

## CALORIMETRIC STUDIES OF SELF-ASSOCIATION OF CYCLOHEXANOL IN BENZENE

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(Received 6 September 1985)

### ABSTRACT

The heat of solution of cyclohexanol in pure benzene and in benzene solutions of cyclohexanol, as well as the heat of dilution of benzene solutions of cyclohexanol with pure benzene or with dilute benzene solution of cyclohexanol were measured at 298.15 K. The concentration dependence of the relative apparent molar enthalpy of the solute in the concentration range up to  $1.3 \text{ mol kg}^{-1}$  was expressed as a second degree polynomial. On the basis of the relative partial molal enthalpies of solvent and solute, the values of the practical osmotic coefficient and molal activity coefficient of solute at 298.15 K were obtained from the respective values at the freezing point of benzene. The non-ideality of the system investigated is discussed in terms of the excess thermodynamic functions and with a semi-ideal association model including an extended series of multimers, in which the stepwise association constants for the successive association reactions are equal. The fractions of non-H-bonded molecules were obtained from the thermochemical data. The stepwise association constant at 298.15 K was determined by a curve-fitting method. The values of enthalpy and entropy changes, accompanying the stepwise association reactions, were calculated from the temperature dependence of the stepwise association constants via the van't Hoff relation, and the thermodynamic data discussed on the basis of formation of linear oligomeric species only.

### INTRODUCTION

Due to the extremely non-ideal behaviour of alcohol solutions in non-polar solvents, their physico-chemical properties have been extensively studied by many investigators [1]. The experimental work has been mainly based on the analysis of colligative properties, IR absorption, and dielectric studies, as well as on calorimetric measurements. These data suggested the presence of associated alcohol species, either in the linear or cyclic form, or both. With the assumption that the heat effects are due entirely to the breaking of hydrogen bonds between alcohol molecules, from the calorimetric data the chemical association model can be justified [2].

In this paper the heat of solution of cyclohexanol in pure benzene or in benzene solutions of cyclohexanol, as well as the heat of dilution of benzene

solutions of cyclohexanol with pure benzene or with a dilute benzene solution of cyclohexanol, were determined at 298.15 K. The aim of this investigation was to give additional thermochemical information on this system to that obtained previously [3] by cryoscopic, IR spectrophotometric and electric permittivity measurements, and to support the association model adopted for this system on the basis of its colligative and IR spectrophotometric data.

## EXPERIMENTAL

Benzene (Riedel de Hen) was purified as in ref. 4.

Cyclohexanol (Riedel de Hen), was dried over anhydrous calcium chloride, purified by vacuum distillation, and stored over a 0.4-nm molecular sieve in a closed container.

Solutions of cyclohexanol in benzene were prepared from dry cyclohexanol on a molar concentration scale ( $\text{mol l}^{-1}$ ). Their respective molalities ( $\text{mol kg}^{-1}$ ) were calculated by means of solution density [3].

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 ref. 5. The volume of the reaction vessel was  $100 \text{ cm}^3$ . The bath temperature and starting temperature of all runs were both  $298.15 \pm 0.05 \text{ K}$ . The system was tested by measuring the heat of solution of potassium chloride in water up to  $0.04 \text{ mol l}^{-1}$  at 298.15 K. The value of  $17.361 \pm 0.054 \text{ kJ mol}^{-1}$  determined is close to the value of the heat of solution for potassium chloride given in ref. 6. The heat of solution and the heat of dilution were determined by the glass ampoule technique.

In solution experiments a known amount of cyclohexanol was sealed in a glass ampoule of  $1 \text{ cm}^3$  volume. After thermostating, the ampoule was broken and solute dissolved in  $100 \text{ cm}^3$  of pure benzene ( $n_1 = 1.118 \text{ mol}$ ) (experiment (A)), or in  $100 \text{ cm}^3$  of benzene solutions of cyclohexanol up to  $0.40 \text{ mol l}^{-1}$  (experiments (B)–(F)). On the other hand, in dilution experiments a known amount of a benzene solution of cyclohexanol from 0.26 to  $1.00 \text{ mol l}^{-1}$  was sealed in a glass ampoule of  $1 \text{ cm}^3$  volume. After thermostating and breaking the ampoule, the solution was mixed either with  $100 \text{ cm}^3$  of pure benzene (experiment (A)) or with  $100 \text{ cm}^3$  of a dilute benzene solution of cyclohexanol,  $0.02 \text{ mol l}^{-1}$  (experiment (B)). In both solution and dilution procedures the heats absorbed were recorded.

## RESULTS AND DISCUSSION

From the solution of  $n'_2$  moles of solute in  $n_1$  moles of solvent, a mixture

of composition  $n'_2\text{N}(n_1/n'_2\text{S})$  is obtained [7]

$$n'_2\text{N} + n_1\text{S} = n'_2\text{N}\left(\frac{n_1}{n'_2}\text{S}\right) \quad (1)$$

where N and S stand for solute and solvent, respectively. For this process the enthalpy change is  $n'_2 \Delta_{\text{sol}} H_{\text{int}}(n_1/n'_2\text{S})$  (J), where  $\Delta_{\text{sol}} H_{\text{int}}(n_1/n'_2\text{S})$  ( $\text{J mol}^{-1}$ ) is the integral heat of solution per mole of solute.

If  $n''_2$  moles of solute are added to solution (1), the following mixture results

$$n''_2\text{N} + n'_2\text{N}\left(\frac{n_1}{n'_2}\text{S}\right) = n_2\text{N}\left(\frac{n_1}{n_2}\text{S}\right); n_2 = n'_2 + n''_2 \quad (2)$$

The enthalpy change accompanying this process in  $n''_2 \Delta_{\text{sol}} H_{\text{inter}}$  (J), where  $\Delta_{\text{sol}} H_{\text{inter}}$  ( $\text{J mol}^{-1}$ ) is the enthalpy change per mole of solute added to the initial solution. Thus, the enthalpy change of solution of  $n_2$  moles of solute in  $n_1$  moles of solvent can be calculated from

$$n_2 \Delta_{\text{sol}} H_{\text{int}}\left(\frac{n_1}{n_2}\text{S}\right) = n'_2 \Delta_{\text{sol}} H_{\text{int}}\left(\frac{n_1}{n'_2}\text{S}\right) + n''_2 \Delta_{\text{sol}} H_{\text{inter}} \quad (3)$$

The experimental results, compiled in Table 1, were treated as follows: in experiment (A) the values of enthalpy change  $n'_2 \Delta_{\text{sol}} H_{\text{int}}(n_1/n'_2\text{S})$  (J) were plotted as a function of  $n'_2$  moles of solute dissolved. A smoothed curve was drawn through the experimental points. On the other hand, the smoothed curve values of  $n'_2 \Delta_{\text{sol}} H_{\text{int}}(n_1/n'_2\text{S})$  (J), relating to the initial solutions in the calorimetric cell, were added to the values of the enthalpy change  $n''_2 \Delta_{\text{sol}} H_{\text{inter}}$  (J) obtained from experiments (B) – (F). In such a way, the enthalpy changes of solution of  $n_2 = (n'_2 + n''_2)$  moles of cyclohexanol in  $100 \text{ cm}^3$  of benzene up to  $0.6 \text{ mol kg}^{-1}$  were obtained (see relation (3)). The smoothed curve data as a function of  $n_2$  were given by a polynomial

$$n_2 \Delta_{\text{sol}} H_{\text{int}}\left(\frac{n_1}{n_2}\text{S}\right) = an_2 + bn_2^2 + cn_2^3 \quad (4)$$

with the regression coefficients of  $a = 16\,035$ ,  $b = -121\,440$ ,  $c = 489\,355$  and the standard error of the estimate  $s = 1.4$  J, as calculated by the method of least squares.

From the integral heat of solution,  $n_2 \Delta_{\text{sol}} H_{\text{int}}(n_1/n_2\text{S})$  (J), given by [8]

$$n_2 \Delta_{\text{sol}} H_{\text{int}}\left(\frac{n_1}{n_2}\text{S}\right) = n_1 \bar{L}_1 + n_2 (\bar{L}_2 - L_2^*) \quad (5)$$

where  $\bar{L}_1$  ( $\text{J mol}^{-1}$ ) and  $\bar{L}_2$  ( $\text{J mol}^{-1}$ ) are the relative partial molar enthalpies of solvent and solute, respectively, and  $L_2^*$  ( $\text{J mol}^{-1}$ ) is the relative molar enthalpy of pure solute, the value of  $L_2^*$  was obtained as the limiting value of the derivative  $\delta[n_2 \Delta_{\text{sol}} H_{\text{int}}(n_1/n_2\text{S})]/\delta n_2$  for constant  $n_1$  and as  $n_2 \rightarrow 0$ . On the basis of relation (4), the value of the relative molar enthalpy of pure

TABLE 1

Enthalpies of solution of cyclohexanol in pure benzene,  $n'_2 \Delta_{\text{sol}} H_{\text{int}} \left( \frac{n_1}{n'_2} \text{S} \right)$ , or in benzene solutions of cyclohexanol of concentration  $m'$  (mol kg<sup>-1</sup>),  $n''_2 \Delta_{\text{sol}} H_{\text{inter}}$ , at 298.15 K

$n'_2$ (mol)	$m$ (mol kg <sup>-1</sup> )	$n'_2 \Delta_{\text{sol}} H_{\text{int}} \left( \frac{n_1}{n'_2} \text{S} \right)$ (J)	$\delta^a$ (J)
<i>Experiment (A): pure benzene</i>			
0.00008	0.0009	1.30	0.04
0.00027	0.0031	4.40	0.07
0.00076	0.0087	12.32	0.19
0.00103	0.0117	16.79	0.53
0.00174	0.0200	27.66	0.00
0.00221	0.0253	34.44	-0.43
0.00314	0.0360	48.65	-0.62
0.00373	0.0427	57.34	-0.86
0.00479	0.0548	73.34	-0.78
0.00567	0.0649	85.59	-1.62
0.00637	0.0729	97.50	0.03
0.00735	0.0842	112.03	0.26
0.00855	0.0979	127.25	-0.36
$n''_2$ (mol)	$m$ (mol kg <sup>-1</sup> )	$n''_2 \Delta_{\text{sol}} H_{\text{inter}}$ (J)	$\delta^b$ (J)
<i>Experiment (B): <math>m' = 0.0576</math></i>			
0.00214	0.0823	32.10	0.74
0.00433	0.1075	61.94	-0.50
0.00544	0.1203	77.90	0.10
0.00654	0.1330	92.55	-0.21
0.00796	0.1493	112.00	0.27
<i>Experiment (C): <math>m' = 0.1158</math></i>			
0.00091	0.1264	12.97	0.50
0.00162	0.1346	22.94	0.85
0.00317	0.1525	43.36	0.64
0.00572	0.1820	75.80	0.18
0.00813	0.2100	106.42	0.88
<i>Experiment (D): <math>m' = 0.2341</math></i>			
0.00107	0.2466	11.96	-0.58
0.00200	0.2575	24.13	0.87
0.00268	0.2655	31.86	0.86
0.00574	0.3013	64.86	0.03
0.00847	0.3332	92.85	-0.87
<i>Experiment (E): <math>m' = 0.3551</math></i>			
0.00111	0.3682	11.46	0.36
0.00203	0.3791	20.23	0.10
0.00394	0.4017	39.09	0.61
0.00566	0.4220	54.36	-0.20
0.00832	0.4536	77.89	-0.68

cyclohexanol is equal to  $-16035 \text{ J mol}^{-1}$ , i.e., the negative value of regression coefficient  $a$ . Thereby, the number of moles of solvent,  $n_1$ , for the system investigated was considered constant, due to the small difference in

TABLE 1 (continued)

$n_2''$ (mol)	$m$ (mol kg <sup>-1</sup> )	$n_2''\Delta_{\text{sol}}H_{\text{inter}}$ (J)	$\delta^b$ (J)
<i>Experiment (F): <math>m' = 0.4787</math></i>			
0.00117	0.4927	9.89	-0.06
0.00191	0.5016	16.25	0.10
0.00382	0.5244	31.92	0.04
0.00581	0.5482	47.95	0.18
0.00821	0.5770	65.61	-0.77

$$\delta^a = n_2''\Delta_{\text{sol}}H_{\text{int}}(n_1/n_2\text{S})(\text{exp.}) - n_2''(\phi L_2' - L_2')(\text{calc.}).$$

$$\delta^b = n_2''\Delta_{\text{sol}}H_{\text{inter}}(\text{exp.}) - (n_2\phi L_2 - n_2'\phi L_2' - n_2''L_2')(\text{calc.}).$$

its values throughout the experiments. On the other hand, the integral heat of solution per mole of solute at infinite dilution,  $\Delta_{\text{sol}}H_{\text{int}}^0(n_1/n_2\text{S})$  (J mol<sup>-1</sup>) is equal to the value of regression coefficient  $a$  of relation (4).

The relative apparent molar enthalpy of solute,  $\phi L_2$  (J mol<sup>-1</sup>), can be calculated from the integral heat of solution per mole of solute and the relative molar enthalpy of pure solute via the relation [8]

$$\phi L_2 = \Delta_{\text{sol}}H_{\text{int}}\left(\frac{n_1}{n_2}\text{S}\right) + L_2' \quad (6)$$

Taking into account relations (4) and (6), the following analytical expression for  $\phi L_2$  as a function of  $n_2$  was obtained from solution experiments

$$\phi L_2 = bn_2 + cn_2^2 \quad (7)$$

In the dilution experiments, experiment (A) included measuring the enthalpy change when a solution containing  $n_2'$  moles of solute with an initial molality  $m'$  was diluted with 100 cm<sup>3</sup> of pure benzene to give a final solution of molality  $m$ . The enthalpy change,  $\Delta_{\text{dil}}H$  (J), is given by [8]

$$\Delta_{\text{dil}}H = n_2'(\phi L_2 - \phi L_2') \quad (8)$$

where  $\phi L_2$  and  $\phi L_2'$  are the relative apparent molar enthalpies at concentration  $m$  and  $m'$ , respectively. Since for the system investigated the relative apparent molar enthalpy of solute can be expressed as a second degree polynomial

$$\phi L_2 = Bm + Cm^2 \quad (9)$$

where  $B$  and  $C$  are the regression coefficients, from relations (8) and (9) it follows that

$$\frac{\Delta_{\text{dil}}H}{n_2'(m - m')} = B + C(m + m') \quad (10)$$

Taking into account the experimental data from Table 2, for experiment (A), the values of coefficients  $B = -(10\,135 \pm 10)$  and  $C = (3300 \pm 100)$  were obtained from relation (10) by a least-squares analysis.

TABLE 2

Enthalpies of dilution,  $\Delta_{\text{dil}}H$ , of benzene solutions of cyclohexanol with pure benzene, or with dilute benzene solution of cyclohexanol of concentration  $m'$  (mol kg<sup>-1</sup>) at 298.15 K

$n'_2$ (mol)	$m$ (mol kg <sup>-1</sup> )	$\Delta_{\text{dil}}H$ (J)	$\delta^a$ (J)	
<i>Experiment (A) (pure benzene): <math>m' = 1.2826</math></i>				
0.00084	0.0095	6.24	0.07	
0.00068	0.0078	5.07	-0.01	
0.00055	0.0062	4.08	0.04	
0.00040	0.0046	3.02	0.01	
0.00026	0.0030	1.95	-0.02	
0.00016	0.0018	1.19	0.01	
0.00009	0.0010	0.66	0.00	
$m' = 0.9340$				
0.00062	0.0071	4.11	0.07	
0.00049	0.0056	3.24	0.05	
0.00035	0.0039	2.28	0.05	
0.00022	0.0026	1.48	-0.01	
0.00012	0.0014	0.77	-0.03	
$m' = 0.6052$				
0.00044	0.0050	2.14	0.00	
0.00035	0.0040	1.67	-0.04	
0.00032	0.0037	1.56	-0.03	
0.00025	0.0029	1.25	0.01	
0.00018	0.0020	0.87	0.01	
$n'_2$ (mol)	$m''$ (mol kg <sup>-1</sup> )	$m$ (mol kg <sup>-1</sup> )	$\Delta_{\text{dil}}H$ (J)	$\delta^b$ (J)
<i>Experiment (B): <math>m' = 0.0230</math></i>				
0.00086	1.2820	0.0326	6.04	0.04
0.00069	1.0017	0.0306	4.36	0.01
0.00066	0.9336	0.0303	4.00	0.00
0.00050	0.7341	0.0285	2.58	0.00
0.00043	0.6049	0.0277	1.90	-0.01
0.00021	0.2941	0.0252	0.47	0.00

$\delta^a = \Delta_{\text{dil}}H(\text{exp.}) - n'_2(\phi L_2 - \phi I'_2)(\text{calc.})$ .

$\delta^b = \Delta_{\text{dil}}H(\text{exp.}) - (n_2\phi L_2 - n'_2\phi L'_2 - n''_2\phi L''_2)(\text{calc.})$ .

In dilution experiment (B), the enthalpy change is measured when a concentrated solution of molality  $m''$  is mixed with a dilute solution of molality  $m'$  to give a final solution of molality  $m$ . The enthalpy change for such an experiment is given by [8]

$$\Delta_{\text{dil}}H = n_2\phi L_2 - n'_2\phi L'_2 - n''_2\phi L''_2 \quad (11)$$

where  $n_2 = n'_2 + n''_2$ ,  $n'_2$  and  $n''_2$  denote the number of moles of solute in the final solution, the calorimetric cell before mixing and in the added solution, respectively. Considering relations (9) and (11), the following expression

$$\frac{\Delta_{\text{dil}}H}{n_2m - n'_2m' - n''_2m''} = B + C \frac{n_2m^2 - n'_2m'^2 - n''_2m''^2}{n_2m - n'_2m' - n''_2m''} \quad (12)$$

was applied for calculation of the coefficients  $B$  and  $C$  of relation (9). Values for the coefficients  $B$  and  $C$  of  $-(10145 \pm 15)$  and  $(3310 \pm 16)$ , respectively, were obtained on the basis of relation (12) by the method of least squares. Thus, from both the solution and dilution experiments, the relative apparent molar enthalpies of cyclohexanol in benzene solutions as a function of molality up to  $1.3 \text{ mol kg}^{-1}$  at  $298.15 \text{ K}$  can be calculated from relation (9), with the average values of coefficients  $B = -(10220 \pm 50)$  and  $C = (3390 \pm 40)$ ; the standard error of the estimate,  $s$ , amounts to  $40 \text{ J mol}^{-1}$ .

All the experimental data were recalculated: for the solution experiment (A) from the relation

$$n'_2 \Delta_{\text{sol}} H_{\text{int}} \left( \frac{n_1}{n'_2} S \right) = n'_2 (\phi L'_2 - L_2) \quad (13)$$

for the solution experiments (B) – (F) through

$$n''_2 \Delta_{\text{sol}} H_{\text{inter}} = n_2 \phi L_2 - n'_2 \phi L'_2 - n''_2 L_2 \quad (14)$$

and for the dilution experiments (A) and (B) via relations (8) and (11), respectively. In the recalculations, the average values of coefficients  $B$  and  $C$ , and  $L_2 = -16035 \text{ J mol}^{-1}$  were used. The recalculated values are, within experimental error, equal to the experimental data (see Tables 1 and 2).

In addition, the relative partial molar enthalpies of solvent,  $\bar{L}_1$  ( $\text{J mol}^{-1}$ ), and solute,  $\bar{L}_2$  ( $\text{J mol}^{-1}$ ), for the system investigated, were calculated from the relations [8]

$$\bar{L}_1 = -\frac{1}{n_1} (Bm^2 + 2Cm^3) \quad (15)$$

and

$$\bar{L}_2 = 2Bm + 3Cm^2 \quad (16)$$

respectively, taking into account the average values of coefficients  $B$  and  $C$ , and for  $n_1 = 12.802 \text{ mol kg}^{-1}$  of benzene. The concentration dependence of  $\phi L_2$ ,  $\bar{L}_1$  and  $\bar{L}_2$  are given in Fig. 1.

With the assumption that the relative partial molar enthalpies of solvent and solute are temperature independent in the temperature range from  $T' = 278.68 \text{ K}$ , i.e., the freezing point of benzene, to  $T = 298.15 \text{ K}$ , the values of the practical osmotic coefficient,  $\phi$ , and the molal activity coefficient of solute,  $\gamma_2$ , at concentrations up to  $\sim 0.25 \text{ mol kg}^{-1}$  and  $298.15 \text{ K}$  were calculated from their values at the freezing point of benzene [3] via the relations [8,9]

$$\phi = \phi' + x(Bm + 2Cm^2) \quad (17)$$

where  $\phi'$  is the practical osmotic coefficient at  $T'$  and

$$x = -\frac{T - T'}{n_1 M_1 R T T'} = -2.82 \times 10^{-5} \text{ mol J}^{-1} \quad (18)$$

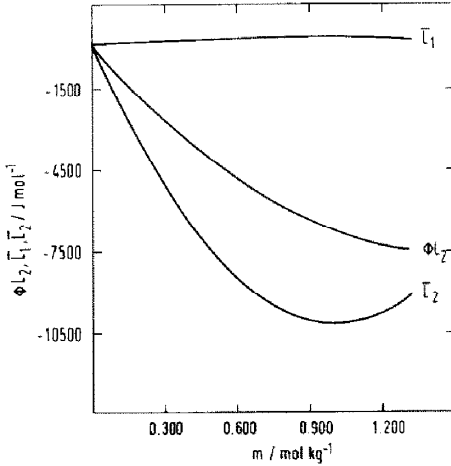


Fig. 1. Concentration dependence of  $\phi L_2$ ,  $\bar{L}_1$  and  $\bar{L}_2$  for cyclohexanol + benzene mixtures at 298.15 K.

where  $M_1$  ( $\text{kg mol}^{-1}$ ) is the molar mass of the solvent,  $R$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) is the gas constant, and

$$\ln \gamma_2 = \ln \gamma'_2 + y(2Bm + 3Cm^2) \quad (19)$$

where  $\ln \gamma'_2$  is the molal activity coefficient of solute at  $T'$  and

$$y = -\frac{T - T'}{RTT'} = -2.82 \times 10^{-5} \text{ mol J}^{-1} \quad (20)$$

From relations (17) and (19) it follows that at concentrations up to  $\sim 0.25 \text{ mol kg}^{-1}$  the values of  $\phi$  and  $\gamma_2$  at 298.15 K are  $\sim 10\%$  higher than their values at the freezing point of benzene.

The non-ideality of the system up to  $0.25 \text{ mol kg}^{-1}$  was interpreted in terms of the excess thermodynamic functions, i.e., the excess Gibbs free energy,  $G^{\text{ex}}$  ( $\text{J kg}^{-1}$ ), excess enthalpy,  $H^{\text{ex}}$  ( $\text{J kg}^{-1}$ ) and excess entropy,  $S^{\text{ex}}$  ( $\text{J kg}^{-1} \text{K}^{-1}$ ) at 298.15 K, following the expressions [10]

$$G^{\text{ex}} = mRT[1 - \phi' - x(Bm + 2Cm^2) + \ln \gamma'_2 + y(2Bm + 3Cm^2)] \quad (21)$$

$$H^{\text{ex}} \equiv \phi L_2 = Bm^2 + Cm^3 \quad (22)$$

and

$$TS^{\text{ex}} = (\phi' - \ln \gamma'_2 - 1)RTm + [1 + (x - 2y)RT]Bm^2 + [1 + (2x - 3y)RT]Cm^3 \quad (23)$$

respectively. The excess thermodynamic functions, together with the excess Gibbs free energy,  $G^{\text{ex}'}$ , at 278.68 K [3] as a function of molality ( $\text{mol kg}^{-1}$ ) are shown in Fig. 2. From Fig. 2 it can be seen that the values of  $H^{\text{ex}}$  and  $TS^{\text{ex}}$  are equal and much more negative than the values of  $G^{\text{ex}}$  at 298.15 K. Since  $G^{\text{ex}}$  values are practically zero, the non-ideality is primarily manifest from  $H^{\text{ex}}$  and  $TS^{\text{ex}}$  values.



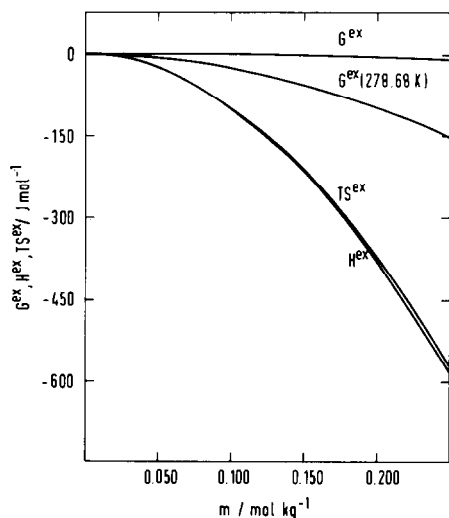


Fig. 2. Concentration dependence of excess thermodynamic functions for cyclohexanol + benzene mixtures at 298.15 K, together with excess Gibbs free energy at 278.68 K.

In addition, the non-ideal behaviour of the system up to  $1.3 \text{ mol kg}^{-1}$  was interpreted on the basis of the association processes which occur among solute monomeric units to form higher oligomeric species. As before [3], the simplest type of association for solute molecules was postulated, i.e., the values of stepwise association constant,  $K_q$ , for the successive association reactions are assumed equal;  $K_q \equiv K$ .

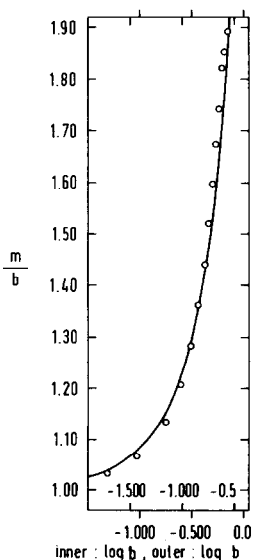


Fig. 3. Normalized curve  $m/b(\log b)$  superimposed on the experimental data  $m/b(\log b)$  for cyclohexanol + benzene mixtures at 298.15 K.

Postulating that the heat of solution per mole of cyclohexanol in benzene is entirely due to breaking hydrogen bonds among alcohol molecules, the fraction of non-H-bonded molecules,  $\alpha_1$ , is given by [11]

$$\alpha_1 = \frac{\Delta_{\text{sol}} H_{\text{int}}(n_1/n_2 S)}{\Delta_{\text{sol}} H_{\text{int}}^0(n_1/n_2 S)} = 1 - \frac{1}{L_2} (Bm + Cm^2) \quad (24)$$

In this case, the concentration of monomer is  $b = \alpha_1 m$ .

In Fig. 3 the experimental points  $m/b$  ( $\log b$ ) are superimposed on the normalized curve  $m/b$  ( $\log b$ ) [12] in the position of the best fit; the normalized variable  $\mathbf{b} = Kb$ . The determined value of  $\log K$  is  $-0.41$ ;  $K = 0.39$ . From the values of constant  $K$  determined by the cryoscopic method at the freezing point of benzene [3], the calorimetric method at 298.15 K and the IR spectrophotometric method at 303.65 K [3], the approximate value of the enthalpy change,  $\Delta H = -41.9 \text{ kJ mol}^{-1}$ , as well as of the entropy change,  $\Delta S = -147 \text{ J mol}^{-1} \text{ K}^{-1}$ , accompanying the stepwise association reactions were calculated via the van't Hoff relation (see Fig. 4).

From the van't Hoff plot, it is evident that the three different experimental techniques give a satisfactory explanation of the experimental data, using a semi-ideal association model including an extended series of multimers, in which the values of the stepwise association constant,  $K$ , are equal, and the self-association constant  $\beta_q$  is  $K^{q-1}$ ;  $q \geq 2$ . Since the values of enthalpy and entropy changes for the stepwise association reactions are constant and independent of the number of monomer units in the oligomeric species, a linear structure for the oligomeric species of cyclohexanol in benzene solutions seems to be indicated.

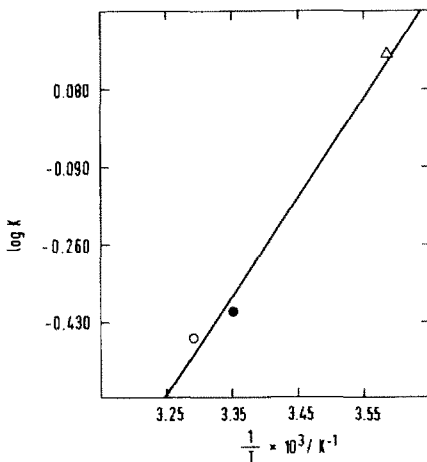


Fig. 4. Temperature dependence of stepwise association constants for cyclohexanol + benzene mixtures; ( $\Delta$ ) cryoscopic method, ( $\bullet$ ) calorimetric method, and ( $\circ$ ) IR spectrophotometric method.

## ACKNOWLEDGEMENTS

The authors thank Mrs. J. Burger for her skilful technical assistance. Financial support for this work was provided by the Slovene Research Community, Ljubljana, and the National Science Foundation, Washington, DC.

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