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Experimental Results for the Limiting Activity Coefficients in Some Binary and Ternary Mixtures of Organic Components

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Experimental results for the activity coefficients at infinite dilution of 13 binary systems of either hexane or heptane or cyclohexane with 1-propanol or 2-propanol or 1-butanol and those compounds with either perfluorohexane or perfluoroheptane are reported for temperatures from 298 K to 343 K. Furthermore, experimental results for the activity coefficients of these perfluoroalkanes at infinite dilution in binary mixtures of one of those alkanes and one of those alcohols at 298 K are reported. Some of the new experimental results agree well with literature data. The new experimental data are also compared to predictions from several group contribution methods. The best predictions are achieved with a UNIFAC model with corrections for "free volume" contributions and with a modification of Kehiaian's method. The differences between predictions from those models and the new experimental data typically amount to about 10%.

Introduction

The knowledge of the thermodynamic properties of highly diluted liquid mixtures is required in various fields, for example, for the design of equipment to produce high-purity chemicals by distillation, extraction, and absorption, in environmental protection such as the design of equipment to treat liquid wastes, and in problems related to interest in the chemical fate of poisonous substances in the environment. But infinite dilution properties are also used to test and improve thermodynamic methods for correlating and predicting the properties of liquid mixtures. One of the most interesting infinite dilution properties is the infinite dilution activity coefficient of a solute in a pure solvent. Headspace chromatography is a very effective experimental technique to determine infinite dilution activity coefficients of volatile components in binary mixtures. In the present work two variants of that technique are applied to determine the infinite dilution activity coefficients of eight binary mixtures (hexane + (1-propanol or perfluorohexane), heptane + (1-propanol or 1-butanol or perfluorohexane), 1-propanol + (perfluorohexane or perfluoroheptane), and 1-butanol + perfluorohexane) at 298 K, the infinite dilution coefficient of a solute (hexane and cyclohexane) in three solvents (1-propanol, 2-propanol, and 1-butanol) at temperatures between 313 and 343 K, and the infinite dilution coefficient of a solute (perfluorohexane and perfluoroheptane) in a binary solvent mixture (hexane + 1-propanol and heptane + 1-butanol) at 298 K. The research was initiated by our interest in the thermodynamic properties of fluid mixtures containing associating components, for example, alcohols. The experimental procedures are described. The experimental results are reported and compared to literature data.

Experimental Section

Experimental Methods. Various methods for measuring infinite dilution activity coefficients have been described in the literature, for example, the inert gas stripping method (cf. Burnett, 1963; Foulis et al., 1963), the inverse gas chromatography method (cf. James and Martin, 1952), the ebulliometric method (cf. Thomas et al., 1982), as well as some headspace gas chromatographic methods (cf. Hachenberg and Schmidt, 1977; Hussam and Carr, 1985; Hachenberg and Behringer, 1996). For a recent review, see, for example, Kojima et al., 1997. Each method has some specific advantages as well as some disadvantages. The ebulliometric method is typically restricted to mixtures of components with similar volatilities; that is, the ratio $R_{12} = (y_1/x_1)/(y_2/x_2)$—where x and y represent the mole fractions of the solute (1) and the solvent (2) in the liquid phase and the vapor phase, respectively—should be between 0.1 and 10. The inert gas stripping method and inverse chromatography are well suited for mixtures of a volatile solute and a nearly nonvolatile solvent. Most published data on limiting activity coefficients were determined by those methods. Non-steady-state gas liquid chromatography (cf. Landau et al., 1991) and headspace gas chromatography (cf. Kolb, 1975, 1992; Hussam and Carr, 1985) have also often been used. Headspace analysis is appropriate for systems with rather small differences in the volatility, whereas the use of non-steady-state gas−liquid chromatography is recommended only for systems with higher differences in the volatility.

In the present work two variants of the headspace gas chromatographic technique are applied to measure infinite dilution activity coefficients. One method is called the "isobaric, variable volume vessel method", hereafter denoted as method I. The principles of that method are shown in Figure 1. A small amount (typically a few milliliters) of a volatile liquid or gaseous solute (1) is added to a small, thermostated vessel (e.g. a syringe) filled with air at atmospheric pressure. The volume of that vessel (typically

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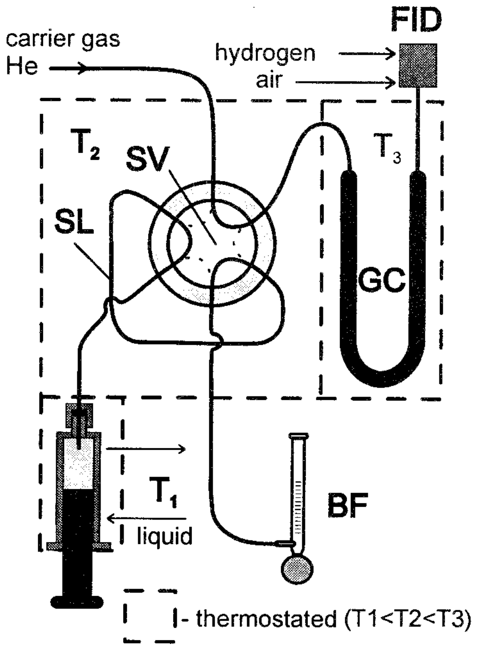

Figure 1. Schematic of the isobaric, variable-volume vessel method (method I) for measuring infinite dilution activity coefficients: BF = bubble flow meter; CG = carrier gas; FID = flame ionization detector; GC = gas chromatograph; N = needle; SL = sample loop; SP = syringe plunger; SV = sample valve; T_1, T_2, T_3 = constant temperature baths; V = thermostated vessel.

about 50 to 100 cm^3) is precisely known from a calibration with pure water. After vapor−liquid equilibrium is achieved (typically after about 20 to 30 min), a small needle-like tube is inserted into that vessel through an elastic rubber septum coated with PTFE. That needle links the vessel to the sample valve (SV) of a gas chromatograph (GC). The volume of the vessel is reduced at constant pressure (e.g. by pushing the syringe plunger), and the resulting gas flow transports a gaseous sample to the sample loop (SL). The gas flow is checked with a bubble flow meter (BF). To avoid condensation, the tubing and the sampling valves are heated to about 2 to 3 K (T_2) above the equilibration temperature of the vessel (T_1). The vapor sample is taken to the column of the gas chromatograph (GC) by a carrier gas. The volume of the sampling loop is so small (about 0.5 cm^3) that the peak area determined by a detector is proportional to the amount of solute in the sample loop. That procedure is repeated several times. Then a precisely known amount of the solvent (solv) is added by a second, smaller syringe to the vessel through the elastic rubber septum. The amount of that solvent is determined accurately from the difference in mass of the syringe before and after the filling. During that filling process the plunger of the (larger) syringe should be in a position where the volume of that syringe is precisely known from calibration experiments. This position is set by means of special stencil that limits the motion of the plunger. After the introduction of the liquid the system is equilibrated. When the vapor−liquid equilibrium is established, the gas phase is injected into the gas chromatograph as described before (when the vessel was filled only with a gaseous mixture of air and the solute) and the peak area caused by the solute is determined. That peak area corresponds to the partial pressure of the solute (1) above the liquid mixture.

Assuming that the vapor phase behaves like an ideal gas, the limiting activity coefficient of the solute (1) in the solvent (solv) $\gamma^{\infty}_{1,\mathrm{solv}}$ is

$$\gamma^{\infty}_{1,\mathrm{solv}} = \frac{RT\rho_{\mathrm{solv}}}{K^{\infty}_{1,\mathrm{solv}}\, p^{\mathrm{s}}_1} \tag{1}$$

where

$$K^{\infty}_{1,\mathrm{solv}} = \lim_{n_1 \to 0} K_{1,\mathrm{solv}} \tag{2}$$

and

$$K_{1,\mathrm{solv}} = \frac{c_1^{\mathrm{liq}}}{c_1^{\mathrm{vap}}} = 1 + \frac{V}{V^{\mathrm{liq}}} \cdot \frac{A_{1,0} - A_{1,\mathrm{solv}}}{A_{1,\mathrm{solv}}} \tag{3}$$

R, T, ρ_{solv}, p^{s}_1, V, V^{liq}, n_1, c_1^{liq} and c_1^{vap} are the universal gas constant, the thermodynamic temperature, the molar density of the liquid solvent, the partial pressure of the solute, the volume of the vessel (when n_{solv} moles of the solvent is added), the volume of the liquid ($V^{\mathrm{liq}} = n_{\mathrm{solv}}\rho_{\mathrm{solv}}$), the number of moles of solute added to the vessel, and the molarity of the solute (1) in the liquid phase and the vapor phase, respectively. $A_{1,0}$ and $A_{1,\mathrm{solv}}$ are the gas chromatographic peak areas due to the solute in the initial experiment (without the solvent) and the experiment with the solvent, respectively.

Besides method I, another headspace method was applied in the present work. That method (method II) uses an external calibration procedure for the solute. In headspace chromatography, the vapor phase coexisting with a solvent-rich liquid phase in a thermostated vial is analyzed by gas chromatography to determine the vapor-phase composition. When the composition of the liquid is known, the results can be evaluated to determine the infinite dilution activity coefficient of the solute (1) in the solvent (2) (cf. Kolb, 1992). In the present work four to six glass vials of even volume (≈22.3 cm^3) were charged with the same, exactly known amount of the solvent (≈5 cm^3) and sealed with rubber septa. Small amounts (≈0.002 to 0.005 cm^3) of the liquid, volatile solute were added by means of a microsyringe. Four more similar glass vials were prepared in the same way, but without adding the solvent. The vials were thermostated to establish thermodynamic equilibrium, that is, vapor−liquid equilibrium in the vials containing the solute as well as the solvent and a homogeneous vapor phase in the solvent-free vials. Then small samples of the vapor phase were taken with an electropneumatic sampling system and transferred to the gas chromatograph, where the solute was detected. Assuming that the peak area A_1 is proportional to the mole number of solute n_1 yields a relation between the detected peak area and the amount of solute:

$$n_1 = \alpha_1 A_1 V_{\mathrm{g}} \tag{4}$$

were α_1 and V_{g} are a calibration factor for the solute and the volume of the vapor phase, respectively. Applying similar assumptions as discussed before (i.e., ideal gas behavior, very small partial pressure of the solvent, etc.) results in the following expression for the infinite dilution activity coefficient of the solute (1) in the solvent (2):

$$\gamma^{\infty}_{1,2} = \frac{RT\rho_2}{K^{\infty}_{1,2}\, p^{\mathrm{s}}_1} \tag{1a}$$

where

$$K^{\infty}_{1,2} = \lim_{n_1 \to 0} K_{1,2} \tag{2a}$$

Table 1. Experimental and Calculated Results for the Limiting Activity Coefficients $\gamma_{1,2}^{\infty}$ and $\gamma_{2,1}^{\infty}$ in Binary Systems

				UNIFAC		UNIFAC-FV		
components 1 + 2		temp, T/K	$\gamma_{i,j}^{\infty}$ exp	Set I	Set II	Set I	Set II	MODKEQ
hexane + 1-propanol	$\gamma_{1,2}^{\infty}$	298.15	9.7	4.9	5.3	5.1	10.3	6.4
		313.15	8.9	4.8	5.2	5.0	9.4	6.1
		323.15	8.2	4.8	5.1	5.0	8.8	6.0
		333.15	7.3	4.8	5.0	5.0	8.4	5.8
	$\gamma_{2,1}^{\infty}$	298.15	45	20.5	26	21.5	80.2	44
hexane + 2-propanol	$\gamma_{1,2}^{\infty}$	323.15	7.9	4.8	5.1	4.9	7.5	6.0
		333.15	7.6	4.7	5.0	4.8	7.1	5.9
		343.15	7	4.7	4.9	4.8	6.8	5.7
hexane + 1-butanol	$\gamma_{1,2}^{\infty}$	323.15	5.6	3.9	3.8	4.1	6.1	4.3
		333.15	5.3	3.8	3.7	4.1	5.9	4.2
hexane + perfluorohexane	$\gamma_{1,2}^{\infty}$	298.15	5.6	6.5		6.5		5.5
	$\gamma_{2,1}^{\infty}$	298.15	18	11.9		11.9		17.5
cyclohexane + 1-propanol	$\gamma_{1,2}^{\infty}$	313.15	8.8	4.3	4.9	4.3	6.9	5.2
		323.15	7.7	4.3	4.8	4.3	6.6	5.0
		343.15	6	4.2	4.6	4.2	6.1	4.8
cyclohexane + 2-propanol	$\gamma_{1,2}^{\infty}$	323.15	5.8	4.3	4.8	4.3	5.8	5.1
		333.15	5.5	4.2	4.7	4.2	5.6	5.0
cyclohexane + 1-butanol	$\gamma_{1,2}^{\infty}$	313.15	4.2	3.5	3.6	3.5	4.8	3.8
		323.15	4	3.4	3.6	3.4	4.6	3.7
		333.15	3.6	3.4	3.5	3.4	4.5	3.6
		343.15	3.4	3.4	3.5	3.4	4.4	3.6
heptane + 1-propanol	$\gamma_{1,2}^{\infty}$	298.15	7.6	5.7	6.5	5.8	11.6	7.6
	$\gamma_{2,1}^{\infty}$	298.15	41	19.5	25.3	19.9	65.4	41.5
heptane + 1-butanol	$\gamma_{1,2}^{\infty}$	298.15	5.2	4.6	4.7	4.8	7.6	5.3
	$\gamma_{2,1}^{\infty}$	298.15	37	16.9	21.1	17.6	44.7	35
heptane + perfluoroheptane	$\gamma_{1,2}^{\infty}$	298.15	8.2	8.7		8.7		7.1
	$\gamma_{2,1}^{\infty}$	298.15	31	17.5		17.5		27
1-propanol + perfluorohexane	$\gamma_{1,2}^{\infty}$	298.15	233	241		254		119
	$\gamma_{2,1}^{\infty}$	298.15	225	238		249		217
1-propanol + perfluoroheptane	$\gamma_{1,2}^{\infty}$	298.15	225	221		227		109
	$\gamma_{2,1}^{\infty}$	298.15	400	447		459		403
1-butanol + perfluoroheptane	$\gamma_{1,2}^{\infty}$	298.15	300	268		282		126
	$\gamma_{2,1}^{\infty}$	298.15	300	328		343		270

and

$$K_{1,2} = \frac{c_1^{\mathrm{liq}}}{c_1^{\mathrm{vap}}} = 1 + \frac{V_0}{n_2\rho_2}\cdot\frac{A_{1,0} - A_{1,2}}{A_{1,2}} \qquad (3a)$$

where V_0 and ρ_2 are the volume of a vial and the molar density of the liquid solvent, respectively. $A_{1,0}$ and $A_{1,2}$ are the peak areas of the solute detected in the solvent-free and solvent-containing vapor samples.

In both methods results from about 10 single measurements at low solute concentrations were used to perform the extrapolations (cf. eqs 2 and 2a). The accuracy of the experimental data for the temperature is ±0.1 K.

Experimental Equipment. The equipment used in the present work is not a new design. It has been used (with some updates) for measuring activity coefficients for more than two decades (cf. Vitenberg et al., 1975; Mokrushina and Balashova, 1996, 1997). In the investigations applying method I the gas chromatograph was a type 102 model by TSVET, whereas in the investigations applying method II a multifract F 45 model by Perkin-Elmer was used. The gas chromatographic columns were always from Perkin-Elmer (packed—(2 m × 1/8 in.)—15% polyethylene on Celite, 60−80 mesh). Flame ionization detectors were used in both cases.

Materials. All chemicals were bought in the highest available quality (p.a.) from Reachim, Tcherkassk, Russia, and further purified by batch distillation (high reflux, about 10 theoretical plates). For those distillation procedures potassium carbonate (at a concentration of about 10 mass %) was added to the alcohols to improve the dewatering process. The liquid distillate fractions were investigated by measuring their refractive indices. The head-running fractions were discarded as long as those measurements did not result in a constant number for the refractive index. The sum of all discarded head-running fractions was about 5% of the pure chemical charged to the distillation equipment. Similarly, about 10% of that pure chemical was discarded as residue. The remaining distillate was further tested by gas chromatographic analysis. Within the usually small noise of the baseline, no impurity could be detected.

Experimental Results

Method I was applied to determine the infinite dilution activity coefficients at 298.15 K of both components in eight binary mixtures (hexane + (1-propanol or perfluorohexane), heptane + (1-propanol or 1-butanol or perfluorohexane), 1-propanol + (perfluorohexane or perfluoroheptane), and 1-butanol + perfluorohexane) and the infinite dilution coefficient of two solutes (perfluorohexane and perfluoroheptane) in two binary solvent mixtures (hexane +1-

Table 2. Infinite Dilution Activity Coefficient of Component 1 $\gamma^\infty_{1,(2+3)}$ in Binary Mixtures of Components 2 and 3 at 298.15 K

	liquid phase		$\gamma^\infty_{1,(2+3)}$			
				prediction		
ternary system	mole fraction, x_3	specific density, $\tilde{\rho}$/(g cm^{-3})	exp	UNIFAC (Set I)	UNIFAC-FV (Set I)	MODKEQ
perfluorohexane (1) + hexane (2) + 1-propanol (3)	0.00	0.6550	18	11.9	11.9	17.5
	0.21	0.6732	23	18.3	18.3	22
	0.59	0.7167	45	54.0	54.5	48
	0.86	0.7610	103	138	142	116
	0.91	0.7703	125	167	172	143
	1.00	0.7995	225	238	249	217
perfluoroheptane (1) + heptane (2) + 1-propanol (3)	0.00	0.6795	31	17.5	17.5	27
	0.31	0.6990	44	34.3	34.4	40
	0.59	0.7231	67	81.9	82.4	74
	0.88	0.7655	150	256	261	211
	1.00	0.7995	400	447	459	403
perfluoroheptane (1) + heptane (2) + 1-butanol (3)	0.00	0.6795	31	17.5	17.5	27
	0.34	0.7149	58	37.4	37.6	43
	0.59	0.7467	100	78.0	78.9	72
	0.85	0.7787	200	187	193	153
	1.00	0.8057	300	328	343	270

propanol and heptane + 1-butanol) at 298.15 K. Method II was applied to determine the limiting activity coefficients of the solutes hexane and cyclohexane in three solvents (1-propanol or 2-propanol or 1-butanol) in the temperature range from 313.15 K to 343.15 K.

For converting the direct experimental data (gas chromatographic peak areas) to infinite dilution activity coefficients, the liquid densities of the pure solvents and the binary solvent mixtures as well as the saturation pressures of the pure solvents are needed. The pure component properties were taken from the literature (Reid et al., 1977; Smith and Srivastava, 1986; Cibulka, 1993)—cf. Appendix I. The specific densities of hexane, heptane, and the fluoroalkanes as well as of the binary solvent mixtures were measured by pycnometry with an accuracy of ±0.0002 g cm^{-3}. For the pure liquids they are given in Table 3. For the binary solvent mixtures they are given together with the experimental results for the infinite dilution activity coefficients in Table 2.

The experimental results for the infinite dilution activity coefficients in binary mixtures are given in Table 1. The results for the infinite dilution coefficient of a solute in a binary solvent mixture are given in Table 2.

As the experimental techniques and equipment have been intensively tested and used over more than two decades, the uncertainty of the reported numbers for the infinite dilution activity coefficients from method I was adopted from such earlier investigations (cf. Vitenberg et al., 1975): about 3% for numbers below about 100 and 5% for larger numbers for the infinite dilution activity coefficient. As the procedure of method II is very similar to that of method I, those estimates were also adopted for method II.

All investigated systems reveal positive deviations from Raoult's law. The experimental data for the infinite dilution activity coefficient range from about 5 (for hexane in perfluorohexane) to about 400 (for perfluoroheptane in 1-propanol). The large numbers for the infinite dilution activity coefficient of a perfluoroalkane in an alcohol also indicate that these binary systems reveal liquid−liquid miscibility gaps. As was expected, in the binary systems alcohol + alkane, the associating component, that is, the alcohol, has a much larger limiting activity coefficient than the alkane in the alcohol.

Comparison with Literature Data. Figure 2 shows a comparison with literature data for both infinite dilution activity coefficients of the binary system hexane (1) + 1-propanol (2). The new experimental data for $\gamma^\infty_{2,1}$ agree with the data of Thomas et al. (1982) within the experimental uncertainty of the new data, whereas the data reported by Brown et al. (1964) as well as by Belousov et al. (1975) are smaller by nearly 35%. Therefore, it is no surprise that the results by those two authors for $\gamma^\infty_{2,1}$ are also >30% smaller than the new experimental data. The publication of Trampe et al. (1990) is the only literature source for $\gamma^\infty_{2,1}$ in the binary system hexane (1) + 2-propanol (2). The comparison with the new experimental data is not as favorable as that for the binary system hexane (1) + 1-propanol (2), as the new experimental data are about 30% larger than the data of Trampe et al. (1990)—cf. also Figure 3. As is shown in Figure 4, literature data for $\gamma^\infty_{2,1}$ in the binary system hexane (1) + 1-butanol (2) agree within about 5% but are about 15% below the new experimental data. The new experimental data for $\gamma^\infty_{2,1}$ in the system cyclohexane (1) + 2-propanol (2) agree with the data of Pividal and Sandler (1990) within experimental uncertainty, whereas they are a gain about 15% larger than the results of Trampe et al. (1990)—cf. Figure 5. Literature data for $\gamma^\infty_{1,2}$ in the binary system cyclohexane (1) +

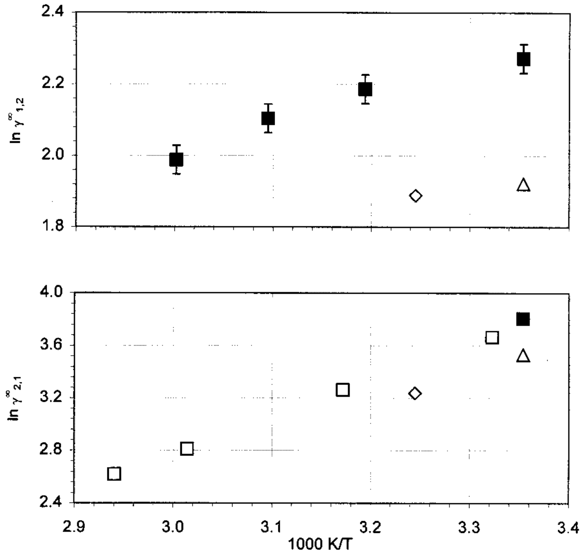

Figure 2. Hexane (1) + 1-propanol (2). Experimental data for the infinite dilution coefficients $\gamma^\infty_{1,2}$ and $\gamma^\infty_{2,1}$: △, Brown et al. (1964); ◇, Belousov et al. (1975); □, Thomas et al. (1982); ■, this work.

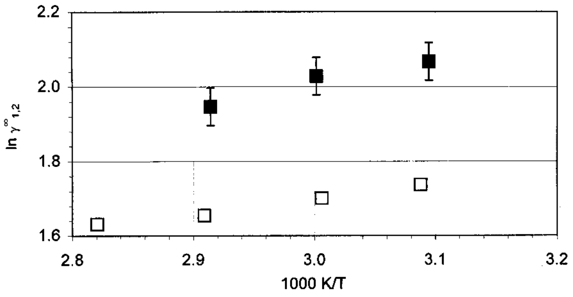

Figure 3. Hexane (1) + 2-propanol (2). Experimental data for the infinite dilution coefficient $\gamma_{1,2}^{\infty}$: □, Trampe and Eckert (1990); ■, this work.

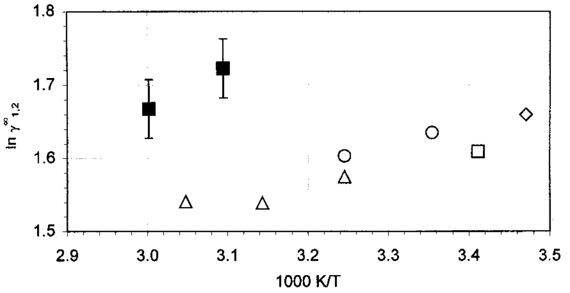

Figure 4. Hexane (1) + 1-butanol (2). Experimental data for the infinite dilution coefficient $\gamma_{1,2}^{\infty}$: △, Landau et al. (1991); ○, Brown et al. (1964); ◇, Nguyen and Ratcliff (1975); □, Thomas et al. (1982; ■, this work.

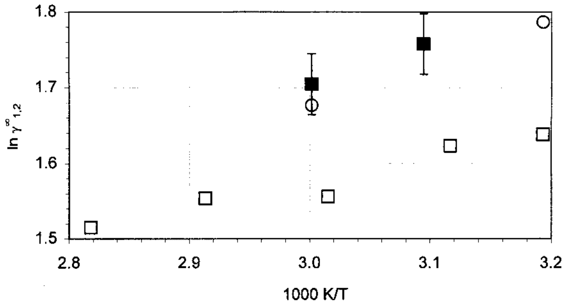

Figure 5. Cyclohexane (1) + 2-propanol (2). Experimental data for the infinite dilution coefficient $\gamma_{1,2}^{\infty}$: ○, Pividal and Sandler (1990); □, Trampe and Eckert (1990); ■, this work.

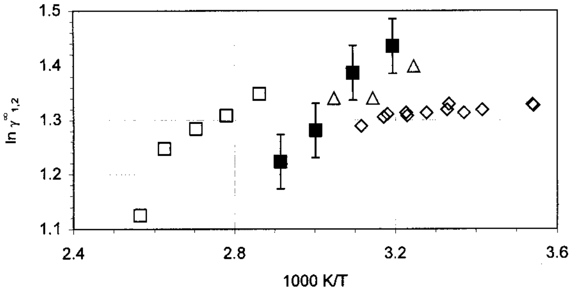

Figure 6. Cyclohexane (1) + 1-butanol (2). Experimental data for the infinite dilution coefficient $\gamma_{1,2}^{\infty}$: △, Landau et al. (1991); □, Trampe and Eckert (1990); ◇, Vernier et al. (1969); ■, this work.

1-butanol (2) scatter around the new data by about ±10%—cf. Figure 6. A comparison for $\gamma_{1,2}^{\infty}$ as well as $\gamma_{2,1}^{\infty}$ in the system heptane (1) + 1-propanol (2) is shown in Figure 7. The new experimental data perfectly agree with the results obtained by linear extrapolation of the data of Pividal and Sandler (1990) (in a plot of ln $\gamma_{i,j}^{\infty}$ over $1/T$) and deviate from other literature sources by up to 7% ($\gamma_{1,2}^{\infty}$) and 25% ($\gamma_{2,1}^{\infty}$). The comparison with literature data for the binary system heptane (1) + 1-butanol (2) is shown in Figure 8.

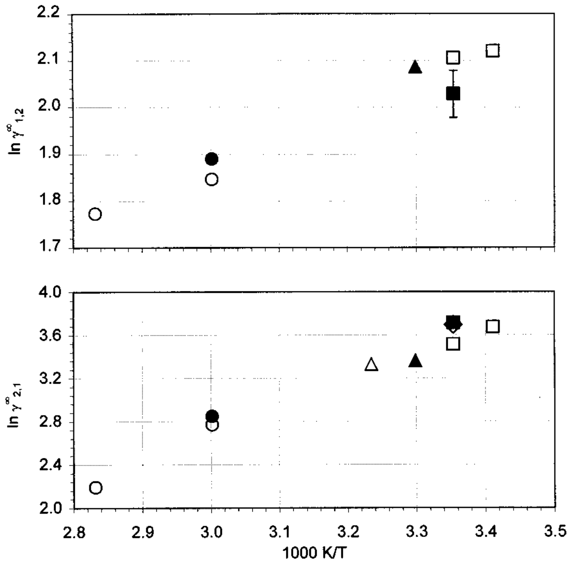

Figure 7. Heptane (1) + 1-propanol (2). Experimental data for the infinite dilution coefficients $\gamma_{1,2}^{\infty}$ and $\gamma_{2,1}^{\infty}$: □, Ramalho and Ruel (1968); ◇, Savini et al. (1976); △, Shen et al. (1978); ▲, Rytting et al. (1978); ○, Pividal and Sandler (1990); ●, Park et al. (1996); ■, this work.

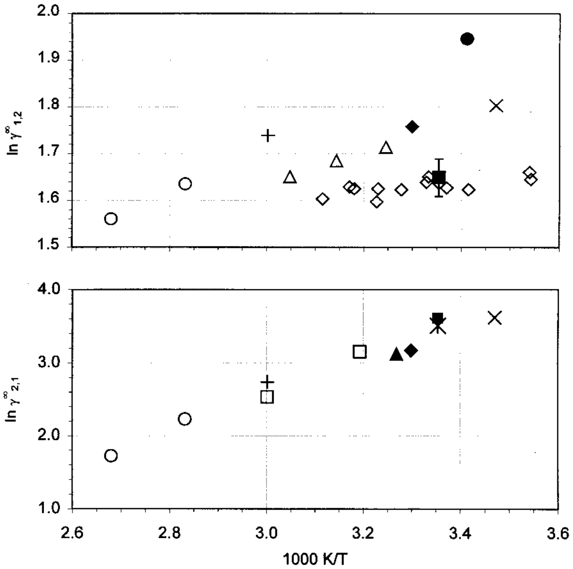

Figure 8. Heptane (1) + 1-butanol (2). Experimental data for the infinite dilution coefficients $\gamma_{1,2}^{\infty}$ and $\gamma_{2,1}^{\infty}$: □, Hofstee et al. (1960); ◇, Vernier et al. (1967); ×, Nguyen and Ratcliff (1975); ◆, Savini et al. (1976); ▲, Shen et al. (1978); ∗, Rytting et al. (1978); ●, Thomas et al. (1982); ○, Pividal and Sandler (1990); △, Landau et al. (1991); +, Park et al. (1996); ■, this work.

The new experimental results for $\gamma_{1,2}^{\infty}$ agree with most literature data within the experimental uncertainty. The literature data for $\gamma_{2,1}^{\infty}$ reveal some larger scattering. The data of Vernier (1967) show the best agreement with the new data. The deviation is within the small scattering of that data.

For all other systems no infinte dilution activity data are available in the literature.

Comparison with Predictions from Group Contribution Methods. The group contribution methods UNIFAC (Fredenslund et al., 1975), MODKEQ (Kehiaian et al., 1978), and UNIFAC-FV (Oishi and Prausnitz, 1978) were used to predict infinite dilution activity coefficients for comparison with the results of the present work. That

Table 3. Coefficients a_1 to a_6 of Eqs I.1 and I.2

parameter	1-propanol	2-propanol	1-butanol
ρ_c/(g cm^{-3})	0.274		0.271
T_c/K	536.74		563.01
a_1	0.940 533 6	1.067 065 2	−3.573 785
a_2	12.944 24	$5.805\,851 \times 10^{-4}$	50.244 97
a_3	−53.951 90	38.930 74	−175.9335
a_4	113.6388	644.123 29	308.5883
a_5	−113.8656		−265.6281
a_6	43.383 24		89.499 66
T_{min}/K	153.2	196	186.2
T_{max}/K	529.8	361	559.2

comparison is also shown in Tables 1 and 2. Some details of those methods are given in Appendix II.

Predictions of the infinite dilution activity coefficients in the binary mixtures from the UNIFAC method with binary interaction parameters from Fredenslund et al. (1977) and Morachevskii et al. (1989)—denoted by Set I—generally reveal rather large deviations from the new experimental data. Only for $\gamma_{1,2}^{\infty}$ in the systems cyclohexane (1) + 1-butanol (2) and heptane (1) + perfluoroheptane (2) and for $\gamma_{1,2}^{\infty}$ and $\gamma_{2,1}^{\infty}$ in the systems alcohol (1) + either perfluorohexane or perfluoroheptane (2) are the differences below about 10%. Such a result might have been expected, as the set of interaction parameters was not particularly adjusted to give good results for infinite dilution activity coefficients. However, using the set of interaction parameters reported by Bastos et al. (1988)—denoted by Set II—gives only a minor improvement, although that set of interaction parameters was fitted to infinite dilution activity coefficients. Combining that set of UNIFAC parameters with “free-volume” corrections results in an essential improvement. But, as no interaction parameters for fluoro groups were given by Bastos et al. (1988), that procedure cannot be applied to binary systems with fluoro compounds.

The MODKEQ model gives in most cases a somewhat better agreement with the new experimental data than the UNIFAC-FV−Set II model. But it performs much better than the other UNIFAC models. For example, there is nearly a perfect agreement in the binary systems hexane + perfluorohexane, heptane + 1-propanol, and heptane + 1-butanol. For the binary systems of an alcohol and a fluoroalkane the predictions for the infinite dilution activity coefficient of the fluoroalkane in the alcohol agree with the experimental results within experimental uncertainty while there are quite large deviations between the experimental data and the prediction for the activity coefficient of an alcohol at infinite dilution in an fluoroalkane.

That model also gives the best agreement for the activity coefficients of the perfluoroalkanes at infinite dilution in the binary solvent mixtures.

Appendix I

Pure Component Properties. The densities of the liquids 1-propanol and 1-butanol were calculated from the equation by Cibulka (1993):

$$\rho/\rho_c = 1 + \sum_{i=1}^{6} a_i (1 - T/T_c)^{i/3} \qquad \text{(I.1)}$$

The density of liquid 2-propanol was taken from Smith and Srivastava (1986):

$$\rho/(\text{g}\cdot\text{cm}^{-3}) = a_1 - a_2(T/\text{K}) - \frac{a_3}{a_4 - (T/\text{K})} \qquad \text{(I.2)}$$

The constants are given in Table 3.

Table 4. Experimental Results for the Densities of Some Pure Liquids at 298.15 K

liquid	ρ_{liq}/(g cm $^{-3}$)
hexane	0.6550
heptane	0.6795
perfluorohexane	1.6798
perfluoroheptane	1.7178

Table 5. Antoine Parameters for Pure Component Vapor Pressure Curve

component	A	B	C
1-propanol	17.5439	3166.38	−80.15
2-propanol	18.6929	3640.20	−53.54
1-butanol	17.2160	3137.02	−94.43
cyclohexane	15.7527	2766.63	−50.50
hexane	15.8366	2697.55	−48.78
heptane	15.8737	2911.32	−56.51
perfluorohexane	15.8307	2488.59	−59.73
perfluoroheptane	15.9747	2719.68	−64.50

Table 6. UNIFAC Size *r* and Surface *q* Parameters

group	r	q
CH_3	0.9011	0.848
CH_2	0.6744	0.540
CH	0.4469	0.228
OH	1.0000	1.200
CF_3	1.4060	1.380
CF_2	1.0105	0.920
CH_2CH_2OH	1.8788	1.664
$CHOHCH_3$	1.8780	1.660

The densities of the pure liquids hexane, heptane, perfluorohexane, and perfluoroheptane at 298.15 K were measured in the present work. They are given in Table 4.

The vapor pressures of the pure components were calculated from the Antoine equation:

$$\ln p^{s}/(\text{mmHg}) = A - B/\{(T/\text{K}) + C\} \qquad \text{(I.3)}$$

The coefficients *A*, *B*, and *C* were taken from the compilation of Reid et al. (1977). They are given in Table 5.

Appendix II

The original version for the UNIFAC model was used. But two different sets of groups as well as of interaction parameters were used. Set I (given by Fredenslund et al. (1977) and Morachevskii et al. (1989)) is characterized by using the groups CH_2CH_2OH and $CHOHCH_3$ for describing an alcohol. Its interaction parameters are based on experimental vapor−liquid and liquid−liquid equilibrium data. Set II (from Bastos et al. (1988)) uses the OH group for describing the alcohols, and its binary interaction parameters are exclusively based on infinite dilution activity coefficient data. The UNIFAC parameters for the size *r* and the surface *q* of all groups are given in Table 6.

Both sets of group interaction parameters are given in Table 7.

Free-volume contributions are particularly important in polymer−solvent mixtures. But they might also contribute essentially to the activity coefficients in mixtures with associating components, for example, an alcohol. Therefore, calculations were repeated including a free-volume (FV) contribution to the activity coefficient, as proposed by Oishi and Prausnitz (1978).

$$\gamma_{1,2}^{\infty} = \gamma_{1,2}^{\text{comb},\infty}\, \gamma_{1,2}^{\text{res},\infty}\, \gamma_{1,2}^{\text{FV},\infty} \qquad \text{(II.1)}$$

$\gamma_{1,2}^{\text{comb},\infty}$ and $\gamma_{1,2}^{\text{res},\infty}$ were calculated with the UNIFAC method using parameter set I. $\gamma_{1,2}^{\text{FV},\infty}$ was calculated as

Table 7. UNIFAC Interaction Parameters $a_{i,j}$/K[a]

		$a_{i,j}$/K			
set	i	$j = CH_2$ or CH_3	$j = OH$	$j = CF_2$ or CF_3	$j = CH_2CH_2OH$ or $CHOHCH_3$
I	CH_2 or CH_3	0		−2.861[b]	737.5
II		0	1024.5	n.a.	
I	OH	156.4		411.2[b]	
II		173.32	0	n.a.	
I	CF_2 or CF_3	147.3[b]		0	982.5
II		n.a.	n.a.	0	
I II	CH_2CH_2OH or $CHOHCH_3$	−87.93		65.74	0

[a] Set I: from VLE and LLE (Fredenslund et al., 1977; Morachevskii et al., 1989). Set II: from infinite dilution activity coefficient data (Bastos et al., 1988). [b] From Sokolovskaya (1981).

recommended by Oishi and Prausnitz (1978):

$$\ln \gamma_{1,2}^{FV,\infty} = 3.3 \ln\left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1}\right] - 1.1\left[\frac{\dfrac{\tilde{v}_1}{\tilde{v}_2} - 1}{1 - \dfrac{1}{\tilde{v}_1^{1/3}}}\right] \tag{II.2}$$

$\tilde{v}_i$ is the reduced liquid volume of pure liquid i:

$$\tilde{v}_i = v_i\ (\mathrm{cm^3\ mol^{-1}})/(19.4176 r_i)$$

where v_i and r_i are the molar volume and the UNIFAC size parameter of pure liquid i, respectively. The molar volumes of the pure liquids were taken at 298.15 K.

Modification of the Generalized Quasichemical Group Contribution Theory of Kehiaian. The theory of Kehiaian is based on the Barker−Guggenheim quasi-lattice theory (cf. Kehiaian et al. (1978)). The activity coefficient of component 1 infinitely diluted in a liquid mixture of solvents 2 and 3 is given by

$$\gamma_{1,2+3}^{\infty} = \gamma_{1,2+3}^{comb,\infty}\ \gamma_{1,2+3}^{res,\infty} \tag{II.3}$$

$$\ln \gamma_{1,2+3}^{comb,\infty} = \ln\left[\frac{r_1}{r_2x_2 + r_3x_3}\right] + \frac{Zq_1}{2}\ln\left[\frac{q_1}{r_1}\,\frac{r_2x_2 + r_3x_3}{q_2x_2 + q_3x_3}\right] + l_1 - r_1\frac{l_2x_2 + l_3x_3}{r_2x_2 + r_3x_3} \tag{II.4}$$

r_i and q_i are the size and surface parameters of component i, and x_j is the mole fraction of solvent j in the solvent mixture (i.e. $x_2 + x_3 = 1$). Z is the coordination number of the lattice (here $Z = 10$), and

$$l_i = \frac{Z}{2}(r_i - q_i) - r_i + 1 \tag{II.5}$$

The size and surface parameters were calculated from the number $\nu_s^{(i)}$ of groups s in a molecule of component i and the size $r_s^{(g)}$ and surface $q_s^{(g)}$ parameters of the groups:

$$r_i = \sum_{\substack{\text{all groups } s \text{ in}\\ \text{component } i}} \nu_s^{(i)}\, r_s^{(g)} \tag{II.6a}$$

$$q_i = \sum_{\substack{\text{all groups } s \text{ in}\\ \text{component } i}} \nu_s^{(i)} q_s^{(g)} \tag{II.6b}$$

The surface area and the volume of a group (a_s and v_s, respectively) were calculated as recommended by Bondi (1968). $q_s^{(g)}$ and $r_s^{(g)}$ were calculated by normalizing those

Table 8. Modification of Kehiaian's Generalized Quasichemical Group Contribution Theory: Volume Parameters $r_s^{(g)}$, Surface Parameters $q_s^{(g)}$, and Binary Group Interaction Parameters ω_{st}

group s	$r_s^{(g)}$	$q_s^{(g)}$
CH_3	0.722	0.6773
CH_2	0.5406	0.4313
CH	0.3581	0.1821
H	0	0.1
O	0.4248	0.3664
CF_3	1.1271	1.1025
CF_2	0.8101	0.7349

type of contact $s-t$ [a]	(ω_{st}/R)/K
CH_3-O CH_2-O $CH-O$ CH_3-H CH_2-H $CH-H$	148
$H-O$	−1301
CH_3-CF_3 CH_3-CF_2 CH_2-CF_3 CH_2-CF_2	16.58
CF_3-O CF_2-O	153.7
CF_3-H CF_2-H	233.4

[a] $\omega_{ss} = 0$ and $\omega_{st} = \omega_{ts}$.

numbers using the standard surface area a_0 and the standard volume v_0 as given by Vera et al. (1977) for a lattice of coordination number $Z = 10$:

$$q_s^{(g)} = a_s/a_0 \text{ and } r_s^{(g)} = v_s/v_0 \text{ with } a_0 = 3.13 \times 10^9\ \mathrm{cm^2/mol} \text{ and } v_0 = 18.92\ \mathrm{cm^3/mol}$$

(for comparison the corresponding parameters in the UNIFAC model are 2.5 × 10^9 cm^2/mol and 15.169 cm^3/mol, respectively).

The residual contribution to the infinite dilution activity coefficient is calculated as follows:

$$\ln \gamma_{1,2+3}^{res,\infty} = q_1 Z \sum_{\text{all groups } s} \alpha_s^{(1)} \ln\left[\frac{\tilde{X}_s^{1,2+3,\infty}}{\tilde{X}_s^{(1)}}\right] \tag{II.7}$$

$\alpha_s^{(1)}$ is the ratio of surface sites of groups s (in a molecule of component 1) to the total number of surface sites in that molcule:

$$\alpha_s^{(1)} = \frac{\nu_s^{(1)}\ q_s^{(g)}}{q_1} \tag{II.8}$$

$\tilde{X}_s^{1,2+3,\infty}$ and $\tilde{X}_s^{(1)}$ are properties of a group s in a solution where component 1 is infinitely diluted in a mixture of components 2 and 3 and in pure component 1, respectively.

$\tilde{X}_s^{1,2+3,\infty}$ is calculated by solving a system of $m_{(1+2+3)}$ equations, where $m_{(1+2+3)}$ is the number of groups in the ternary system of components 1, 2, and 3:

$$\tilde{X}_s^{1,2+3,\infty} \sum_{t=1}^{m_{(1+2+3)}} \alpha_t \tilde{X}_t^{1,2+3,\infty} \eta_{s,t} = 1 \quad (s = 1, 2, ..., m_{(1+2+3)}) \tag{II.9}$$

where α_t is the average surface fraction of groups s in the binary solvent mixture of components 2 and 3:

$$\alpha_t = \frac{(x_2 \nu_t^{(2)} + x_3 \nu_t^{(3)}) q_t^{(g)}}{x_2 q_2 + x_3 q_3} \tag{II.10}$$

and $\eta_{s,t}$ is used to express the interactions between groups s and t:

$$\eta_{s,t} = \exp\left[\frac{-\omega_{st}}{RT}\right] \tag{II.11}$$

ω_{st}, R, and T, are a binary parameter for interactions between groups s and t, the universal gas constant, and the thermodynamic temperature, respectively. ω_{st} is symmetric; that is, $\omega_{st} = \omega_{ts}$. For interactions between the same contacts, $\omega_{ss} = 0$. Information on the influence of temperature on some of these binary interaction parameters is available. But, as taking that influence into account results only in very small changes and those changes were not only for the better, it was neglected in the final calculations.

$\tilde{X}_s^{(1)}$ is calculated in an analogous manner as $\tilde{X}_s^{1,2+3,\infty}$, by replacing in eq II.9 $\tilde{X}_s^{1,2+3,\infty}$ by $\tilde{X}_s^{(1)}$, $\tilde{X}_t^{1,2+3,\infty}$ by $\tilde{X}_t^{(1)}$, α_t by $\alpha_t^{(1)}$ and $m_{(1+2+3)}$ by the number of groups in pure component 1, $m_{(1)}$.

$$\tilde{X}_s^{(1)} \sum_{t=1}^{m_{(1)}} \alpha_t^{(1)} \tilde{X}_t^{(1)} \eta_{s,t} = 1 \quad (s = 1, 2, ..., m_{(1)}) \tag{II.9a}$$

Surface and volume parameters are given in Table 8 for all groups of interest in the present work. The group interaction parameters of the MODKEQ model were fitted to consistent experimental data for the vapor−liquid equilibria of the following binary systems: alkanol + alkane (C_3−C_{10}) (288−328 K), alkanol + perfluoroalkane (C_5−C_7), and alkanol (C_3−C_7) + perfluoroalkane (C_5−C_7). The parameters are also given in Table 8.

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