Limiting Activity Coefficients in Alcohol-Containing Organic Solutions from Headspace Gas Chromatography

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As part of a project on thermodynamic properties of hydrogen-bonding solutions, limiting activity coefficients were measured in 10 binary systems of the type alcohol + solvent at temperatures between 293 K and 333 K. The systems are: methanol + tetrachloromethane, ethanol + hexane, ethanol + heptane, ethanol + cyclohexane, ethanol + tetrachloromethane, 2-methylpropan-2-ol (*tert*-butyl alcohol) + hexane, 1-hexanol + hexane, 1-hexanol + cyclohexane, 1-hexanol + tetrachloromethane, and 1-hexanol + toluene. Furthermore, new experimental results are reported on the vapor−liquid equilibrium for the system ethanol + heptane at 313 K. The measurements were carried out with a newly built headspace gas chromatograph.

Introduction

Developing predictive models for fluid properties of hydrogen-bonding mixtures remains one of the challenges in applied thermodynamics. An extensive, reliable database is crucial for that development. In the present work, results of limiting activity coefficient measurements are presented for binary systems alcohol + solvent at temperatures between 293 K and 333 K. The solvents are both inert (alkanes) and solvating (tetrachloromethane, toluene). The systems are: methanol + tetrachloromethane, ethanol + hexane, ethanol + heptane, ethanol + cyclohexane, ethanol + tetrachloromethane, 2-methylpropan-2-ol (*tert*-butyl alcohol) + hexane, 1-hexanol + hexane, 1-hexanol + cyclohexane, 1-hexanol + tetrachloromethane, and 1-hexanol + toluene. Vapor−liquid equilibria on ethanol + heptane are reported over the whole concentration range at 313 K.

The measurements were carried out in the frame of a project that aims at combining classic thermodynamic data with results on H-bonding obtained by IR spectroscopy (Asprion, 1996; Hasse, 1996). For most of the systems studied here, IR-spectroscopic data on H-bonding are available (Asprion, 1996).

For the measurements, a new headspace gas chromatograph was built. The equipment as well as the operation and calibration are described.

Experimental Section

Outline. Headspace gas chromatography is a suitable method for measuring limiting activity coefficients in liquid mixtures. In such experiments, liquid samples of known composition are filled into small thermostated cells. After equilibrium is reached, the gas above the liquid is analyzed by gas chromatography. From the gas-chromatographic results, partial pressures are calculated using calibration curves. The composition of the liquid is known from the gravimetric preparation of the sample. Activity coefficients are calculated from the partial pressures, the composition of the liquid sample, and pure component saturation pressure data. Limiting activity coefficients are determined by extrapolation to infinite dilution.

Preparation of Samples. All substances were purchased in the highest available quality and used without further purification. Purities and suppliers are summarized in Table 1. The samples (≈20 g) were prepared gravimetrically using an analytical balance with a resolution of 0.0001 g (Mettler AE 240). Care was taken to avoid evaporation during and after the gravimetric preparation.

Equipment and Operation. The main components of the headspace chromatograph used in the present work are the thermostated cell holder, the sampling system, and the gas chromatograph. The general features of the new headspace chromatograph are similar to those of the apparatus of Hussam and Carr (1985). Figure 1 shows a schematic of the apparatus.

Eight sample cells are mounted in a liquid-thermostated cell holder. (Only one of them is shown in Figure 1.) The sample cells are glass vials closed by multilayer rubber-PTFE seals. The vials (volume: ~8 mL) are filled with about 3 mL of the liquid mixture. The temperature is measured in the thermostating bath of the cell holder with a platinum resistance thermometer. From test measurements, it is known that the difference between the measured temperature and the temperature in the cells is less than ±0.05 K. The overall accuracy of the temperature measurement is about ±0.1 K.

The sample cells are connected to a multiposition valve (Vici Valco, type CSD16E) by stainless steel capillaries with needlelike ends. The multiposition valve allows to connect each of the sample cells to a sample valve (Vici Valco, type C6WE), in which the samples for the gas-chromatographic analysis are taken. Both the multiposition and the sample valve are mounted in the same liquid-thermostated valve holder and are operated pneumatically. The multiposition valve has 16 positions, 8 of which allow an individual connection of each of the cells to the sample valve. The remaining eight positions are used for purging. The sample valve has two positions: one is used for the pressurization of the cells, purging and sampling; in the

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S0021-9568(97)00136-2 CCC: $15.00

Table 1. Substances, Suppliers, and Purities

substance	supplier	purity/mass %
methanol	Merck	99.7
ethanol	Berkel[a]	99.9
2-methylpropan-2-ol	Riedel-de Haën	99.5
1-hexanol	Fluka	99.0
tetrachloromethane	Merck	99.7
cyclohexane	Merck	99.7
hexane	Merck	99.0
toluene	Merck	99.7
heptane	Riedel-de Haën	99.0

[a] Pfälzische Sprit- und chemische Fabrik, H. Berkel.

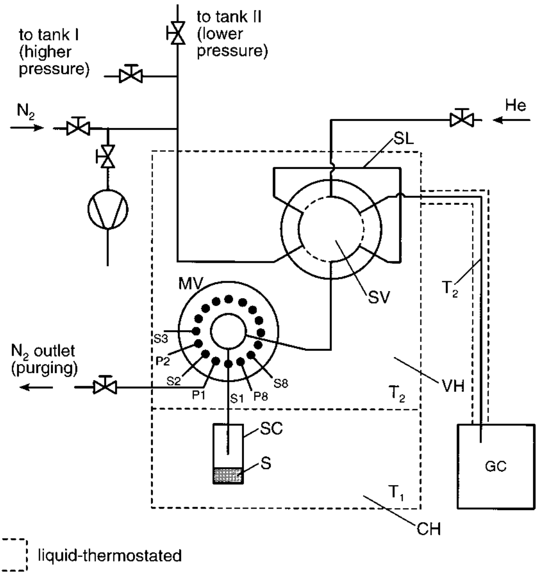

Figure 1. Schema of the headspace chromatograph (GC gas chromatograph, He helium (carrier gas), MV multiposition valve, (S1–S8 sample positions, P1–P8 purge positions), N_2 nitrogen, S sample, CH liquid-thermostated cell holder (temperature T_1), SC sample cell, SL sample loop, SV sample valve, VH liquid-thermostated valve holder (temperature $T_2 > T_1$)).

other the sample is transferred to the gas chromatograph (Hewlett-Packard, type 5890 series II, integration: HP 3393 A). The gas chromatograph was equipped with a Porapak P packed column and a thermal conductivity detector. The feed line was directly connected to the column without passing the injection block.

The temperature of the valve holder was kept constant at 353 K for the measurements of the present work (the temperature of the cell holder was never above 333 K). Also the feed line to the gas chromatograph was thermostated to about 353 K. No problems with condensation in the sampling system were observed.

The operation of the headspace chromatograph consists of a pressurization and a sampling run. First, the eight cells are pressurized one after another in a pressurization run with high-purity nitrogen to a constant pressure of about 130 kPa. That pressure is maintained constant by a large (~300 dm^3) tank filled with nitrogen and kept at a constant temperature, as it is deposited deep in the ground outside the laboratory. In the sample run, the pressurized cells are connected one after another to the sample valve (switching of the multiposition valve). The gas phase in pressurized cell (130 kPa) expands to a pressure of about 100 kPa, and the loop of the sample valve is filled. That lower pressure is kept constant in the same way as the higher pressure, using a second large tank (~300 dm^3) also deposited in the ground outside the laboratory. The sample valve is then switched, and the sample is transferred to the gas chromatograph. After the sample is taken, the multiposition valve is switched into a purge position and the sampling system is purged with nitrogen.

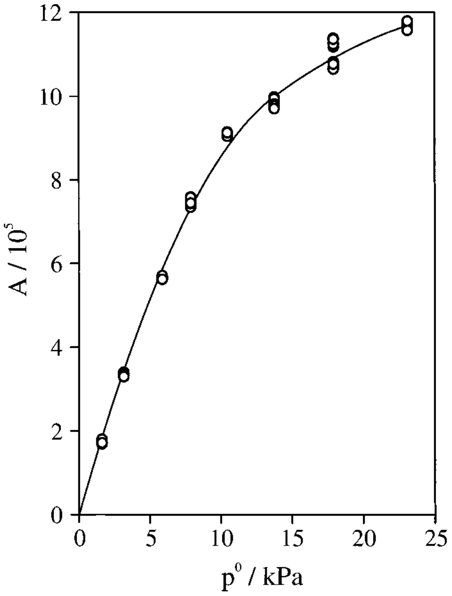

Figure 2. Typical calibration curve: relation between peak area *A* and partial pressure for ethanol; ○ exptl; — corr.

The switching cycles of the pressurization and the sampling run were optimized in test runs. In these runs, it was also verified that equilibrium is reached in the cells before sampling. The operating conditions were kept constant during calibration and measurements. For the operation of the pneumatic valves an electronic controller was used.

Calibration

The primary data collected in headspace chromatographic measurements of limiting activity coefficients is the peak area of the diluted component. From that peak area, in a first step, the partial pressure of the dilute component has to be determined. The peak area is a function of the mass of the component passing the detector. In our experiments, that mass is identical with the mass of the component in the loop of the sample valve. As volume and temperature of the sample in the valve are kept constant, the peak area is proportional to the partial pressure of the component in the sample loop and, hence, directly related to the partial pressure in the sample cell. However, there is no strict proportionality between peak area and partial pressure over the entire partial pressure range of interest. Therefore, the functional relation between peak area and partial pressure had to be determined from calibration measurements.

For the calibration, pure components were investigated at different temperatures. The peak area depends on the vapor pressure of the pure component in the sample cell. Figure 2 shows a typical result of such a calibration. The vapor pressures of the pure components used to derive the calibration are given in Table 2.

For the determination of the limiting activity coefficient, only the partial pressure of the diluted component was determined from such calibration curves. Only for the test measurements of vapor–liquid equilibria in the system ethanol–heptane, calibration curves for both components covering partial pressures over the entire concentration range were determined.

Table 2. Vapor Pressures of Pure Substances (Reid et al., 1987)

$$\ln(p^0/p_C) = (1 - \Theta)^{-1}[a\Theta + b\Theta^{1.5} + c\Theta^3 + d\Theta^6]$$
$$\Theta = 1 - T/T_C; \quad T_{min} \le T \le T_C$$

substance	p_c/MPa	T_c/K	a	b	c	d	T_{min}/K
methanol	8.09	512.6	−8.547 96	0.769 82	−3.108 50	1.544 81	288
ethanol	6.14	513.9	−8.518 38	0.341 63	−5.736 83	8.325 81	293
hexane	3.01	507.5	−7.467 65	1.442 11	−3.282 22	−2.509 41	220
heptane	2.74	540.3	−7.674 68	1.370 68	−3.536 20	−3.202 43	240
cyclohexane	4.07	553.5	−6.960 09	1.313 28	−2.756 83	−2.454 91	293
tetrachloromethane	4.56	556.4	−7.071 39	1.714 97	−2.899 30	−2.494 66	250
toluene	4.10	591.8	−7.286 07	1.380 91	−2.834 33	−2.791 68	309

$$\ln(p^0/\mathrm{MPa}) = a - b/(T/\mathrm{K} + c); \quad T_{min} \le T \le T_{max}$$

substance	a	b	c	T_{min}/K	T_{max}/K
2-methylpropan-2-ol	7.9320	2658.29	−95.50	293	376
1-hexanol	9.1766	4055.45	−76.49	308	430

Determination of Limiting Activity Coefficients

From the partial pressure (p_i) and the liquid-phase mole fractions (x_i), which are known from the gravimetric preparation of the samples, activity coefficients (γ_i) are calculated:

$$p^0_i x_i \gamma_i = p_i \tag{1}$$

The vapor pressure (p^0_i) was calculated according to Table 2.

No corrections for the gas-phase nonideality or for the vaporization of some of the liquids upon saturation of the gas phase were made. These corrections are small in comparison to the uncertainty of the experimental results and do not essentially change the results. For example in a most unfavorable case (low liquid volume in the cell, i.e., 3 cm^3; small solute concentration, i.e., mole fraction $x_{solute} \approx$ 0,005; high solute vapor pressure, i.e., for methanol; very high solute activity coefficient, i.e., methanol in tetrachoromethane − $\gamma_{solute} \approx 50$) less than 4% of the liquid solute vaporizes in the cell.

The uncertainty in the activity coefficient γ_i is mainly determined by the accuracy of the measurement of the partial pressure p_i. The influence of the uncertainty in the temperature measurement on $p^0_i(T)$ and the determination of the liquid-phase composition x_i is small. For each data point, the experiment was repeated from three to five times (The experiments with headspace chromatography are not time-consuming.) The standard deviation for these measurements is typically below 2%. Taking into account the uncertainty of the calibration and the noncorrected systematical influences, the overall relative error in the activity coefficient values is estimated to be about 5%.

Limiting activity coefficients were determined by extrapolating the experimental data for the activity coefficients to infinite dilution. Typically, four to six values at concentrations of the dilute component between mole fractions of about 0.005 and 0.04 were used. Extrapolation was achieved by correlating the activity coefficient with three two-parameter G^E models (Wilson, Van Laar, UNIQUAC) (Prausnitz et al., 1986) and calculating the infinite dilution activity coefficient from that correlation. The extrapolations using the Van Laar and the UNIQUAC model usually yield very similar results (relative deviations below 1%). The extrapolation using the Wilson model generally agrees well with those results. Only when the number for the limiting activity coefficient is greater than about 20, significant deviations between the extrapolations from the Wilson model and those from the two other models are observed (cf. example in Figure 3). As there is no indication on which extrapolation method to prefer, the limiting activity coefficient was calculated as the arithmetic mean of the results from the three methods. The relative error in the limiting activity coefficient introduced by the extrapolation does not exceed 5%. The overall error in the limiting activity coefficient is less than 10%.

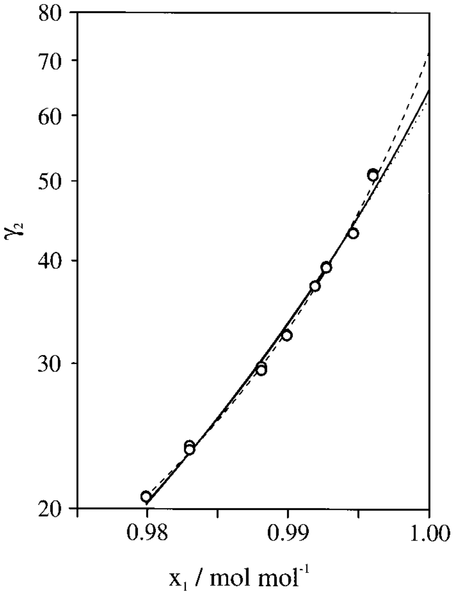

Figure 3. Extrapolation of activity coefficient data γ_2 for the system ethanol (1) + cyclohexane (2) at 293 K to infinite dilution: exptl, ○ this work; corr., — UNIQUAC; - - - Wilson; ··· van Laar.

Results

The results of the determination of limiting activity coefficients are presented in Table 3. Detailed results on the data used for the extrapolation are available elsewhere (Asprion, 1996). Table 3 gives the results from different extrapolation methods (cf. section Determination of Limiting Activity Coefficients), as well as the arithmetic mean value of these results, which is used for further discussion.

The results of the measurements of vapor−liquid equilibria in the system ethanol + heptane at 313 K are presented in Table 4.

Discussion

Vapor−Liquid Equilibria. Figure 4 shows activity coefficients determined from the vapor−liquid equilibrium measurements in the system ethanol + heptane at 313 K and compares them to the literature data of Ratcliff and Chao (1969) and Pena and Cheda (1970). Also given are the results for the limiting activity coefficients taken in

Table 3. Limiting Activity Coefficients in Systems Alcohol (1) + Solvent (2)

		$\gamma^\infty_{1,2}$				$\gamma^\infty_{2,1}$			
system	T/K	van Laar	Wilson	UNIQUAC	mean	van Laar	Wilson	UNIQUAC	mean
methanol (1) + tetrachloromethane (2)	293.2	45.9	50.8	48.1	48.3	7.48	7.48	7.48	7.48
	313.2	26.1	26.7	26.4	26.4	7.21	7.22	7.22	7.22
	333.2	13.1	13.2	13.1	13.1	6.51	6.52	6.52	6.52
ethanol (2) + hexane (1)	293.2					9.57	9.58	9.57	9.57
	313.2					8.21	8.21	8.21	8.21
	333.2					7.24	7.24	7.24	7.24
ethanol (1) + heptane (2)	293.5	46.1	51.2	46.9	48.1	12.7	12.7	12.7	12.7
	303.3	41.6	44.8	42.2	42.9	11.8	11.9	11.9	11.9
	313.1	31.3	32.5	31.5	31.8	11.1	11.1	11.1	11.1
	322.8	21.7	22.1	21.8	21.9	10.5	10.5	10.5	10.5
ethanol (1) + cyclohexane (2)	293.2	63.2	72.0	64.7	66.6				
	313.2	35.4	36.1	35.6	35.7				
	333.2	17.4	17.4	17.4	17.4				
ethanol (1) + tetrachloromethane (2)	293.2	33.0	36.6	33.5	34.4				
	313.2	19.2	19.6	19.3	19.4	4.43	4.43	4.43	4.43
	333.2	10.2	10.2	10.2	10.2	4.05	4.05	4.05	4.05
2-methylpropan-2-ol (1) + hexane (2)	303.3	16.6	17.2	16.6	16.8	3.81	3.81	3.81	3.81
	313.1	12.5	12.7	12.5	12.6	3.55	3.55	3.55	3.55
	322.8	9.49	9.56	9.49	9.51	3.31	3.31	3.31	3.31
1-hexanol (1) + hexane (2)	293.2	43.8	49.1	43.3	45.4	3.16	3.16	3.16	3.16
	313.1					3.05	3.05	3.05	3.05
	313.2	29.0	30.1	29.0	29.4	2.90	2.90	2.92	2.91
	322.8					3.02	3.02	3.02	3.02
	332.6					2.85	2.85	2.85	2.85
	333.2	19.7	19.9	19.7	19.8	2.69	2.69	2.70	2.69
1-hexanol (1) + cyclohexane (2)	293.2	47.4	51.3	47.1	48.6	2.79	2.79	2.78	2.79
	313.2	25.4	25.7	25.4	25.5	2.51	2.51	2.51	2.51
	333.2	15.8	15.9	15.8	15.8	2.32	2.30	2.31	2.31
1-hexanol (1) + tetrachloromethane (2)	293.2					2.02	2.00	2.01	2.01
	313.2	13.5	13.6	13.5	13.5	1.98	1.98	1.98	1.98
	333.2	11.6	11.7	11.6	11.6	1.94	1.94	1.94	1.94
1-hexanol (1) + toluene (2)	293.2					2.53	2.53	2.53	2.53
	313.2					2.39	2.39	2.38	2.39
	333.2					2.26	2.26	2.27	2.26

Table 4. Vapor–Liquid Equilibria in the System Ethanol (1) + Heptane (2) at 313 K

x_1/mol mol^{-1}	y_1/mol mol^{-1}	p/kPa	γ_1	γ_2
0.0292	0.3901	20.256	15.10	1.035
0.1511	0.5030	25.257	4.692	1.202
0.2905	0.5305	25.455	2.594	1.370
0.5521	0.5568	26.407	1.486	2.125
0.8802	0.6652	23.155	0.977	5.262
0.9699	0.8395	20.254	0.978	8.781

Table 5. Literature Data on the Limiting Activity Coefficient of the Investigated Systems (Except Those with Ethanol)

system	T/K	$\gamma^\infty_{1,2}$	$\gamma^\infty_{2,1}$	reference
methanol (1) + tetrachloromethane (2)	298		7.58	Landau et al. (1991)
	328	14.6	8.17	Scatchard et al. (1946)
1-hexanol (1) + hexane (2)	333		2.45	Belfer (1972)

the present work. The measurements of vapor–liquid equilibria and limiting activity coefficients of the present work were carried out independently. From Figure 4, the results from both studies of the present work agree favorably. Figure 4 also shows that the new results are in good agreement with the literature data over the entire concentration range, including the dilute regions.

The correlation shown in Figure 4 was obtained from a G^E model, in which the chemical contributions are determined on the basis of IR-spectroscopic data, while the physical contributions are modeled with UNIQUAC on the basis of limiting activity coefficients (Asprion, 1996).

Limiting Activity Coefficients. Figure 5 shows results from studies of limiting activity coefficients of ethanol (1) in heptane (2) at temperatures between 293 K and 353 K, including those of the present work. The limiting activity coefficient of ethanol (1) in heptane (2) is rather large at low temperatures but decreases rapidly with increasing temperature. This can be explained qualitatively as a result of association: At infinite dilution, the alcohol molecules are present as monomers, whereas in the pure alcohol, they are predominantly associated. Hence, there is a large difference between the state of the alcohol at infinite dilution and in the pure liquid. This results in a

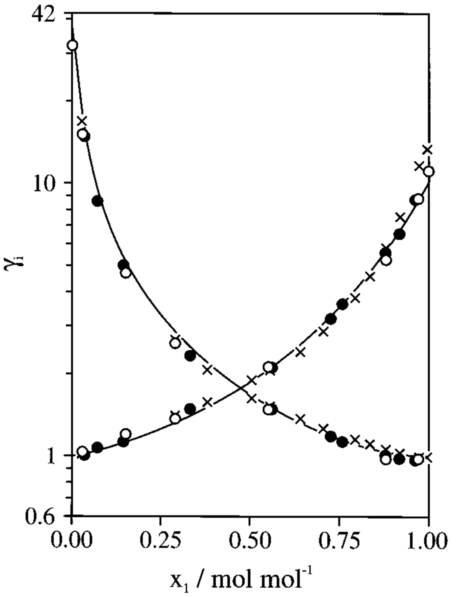

Figure 4. Activity coefficients in the system ethanol (1) + heptane (2) at 313 K: exptl, ● Ratcliff and Chao (1969), × Pena and Cheda (1970), ○ this work; calcd, — UNIQUAC-association model (Asprion, 1996).

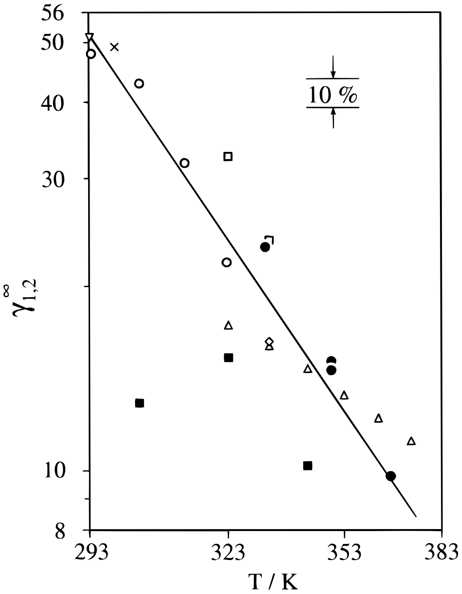

Figure 5. Limiting activity coefficients of ethanol (1) in heptane (2): exptl, × Park et al. (1987), △ Tochigi and Kojima (1976), ▽ Thomas et al. (1982b), ■ Smyth and Engel (1929), ● Cori and Delogu (1986a), ◇ Pividal et al. (1992), □ Dallinga et al. (1993), ○ this work.

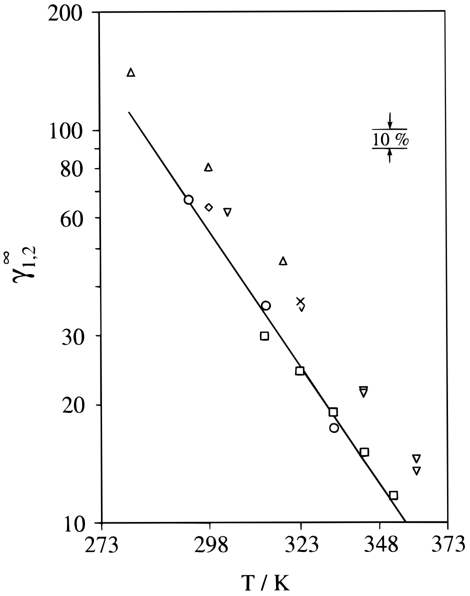

Figure 6. Limiting activity coefficients of ethanol (1) in cyclohexane (2): exptl, △ Wobst et al. (1992), ◇ Park et al. (1987), ▽ Cori and Delogu (1986b), □ Trampe and Eckert (1990), × Yang et al. (1983), ○ this work.

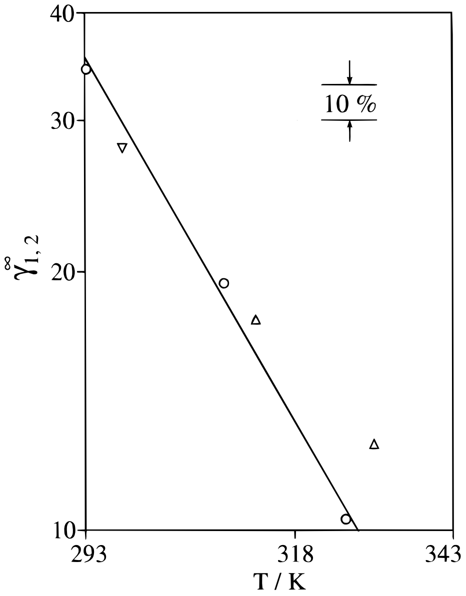

Figure 7. Limiting activity coefficients of ethanol (1) in tetrachloromethane (2): exptl, ▽ Park et al. (1987), △ Barker et al. (1953), ○ this work.

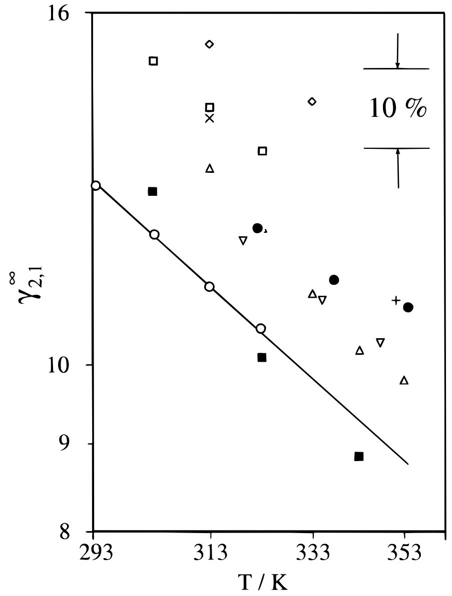

Figure 8. Limiting activity coefficients of heptane (2) in ethanol (1): exptl, × Hofstee et al. (1960), △ Tochigi and Kojima (1976), ▽ Thomas et al. (1982a), + Thomas and Eckert (1982), ■ Smyth and Engel (1929), ● Cori and Delogu (1986a), ◇ Pividal et al. (1992), □ Dallinga et al. (1993), ○ this work.

large number for the limiting activity coefficient of the alcohol. As association becomes less important at higher temperatures, also the difference of the state of the alcohol molecules at infinite dilution and in the pure liquid becomes less important and the number for the limiting activity coefficient of the alcohol decreases.

The limiting activity coefficients of ethanol (1) in heptane (2) measured in the present work generally agree well with most literature data as shown in Figure 5. Similar results were obtained for other systems (ethanol in cyclohexane, Figure 6; ethanol in tetrachloromethane, Figure 7).

Figure 8 shows data for the limiting activity coefficient of heptane (2) in ethanol (1). The limiting activity coefficient of heptane (2) in ethanol (1), $\gamma_{2,1}^{\infty}$, is distinctly smaller than the limiting activity coefficient of ethanol (1) in heptane (2), $\gamma_{1,2}^{\infty}$ (Figure 5). The influence of temperature on $\gamma_{2,1}^{\infty}$ is smaller than on $\gamma_{1,2}^{\infty}$. (The different scales of the limiting activity coefficient axis should be taken into account when Figures 5 and 8 are compared.) The results for $\gamma_{2,1}^{\infty}$ (i.e., heptane in ethanol) from the present work are predominantly lower (by up to about 25%), than the literature. However, literature data reveal a large scattering (± 25%) and the new experimental data agree within ±4% with the results by Smyth and Engel (1929). Also for other systems, for which literature data on the limiting activity coefficient of a solvent (2) in an alcohol (1) are available (cf. Figures 9 and 10 for hexane in ethanol and tetrachloromethane in ethanol, respectively), the new experimental data are lower than the literature data. Therefore, sources for systematic errors in our data on

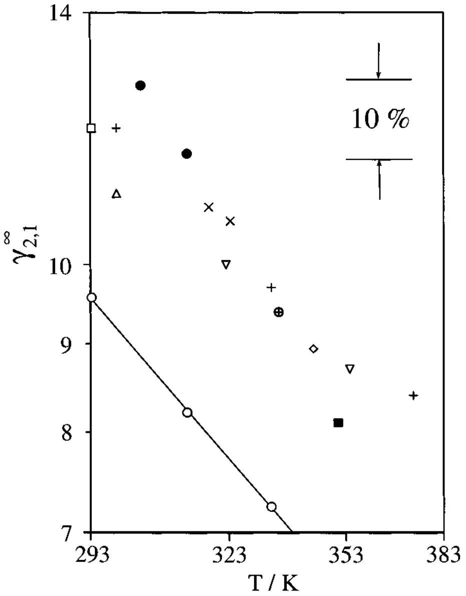

Figure 9. Limiting activity coefficients of hexane (2) in ethanol (1): exptl, ⊕ Wehe and Coates (1955), ◇ Sinor and Weber (1960), × Yang et al. (1983), △ Yang et al. (1988), ▽ Cori and Delogu (1986a), + Deal and Derr (1964), ■ Thomas et al. (1982a), □ Thomas et al. (1982b), ● Dallinga et al. (1993), ○ this work.

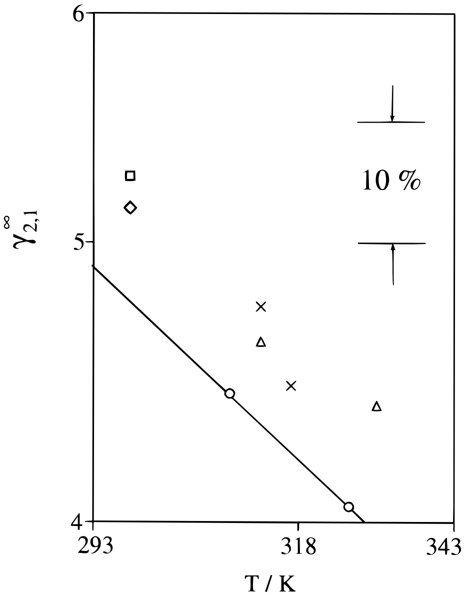

Figure 10. Limiting activity coefficients of tetrachloromethane (2) in ethanol (1); exptl, △ Barker et al. (1953), × Yang et al. (1983), □ Yang et al. (1988), ◇ Landau et al. (1991), ○ this work.

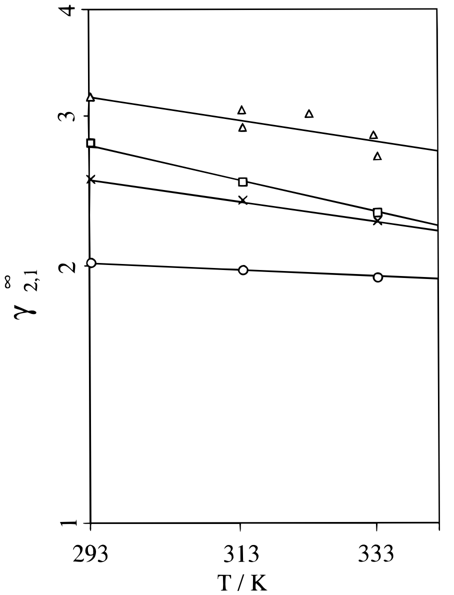

Figure 11. Limiting activity coefficients of different solvents (2) in 1-hexanol (1): exptl, this work, ○ tetrachloromethane; □ cyclohexane; △ hexane; × toluene.

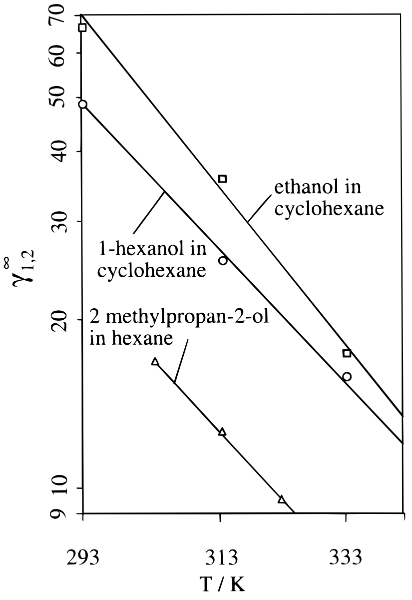

Figure 12. Limiting activity coefficients of ethanol (1a) and 1-hexanol (1b) in cyclohexane (2a) and of 2-methylpropan-2-ol (*tert*-butyl alcohol) (1c) in hexane (2b): □, ○, △ exptl, this work.

limiting activity coefficients of a solvent (2) in an alcohol (1) were critically rechecked. However, no errors exceeding the limits given above could be found. It should be noted that the measurements of the present work for the limiting activity coefficient of a solvent (2) in an alcohol (1) are generally less susceptible to errors from both experiment and evaluation than those for the limiting activity coefficients of the alcohol (1) in the solvent (2), for which our results agree well with literature data (cf. also Figures 5 to 7).

The new data can be used to discuss the influence of several variables on the limiting activity coefficient. As an example, the influence of temperature on the limiting activity coefficients of different solvents (2) in 1-hexanol (1), $\gamma^{\infty}_{2,1-\mathrm{hexanol}}$, is shown in Figure 11. The scaling of the abscissa in Figure 11 is linear in 1/*T*, and the ordinate is linear in ln $\gamma^{\infty}_{2,1}$. For all solvents (2) the data on $\gamma^{\infty}_{2,1}$ from the present work can be correlated well by straight lines in that diagram. This means that the difference between the partial molar enthalpy of the solvent (2) at infinite dilution (in 1-hexanol) and the pure solvent does not significantly depend on temperature. The numbers obtained for that enthalpy difference depend on the solvent (different slopes in Figure 11) but are rather low (between approximatly 0 for tetrachloromethane and 3.6 kJ/mol for cyclohexane). Figure 11 also shows that limiting activity coefficients of solvating solvents (e.g., toluene and tetrachloromethane) are lower than those of inert solvents (e.g., hexane and cyclohexane).

In Figure 12, limiting activity coefficients of different alcohols in similar solvents are compared. Again, plot of ln $\gamma^{\infty}_{1,\mathrm{cyclohexane}}$ over 1/*T* gives a straight line. This indicates that also the difference between the partial molar enthalpy of the alcohol at infinite dilution and that of the pure alcohol does not depend on temperature. Furthermore, Figure 12 shows that in cyclohexane the limiting activity coefficient of ethanol is larger than that of 1-hexanol. This results from the higher degree of association of pure, liquid ethanol in comparison to pure, liquid hexanol. When the temperature is increased, the limiting activity coefficient of an alcohol in cyclohexane decreases and the difference between ethanol and hexanol decreases also. Again those observations can be explained by the association of the alcohols. They are confirmed by the results for the limiting activity coefficient of 2-methylpropan-2-ol (*tert*-butyl alcohol) in hexane. It is well-known that branched alcohols show a distinctly weaker tendency to associate than linear alcohols. Therefore one expects smaller numbers for the limiting activity coefficient of 2-methylpropan-2-ol (*tert*-butyl alcohol) in hexane as, e.g., for hexanol in cyclohexane. Figure 12 shows that this expectation is in agreement with the experimental results.

Conclusions

In the present work a new headspace gas chromatograph was built and used to study limiting activity coefficients in 10 binary systems of the type alcohol (1) + organic solvent (2) at temperatures between 293 K and 333 K. In this temperature range, the influence of association on the excess properties of the studied systems is strong. Together with new results from spectrocopic investigations and literature data on excess properties of binary systems alcohol (1)−solvent (2), the new data are especially useful to investigate the benefits of physicochemical models of H-bonding solutions based on both thermodynamic and spectroscopic data.

Acknowledgment

We would like to thank undergraduate student N. Pröbsting for his contributions to building up and testing the headspace chromatograph. Thanks are also due to Y. Dobriakov, who carried out experiments as an exchange student from the University of St. Petersburg, Russia.

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Received for review June 3, 1997. Accepted October 8, 1997.[⊗] N.A. and H.H. gratefully acknowledge financial support by Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg.

JE970136L

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.