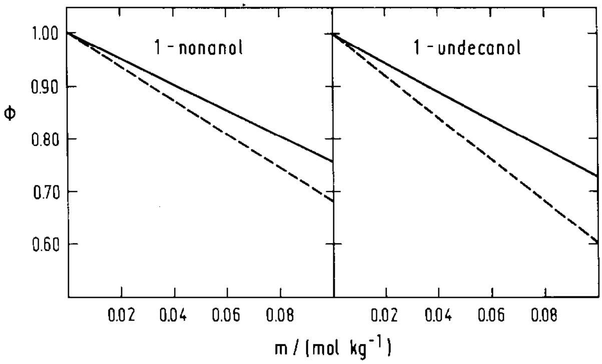

Fig. 4. Concentration dependence of practical osmotic coefficients of systems investigated at 298.15 K: ———, *n*-hexane; – – –, *n*-hexadecane.

The molal activity coefficients of the solute γ_2, defined by asymmetric normalization, are obtained from Bjerrum's relation [28]

$$d[(1-\phi)m] + m \, d \ln \gamma_2 = 0 \tag{19}$$

and are given in the form

$$\ln \gamma_2 = -\left(2C_2M_110^{-3}/\Delta H^0\right)m \tag{20}$$

The concentration dependence of the activity coefficients for both solutes in *n*-hexane and *n*-hexadecane, is given in Fig. 5.

To elucidate the non-ideal behaviour of the systems investigated the excess thermodynamic functions Y_{12}^{ex}, i.e. the excess Gibbs free energy G_{12}^{ex} (J kg^{-1}), excess enthalpy H_{12}^{ex} (J kg^{-1}) and excess entropy TS_{12}^{ex} (J kg^{-1}) were calculated using the following [29]

$$G_{12}^{ex} = RTm(1-\phi+\ln \gamma_2) = -\left(RTC_2M_110^{-3}/\Delta H^0\right)m^2 \tag{21}$$

$$H_{12}^{ex} \equiv m\Phi L_2 = C_2M_110^{-3}m^2 \tag{22}$$

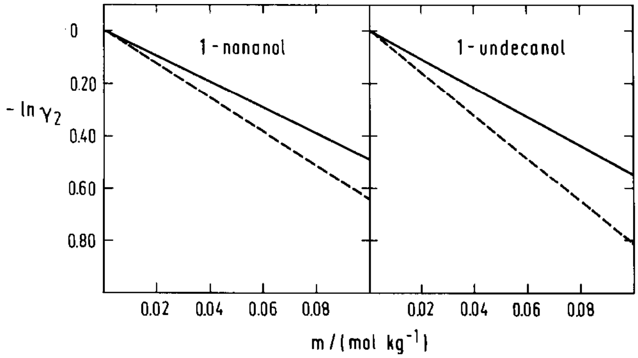

Fig. 5. Concentration dependence of activity coefficients of investigated solutes at 298.15 K: ———, *n*-hexane; – – –, *n*-hexadecane.

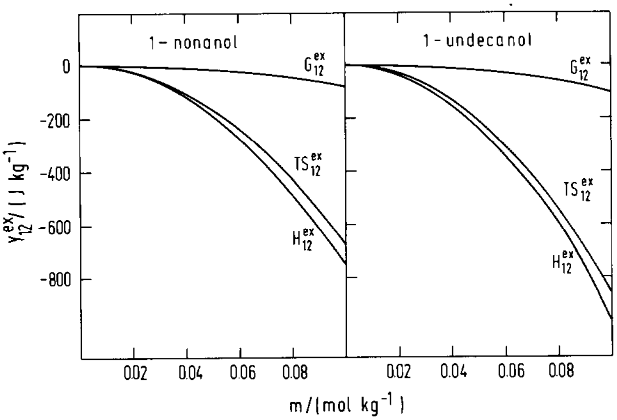

Fig. 6. Concentration dependence of excess thermodynamic functions of solutions of 1-nonanol and 1-undecanol in *n*-hexadecane at 298.15 K.

and

$$TS_{12}^{ex} = H_{12}^{ex} - G_{12}^{ex} = C_2 M_1 10^{-3}\left[1 + \left(RT/\Delta H^0\right)\right] m^2 \tag{23}$$

As an example, Fig. 6 shows the concentration dependence of the excess thermodynamic functions $Y_{12}^{ex} \equiv G_{12}^{ex}$ or H_{12}^{ex} or TS_{12}^{ex} for the systems 1-nonanol + hexadecane and 1-undecanol + hexadecane, respectively. From Fig. 6 it may be observed that for our systems the values of H_{12}^{ex} and TS_{12}^{ex} are negative and almost compensate each other in the G_{12}^{ex} values, which are also negative and small. The negative values of H_{12}^{ex} can be attributed to hydrogen bonding between alkanol molecules. The negative values of S_{12}^{ex} can also be considered to be a consequence of hydrogen bonding, since there is more order in such a mixture than in an ideal system.

The partial molar excess thermodynamic functions of the solute and the solvent $\overline{Y}_i^{ex}$ may also be obtained from [24]

$$Y_{12}^{ex} = n_1 \overline{Y}_1^{ex} + n_2 \overline{Y}_2^{ex} \tag{24}$$

where $\overline{Y}_i^{ex}$ is the derivative of $(\partial Y_{12}^{ex}/\partial n_i)_{n_j}$. Thus, the partial molar excess Gibbs free energies of the solute and the solvent for the systems investigated are calculated from

$$\overline{G}_2^{ex} = RT \ln \gamma_2 = -\left(2RTC_2 M_1 10^{-3}/\Delta H^0\right) m \tag{25}$$

and

$$\overline{G}_1^{ex} = (m/n_1) RT(1-\phi) = \left(RTC_2 M_1^2 10^{-6}/\Delta H^0\right) m^2 \tag{26}$$

As an example, the concentration dependence of the excess Gibbs free energies of solutions of 1-nonanol and 1-undecanol in *n*-hexadecane, and of the partial molar excess Gibbs free energies for both solutes and solvent at 298.15 K are shown in Fig. 7. From Fig. 7 it may be observed that G_{12}^{ex} and $\overline{G}_2^{ex}$ values are negative while $\overline{G}_1^{ex}$ values are positive. This means that the

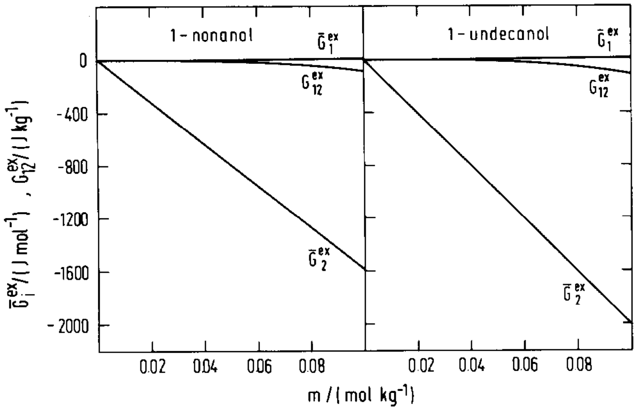

Fig. 7. Concentration dependence of excess Gibbs free energies of solutions of 1-nonanol and 1-undecanol in *n*-hexadecane and of partial molar excess Gibbs free energies for both solutes and solvent at 298.15 K.

contributions of the partial molar excess Gibbs free energy of the solute to the excess Gibbs free energy of the solution prevail over those of the solvent.

In addition, for these systems the formation of an extended series of oligomers is described in terms of two independent parameters, i.e. the dimerization constant β_2 and constant K. The latter is correlated with the stepwise association constant K_l of reaction (9) as [30,31]

$$K_l = [(l-1)/(l-2)]K; \qquad l \geq 3 \tag{27}$$

This means that the first stepwise associations occur more readily than the others, i.e. $K_3 = 2K$, $K_4 = (3/2)K, \ldots, K_l \rightarrow K$ as $l \rightarrow \infty$.

On the other hand, for the adopted model, the self-association constant β_l of the self-association reaction

$$l\mathrm{B}_1 \rightleftharpoons \mathrm{B}_l; \qquad l \geq 2 \tag{28}$$

defined as

$$\beta_l = [\mathrm{B}_l]/[\mathrm{B}_1]^l; \qquad l \geq 2 \tag{29}$$

is correlated with the dimerization constant and constant K through

$$\beta_l = \beta_2(l-1)K^{l-2}; \qquad l \geq 2 \tag{30}$$

The concentration of free monomer b is obtained via Bjerrum's relation in the form

$$\lg(b/b_1) = \int_{m_{r1}}^{m_r} \phi \, \mathrm{d} \lg m_r \quad (\log \equiv \log_{10}) \tag{31}$$

where m_{r1} is the value of m_r corresponding to a known value b_1 of the free monomer concentration. Bjerrum's integral was calculated using Simpson's rule.

The dimerization constant β_2 and constant K 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 normalized curves $\log \mathbf{T}(\log \mathbf{b})$ and $\log \boldsymbol{\Theta}(\log \mathbf{b})$. The normalized variables were calculated from

$$\mathbf{T} = \frac{2\mathbf{b}}{(1 - \mathbf{b})^3} \tag{32}$$

and

$$\boldsymbol{\Theta} = \frac{\mathbf{b}}{(1 - \mathbf{b})^2} \tag{33}$$

In the best fit the values of the parameters β_2 and K were obtained from

$$\log \mathbf{T} - \log T = \log K - \log \beta_2 \tag{34}$$

$$\log \boldsymbol{\Theta} - \log \Theta = \log K - \log \beta_2 \tag{35}$$

and

$$\log \mathbf{b} - \log b = \log K \tag{36}$$

As an example, the normalized curves $\log \mathbf{T}(\log \mathbf{b})$ and $\log \boldsymbol{\Theta}(\log \mathbf{b})$ superimposed on the experimental data $\log T(\log b)$ and $\log \Theta(\log b)$ for the 1-nonanol + n-hexadecane system are shown in Fig. 8. The values of β_2 and K for the systems investigated are given in Table 5. From these data it can be concluded that, within experimental error, the dimerization constant for

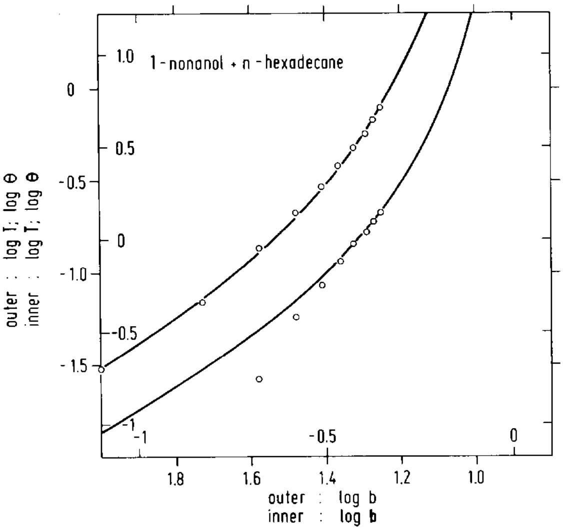

Fig. 8. Normalized curves $\log \mathbf{T}(\log \mathbf{b})$ and $\log \boldsymbol{\Theta}(\log \mathbf{b})$ superimposed on the experimental data $\log T(\log b)$ and $\log \Theta(\log b)$ for the 1-nonanol + n-hexadecane system at 298.15 K.

TABLE 5

Values of dimerization constant β_2 and constant K for extensive self-association reactions according to eqns. (34)–(36) for the systems studied at 298.15 K

System	β_2	K
1-Nonanol +		
n-hexane	1.12	5.62
n-heptane	1.14	6.00
n-decane	1.10	6.76
n-hexadecane	1.20	7.94
1-Undecanol +		
n-hexane	1.14	6.53
n-heptane	1.07	7.59
n-decane	1.15	7.76
n-hexadecane	1.10	11.14

both solutes in the solvents investigated are equal, $\bar{\beta}_2 = 1.13 \pm 0.01$, while the values of the constant K increase from *n*-hexane to *n*-hexadecane and are lower for 1-nonanol than for 1-undecanol. If the semi-ideal association model is considered, the non-ideal behaviour of our systems may be ascribed to the different degree and extent of association of the solutes in the solvents studied, which increase from 1-nonanol to 1-undecanol and from *n*-hexane to *n*-hexadecane. The consequence of this is also evident from the concentration dependence of their practical osmotic coefficients and excess thermodynamic functions.

Furthermore, some information about the intermolecular interactions between solute molecules may be obtained from the enthalpic interaction coefficients. According to the McMillan–Mayer theory for a binary mixture, the total enthalpy $H(m)$ (J) per kg of solvent is given by [32]

$$H(m) = H_s^\circ + \bar{H}_2^\infty m + h_{22}m^2 + h_{222}m^3 + \ldots \tag{37}$$

where H_s° is the enthalpy of 1 kg of pure solvent, $\bar{H}_2^\infty$ (J mol^{-1}) is the standard partial molar enthalpy of the solute, and h_{22}, h_{222} etc. are the virial coefficients which characterize pair, triplet and higher interactions among solute molecules.

The excess enthalpy H^{ex} (J kg^{-1}) as a function of concentration m (mol kg^{-1}) is used in the form

$$H^{ex} = h_{22}m^2 + h_{222}m^3 + \ldots \equiv m\Phi L_2 \tag{38}$$

Owing to the high dilution of the systems investigated this relation may be used in the form

$$H^{ex} = C_2 M_1 10^{-3} m^2 \tag{39}$$

From both eqn. (38) and eqn. (39) it follows that $C_2M_110^{-3}$ is identical to the pair interaction coefficient h_{22} (J mol^{-1} kg). The calculated values of

TABLE 6

Values of the pair interaction coefficient h_{22} for 1-nonanol and 1-undecanol in solvents studied at 298.15 K

System	$-h_{22}$ (J mol^{-2} kg)
1-Nonanol +	
n-hexane	57530
n-heptane	61415
n-decane	62858
n-hexadecane	75176
1-Undecanol +	
n-hexane	64185
n-heptane	70327
n-decane	71377
n-hexadecane	95281

the pair interaction coefficient are given in Table 6. From the values of the pair interaction coefficient h_{22} it may be concluded that intermolecular interactions of 1-alkanol molecules increase from *n*-hexane to *n*-hexadecane, and they are higher in the case of 1-undecanol than in the case of 1-nonanol. This may be ascribed to hydrogen bonding between OH groups of 1-alkanol molecules and interactions resulting from the van der Waals intermolecular forces between 1-alkanol molecules and *n*-alkane molecules, which increase with increasing chain length.

ACKNOWLEDGEMENT

The authors thank the Slovene Research Community, Ljubljana for financial support of this work.

REFERENCES

1 M.K. Wóycicka and W.M. Rećko, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 20 (1972) 783.
2 M.K. Wóycicka and B. Kalinowska, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 25 (1977) 639.
3 A.J. Treszczanowicz and G.C. Benson, J. Chem. Thermodyn., 9 (1977) 1189.
4 A.J. Treszczanowicz and G.C. Benson, J. Chem. Thermodyn., 10 (1978) 967.
5 A.J. Treszczanowicz and G.C. Benson, J. Chem. Thermodyn., 12 (1980) 173.
6 A.J. Treszczanowicz, O. Kiyohara and G.C. Benson, J. Chem. Thermodyn., 13 (1981) 253.
7 M.K. Kumaran and G.C. Benson, J. Chem. Thermodyn., 16 (1984) 175.
8 M. Costas and D. Paterson, J. Chem. Soc., Faraday Trans. 1, 81 (1985) 635.
9 G.C. Benson and P.J. D'Arcy, J. Chem. Thermodyn., 18 (1986) 493.
10 R. O'Shea and R.D. Stokes, J. Chem. Thermodyn., 18 (1986) 691.
11 R. Tanaka, S. Toyama and S. Murakami, J. Chem. Thermodyn., 18 (1986) 6313.

12 I. Brown, W. Fock and F. Smith, Aust. J. Chem., 17 (1964) 1106.
13 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 456.
14 F. Smith and J. Brown, Aust. J. Chem., 26 (1973) 705.
15 J. Stecki and M.K. Wôycicka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 22 (1974) 37.
16 A. Bellemans, Roczniki Chem., 50 (1976) 1749.
17 F. Smith, Aust. J. Chem., 30 (1977) 43.
18 I. Prigogine, A. Bellemans and V. Mathot, The Molecular Theory of Solutions, North-Holland, Amsterdam, 1957, p. 305.
19 S. Wingefors, J. Chem. Tech. Biotechnol., 31 (1981) 530.
20 Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamics Research Center Hydrocarbon Project, Thermodynamics Research Center, Texas A&M University, College Station, TX, 1976, p. 2 (31 October) and 1977, p. 1 (31 October).
21 C. Klofutar and Š. Paljk, J. Chem. Soc., Faraday Trans. 1, 77 (1981) 2705.
22 G. Somsen, J. Coops and M.W. Tolk, Recl. Trav. Chim. Pays-Bas, 82 (1963) 231.
23 V.P. Vasiliev, Thermodynamic Properties of Electrolyte Solutions, Vysshaya Shkola, Moscow, 1962, p. 64.
24 I.M. Klotz and R.M. Rosenberg, Chemical Thermodynamics, Benjamin/Cummings, Menlo Park, CA, 1986, p. 367.
25 C.G. Savini, D.R. Winterhalter and H.C. van Ness, J. Chem. Eng. Data, 10 (1965) 168.
26 V. Brandani, Fluid Phase Equilib., 12 (1983) 87.
27 S.J. Gill, M. Downing and G.F. Sheats, Biochemistry, 6 (1967) 272.
28 E.A. Guggenheim and R.H. Stokes, Equilibrium Properties of Aqueous Solutions of Single Strong Electrolytes, in D.D. Eley, J.E. Mayer and F.C. Tompkins (Eds.), The International Encyclopedia of Physical Chemistry and Chemical Physics, Pergamon, Oxford, 1969, p. 13.
29 H.L. Friedman, Ionic Solution Theory, in I. Prigogine (Ed.), Monographs in Statistical Physics and Thermodynamics, Vol. 3, Wiley, New York, 1962, p. 195.
30 F.J.C. Rossotti and H. Rossotti, J. Phys. Chem., 65 (1961) 926.
31 F.J.C. Rossotti and H. Rossotti, J. Phys. Chem., 65 (1961) 930.
32 W.G. McMillan and J.E. Mayer, J. Chem. Phys., 13 (1945) 276.