Glossary

a	surface tension parameter defined in eq 7
A	constant of MBP apparatus
b	surface tension parameter defined in eq 7
g	gravitational constant
h	tube immersion depth
P_i	pressure in tube i
P	maximum pressure in tube
r	radius of tube
t	temperature
T_c	critical temperature
T_c'	pseudocritical temperature defined in eq 6
T_r'	reduced temperature, T/T_c'
y	mole fraction

Greek Letters

α	surface tension parameter defined in eq 5
β	surface tension parameter defined in eq 5
ρ	density
σ	surface tension

Subscripts

1	fine capillary tube
2	larger capillary tube
A	aqueous component
B	organic component

Registry No. 2-Propanol, 67-63-0; ethylene glycol, 107-21-1.

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Excess Volume, Excess Enthalpy, and Excess Heat Capacity of the Binary Liquid Systems Ethanenitrile or 2-Butanone + 2,2,4-Trimethylpentane

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The excess volumes (at 293.15 and 313.15 K) of the binary liquid mixtures of ethanenitrile (acetonitrile) or 2-butanone (ethyl methyl ketone) + 2,2,4-trimethylpentane (isooctane) have been determined from density measurements at atmospheric pressure. The excess enthalpies (at 293.15 K) and the isobaric heat capacities (at 293.15 and 313.15 K) of the same mixtures have been measured by means of Picker calorimeters at atmospheric pressure. The excess Gibbs energy of ethanenitrile + 2,2,4-trimethylpentane (at the upper critical solution temperature, T_c = 354.55 K) has been estimated from the liquid–liquid equilibrium curve.

Introduction

Data on mixtures containing polar liquids are needed in chemical engineering. We also used these data to develop a classification scheme for these types of systems (*1*) and to test a recently developed equation of state that incorporates information on molecular shape (*2*, *3*).

The thermodynamic excess properties of ethanenitrile or 2-butanone + 2,2,4-trimethylpentane presented here are part of our study on mixtures of polar liquids with a common nonpolar component. In the frame of this study, we have investigated 2,2′-dichlorodiethyl ether + 2,2,4-trimethylpentane (*4*) and ethanenitrile or 2-butanone + 2,4,4-trimethyl-1-pentene or + 2,4,4-trimethyl-2-pentene (*5*, *6*). Moreover, we have surveyed the properties of mixtures of other polar compounds + hydrocarbons (*7*) and their dependence on the dipole moment μ of the polar component (*8*).

Ethanenitrile (μ = 3.91 D in the gas phase) exhibits a miscibility gap in the system with 2,2,4-trimethylpentane at temperatures below 354.55 K and atmospheric pressure, while 2-butanone (μ = 2.88 D) is less polar and completely miscible at the temperatures used in this work.

Experimental Section

Ethanenitrile (J. T. Baker Chemicals, analytical reagent) with a purity of 99.95 mol % and 2-butanone (Merck, p.a.) with a purity of 99.89 mol %, both checked by GLC, were dried over potassium carbonate (Baker, analytical reagent). 2,2,4-Trimethylpentane (Fluka, puriss., or Phillips, research grade), with purities of 99.97 or 99.98 mol %, respectively, by GLC, was stored over Na–Pb (Merck, p.a.). The substances were used without further purification. They were carefully degassed by several pump/thaw cycles prior to each measurement. Relative atomic masses according to IUPAC (1987) (*9*) were used.

The molar excess volumes V^E were calculated from precise density measurements of the liquids with use of a vibrating glass tube densimeter (Model DMA 02 D, Paar) at 293.15 and 313.15 K and atmospheric pressure. The precision of the densities is estimated as 3×10^{-6} g cm^{-3}, and the accuracies are 1×10^{-5} g cm^{-3} at 293.15 K and 1×10^{-4} g cm^{-3} at 313.15 K. Mixtures were prepared from the degassed samples by weighing them into air-tight screw-capped tubes; the masses were corrected for the gas phase. This led to accuracies in the mole fraction x_i of 3×10^{-5} (*10*). V^E is accurate to 0.003 cm^3 mol^{-1} at about equimolar composition but less so at low and high concentration ranges in the partially miscible ethanenitrile + 2,2,4-trimethylpentane system.

The molar excess enthalpies H^E were measured in a dynamic flow microcalorimeter of Picker type (Setaram) at 293.15 K and atmospheric pressure, as described in detail previously (*11*). Here, x_i has an accuracy of 1×10^{-4}. H^E could be measured with a relative error of better than 2.5% at equimolar composition, but again this precision was reduced at the edges

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Table I. Densities ρ and Isobaric Molar Heat Capacities C_p of the Pure Components[a]

substance	T/K	ρ/(g cm^{-3}) exptl	ρ/(g cm^{-3}) lit.	C_p/(J mol^{-1} K^{-1}) exptl	C_p/(J mol^{-1} K^{-1}) lit.
2,2,4-trimethylpentane	293.15	0.691 89	0.691 93 (*20*)	237.85	
	298.15	(0.687 72)*	0.687 81 (*20*)	(240.90)**	238.50 (*20*)
	313.15	0.675 37	0.675 38 (*6*)	252.48	246.80 (*21*)
ethanenitrile	293.15	0.782 03	0.782 2 (*20*)	84.84	
	298.15	(0.776 56)*	0.776 6 (*20*)		
	313.15	0.760 38		88.86	
2-butanone	293.15	0.804 95	0.804 9 (*20*)	156.68	
	298.15	(0.799 64)*	0.799 7 (*20*)	(158.80)**	158.91 (*20*)
	313.15	0.783 91		162.57	

[a] Values marked with a single asterisk were calculated by linear interpolation of ρ between 293.15 K and 313.15 K, those with a double asterisk were calculated by linear interpolation of the volumetric heat capacities between 293.15 and 313.15 K.

Table II. Molar Excess Volumes V^E as a Function of Mole Fraction x_2 at 293.15 or 313.15 K and Atmospheric Pressure

ethanenitrile (1) + 2,2,4-trimethylpentane (2)			2-butanone (1) + 2,2,4-trimethylpentane (2)		
	V^E/(cm^3 mol^{-1})			V^E/(cm^3 mol^{-1})	
x_2	T = 293.15 K	T = 313.15 K	x_2	T = 293.15 K	T = 313.15 K
0.004 66	0.007	0.011	0.027 60	0.060	
0.006 21		0.015	0.043 36		0.116
0.008 00	0.014		0.050 81		0.134
0.012 57	0.021	0.031	0.077 76	0.162	
0.013 17		0.030	0.118 45	0.236	
0.015 95	0.026	0.041	0.147 06		0.351
0.021 70		0.048	0.186 89	0.339	0.409
0.022 40	0.035		0.239 41	0.416	
0.022 91	0.038		0.268 47		0.556
0.024 30		0.053	0.280 06	0.460	0.552
0.035 61	0.056		0.340 91	0.519	0.625
			0.384 33	0.557	
0.947 26	0.196		0.399 62	0.564	0.684
0.956 13	0.164	0.205	0.449 10	0.590	0.714
0.960 59		0.203	0.482 07	0.605	0.728
0.963 75	0.143	0.182	0.501 00		0.748
0.965 42		0.171	0.556 47	0.617	
0.966 74	0.136	0.164	0.568 02		0.759
0.976 39	0.096		0.590 93	0.618	0.743
0.987 00	0.052		0.659 85	0.592	0.719
0.989 43		0.053	0.669 61	0.589	
0.989 48		0.060	0.718 49		0.684
0.990 87	0.037	0.048	0.733 94	0.542	0.653
0.991 01		0.047	0.809 05	0.459	0.544
			0.812 82	0.454	0.538
			0.846 11	0.396	
			0.861 73	0.372	0.444
			0.896 24	0.303	0.355
			0.934 15	0.206	0.244
			0.961 33	0.126	

Table III. Molar Excess Enthalpies H^E as a Function of Mole Fraction x_2 at 293.15 K and Atmospheric Pressure

ethanenitrile (1) + 2,2,4-trimethylpentane (2)		2-butanone (1) + 2,2,4-trimethylpentane (2)	
x_2	H^E/(J mol^{-1})	x_2	H^E/(J mol^{-1})
0.0106	96	0.0639	319
0.0179	160	0.1317	598
0.0232	206	0.1736	771
0.0280	248	0.2245	920
0.0315	277	0.2592	981
0.0381	330	0.3318	1124
0.0397	344	0.3364	1125
		0.4322	1232
0.9222	590	0.4864	1267
0.9260	564	0.5066	1270
0.9438	437	0.5461	1255
0.9568	342	0.5485	1262
		0.6094	1218
		0.6736	1117
		0.7345	994
		0.7796	884
		0.7978	820
		0.8506	633
		0.9102	416

of the concentration range in the case of partially miscible systems.

The isobaric molar excess heat capacities C_p^E were calculated from differences in heat capacities per unit volume between samples of not too different volumetric heat capacities, determined with a differential flow microcalorimeter of Picker Type (Setaram). The calorimeter was thermostated to ±0.5 mK or better and controlled by means of calibrated Pt-100 thermoresistors. The measurements were performed at 293.15 and 313.15 K and atmospheric pressure in the stepwise procedure (*12*). The heat capacities were measured relative to C_p of *n*-heptane (Phillips, research grade, ≥99.92 mol % purity by GLC, dried with Pb-Na, Merck, p.a.) as the ultimate reference liquid; its C_p values at 293.15 K (222.88 J mol^{-1} K^{-1}) and at 313.15 K (230.52 J mol^{-1} K^{-1}) are regarded as the best ones in the literature (*13*). At 293.15 K, the absolute C_p values of 2,2,4-trimethylpentane were estimated to be accurate to 1.2 J mol^{-1} K^{-1}; the errors for C_p of pure ethanenitrile and 2-butanone were estimated to be 1%. At 313.15 K the uncertainties are somewhat larger. The excess quantity C_p^E, where only small differences of volumetric heat capacity are measured, and where the uncertainties in the heat capacity of the pure compounds do not matter, has an accuracy of 0.02 J mol^{-1} K^{-1} at equimolar composition and 293.15 K. As mentioned, the miscibility gap in the ethanenitrile + 2,2,4-trimethylpentane system decreases the accuracy of C_p^E at the concentration edges. The mixtures were prepared in the same way as for the density measurements described above and then pumped into the calorimeter. Thus, the mole fraction has an accuracy of 1×10^{-4}.

The liquid–liquid equilibrium diagram of ethanenitrile + 2,2,4-trimethylpentane was determined visually. The stirred mixtures (with mole fractions accurate to 1×10^{-4}) were cooled very slowly (less than 1 mK s^{-1}) in an isolated bottle, where a Pt resistance thermometer was immersed. The estimated precision of the measured consolute temperatures T is 0.02 K. The T–x curve was fitted to a spline function, with step points chosen at constant temperatures so that measurements near the upper critical solution temperature were weighed more heavily. As H^E is known, the calculation of the molar excess Gibbs energy G^E could be carried out by involving the correction for its temperature dependence (*14*, *15*). This procedure should give G^E with an accuracy of 2%, the miscibility gap extending, in the present case, over nearly the entire concentration range at the low temperatures.

Results and Discussion

In Table I the experimental densities ρ and the isobaric heat capacities C_p of the pure compounds are compared with literature data. The molar excess volumes V^E are presented in Table II, the molar excess enthalpies H^E in Table III, and the

Table IV. Isobaric Molar Excess Heat Capacities C_p^E as a Function of Mole Fraction x_2 at 293.15 or 313.15 K and Atmospheric Pressure

ethanenitrile (1) + 2,2,4-trimethylpentane (2)				2-butanone (1) + 2,2,4-trimethylpentane (2)			
T = 293.15 K		T = 313.15 K		T = 293.15 K		T = 313.15 K	
x_2	C_p^E/(J mol^{-1} K^{-1})	x_2	C_p^E/(J mol^{-1} K^{-1})	x_2	C_p^E/(J mol^{-1} K^{-1})	x_2	C_p^E/(J mol^{-1} K^{-1})
0.0080	0.144	0.0062	0.099	0.0365	0.323	0.0444	0.382
0.0224	0.377	0.0132	0.191	0.0956	0.776	0.0777	0.640
0.0229	0.377	0.0217	0.308	0.1244	0.972	0.1413	1.091
		0.0243	0.331	0.1412	1.084	0.1869	1.379
0.9473	1.044			0.2369	1.581	0.2413	1.706
0.9764	0.491	0.9606	0.735	0.2720	1.715	0.2808	1.856
0.9870	0.284	0.9654	0.648	0.3570	1.958	0.3409	2.086
		0.9895	0.206	0.4395	2.052	0.3996	2.246
		0.9910	0.173	0.5089	2.019	0.4055	2.214
				0.5874	1.937	0.4491	2.329
				0.6021	1.862	0.4945	2.305
				0.6863	1.660	0.6010	2.250
				0.7048	1.623	0.7475	1.751
				0.7868	1.264	0.8204	1.387
				0.8201	1.177	0.8966	0.852
				0.9389	0.466	0.9129	0.616

Table V. Experimental Consolute Temperatures T and Calculated Molar Excess Gibbs Energies G^E of the Liquid System Ethanenitrile (1) + 2,2,4-Trimethylpentane (2) at the Critical Consolute Temperature T_C = 354.55 K and Atmospheric Pressure as a Function of the Mole Fraction x_2

x_2	T/K	G^E/(J mol^{-1})	x_2	T/K	G^E/(J mol^{-1})
0.0305	288.59	248	0.4014	354.51	1674
0.0449	305.16	357	0.4871	353.47	1707
0.0590	316.51	457	0.5258	352.88	1695
0.0628	319.26	483	0.5960	350.22	1633
0.0855	330.96	631	0.6492	347.19	1548
0.0940	333.80	684	0.7007	343.10	1433
0.1340	343.86	911	0.7965	331.75	1132
0.1507	347.12	993	0.8304	325.62	993
0.1941	351.62	1185	0.8827	313.32	746
0.2566	353.82	1403	0.9111	303.90	590
0.3310	354.54	1577	0.9361	292.51	439
0.3778	354.53	1648	0.9480	284.75	366

isobaric molar excess heat capacities C_p^E in Table IV. The measured consolute temperatures of ethanenitrile + 2,2,4-trimethylpentane, as well as the calculated molar excess Gibbs energy G^E at 354.55 K, are given in Table V. All the excess properties have been fitted to Redlich–Kister type polynomials

$$Z^E = x_1x_2[\sum_{i=0}^{k} A_i(x_1 - x_2)^i] \tag{1}$$

where Z^E is V^E/(cm^3 mol^{-1}), H^E/(J mol^{-1}), C_p^E/(J mol^{-1} K^{-1}), or G^E/(J mol^{-1}), respectively. The coefficients A_i are summarized in Table VI, together with the standard deviations σ, defined as

$$\sigma^2 = \sum_N [Z_m - Z_f]^2/(N - m) \tag{2}$$

where Z_m is the measured and Z_f the fitted value, N the number of data points, and m the number of coefficients A_i, and the maximum deviations δ_{max}

$$\delta_{max} = \max |Z_m - Z_f| \tag{3}$$

(σ and δ_{max} are given in units of the fitted excess properties in Table VI). For a qualitative comparison of both systems, we estimated the equimolar excess values of ethanenitrile + 2,2,4-trimethylpentane in the miscibility gap from eq 1.

All the Z^E vs x are positive and almost symmetrical. The equimolar values increase with the dipole moment of the polar component. A better correlation can be achieved when considering the reduced dipole moments, μ^* = 1.647 (ethanenitrile) and μ^* = 0.947 (2-butanone) (*7*, *8*, *16*).

The large positive H^E and V^E values result from the strong dipole–dipole interactions of the polar components with each other and the much weaker interactions with 2,2,4-trimethylpentane. The positive equimolar C_p^E reflects this behavior, too. The values of V^E and C_p^E of the 2-butanone + 2,2,4-trimethylpentane system compare nicely with the values of 2-butanone + *n*-heptane, *n*-decane, and *n*-dodecane (*17*), when 2,2,4-trimethylpentane is considered to be similar to *n*-hexane, as observed previously (*8*, *11*).

Finally, $(G^E/RT)_{x=0.5}$ = 0.578 at the consolute temperature is in close agreement with the values of other partially miscible systems (*18*, *19*).

Glossary

A_i	coefficients in eq 1
C_p	isobaric molar heat capacity, J mol^{-1} K^{-1}
C_p^E	isobaric molar excess heat capacity, J mol^{-1} K^{-1}
G^E	molar excess Gibbs energy, J mol^{-1}
H^E	molar excess enthalpy, J mol^{-1}
T	temperature, K

Table VI. Coefficients A_i of Redlich–Kister Fits to Measured Data, Maximum δ_{max} and Standard Deviations σ for the Liquid Systems Polar Component (1) + 2,2,4-Trimethylpentane (2)

polar component	excess property	T/K	A_0	A_1	A_2	δ_{max}	σ
ethanenitrile[a]	V^E	293.15	2.848	1.272		0.006	0.003
	V^E	313.15	3.762	1.484		0.010	0.004
	H^E	293.15	8104	-410	650	1.2	0.71
	C_p^E	293.15	19.117	2.121		0.012	0.009
	C_p^E	313.15	16.915	2.703		0.009	0.007
	G^E	354.55[b]	6822	-473	1258	1.62	0.90
2-butanone	V^E	293.15	2.435	0.565	0.476	0.007	0.004
	V^E	313.15	2.959	0.657	0.496	0.014	0.007
	H^E	293.15	5066	-82	244	22.0	12.0
	C_p^E	293.15	8.112	-0.953	0.416	0.045	0.024
	C_p^E	313.15	9.348	0.022	-0.599	0.096	0.034

[a] The coefficients of the fits for V^E, H^E, and C_p^E are valid for the single-phase region. [b] Upper critical solution temperature.

V	molar volume, cm^3 mol^{-1}
V^E	molar excess volume, cm^3 mol^{-1}
x_i	mole fraction of component i
Z^E	excess value of quantity Z

Greek Letters

δ_{max}	maximum deviation in units of fitted data
ρ	density, g cm^{-3}
σ	standard deviation in units of fitted data

Subscripts

m,f	measured or fitted values

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Infinite Dilution Diffusion Coefficients of Poly(ethylene glycol) and Poly(propylene glycol) in Water in the Temperature Range 303–318 K

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In this paper, the infinite dilution diffusion coefficients of poly(ethylene glycol) and poly(propylene glycol) in water were measured by using the Taylor dispersion technique. For poly(ethylene glycol), the measurements were performed in the temperature range of 303–318 K at four different polymer molecular weights. The diffusion coefficient was found to increase linearly with temperature but decrease exponentially with molecular weight. In addition, the diffusion coefficient of poly(propylene glycol) (M = 400) was found to be lower than that of poly(ethylene glycol) at the same molecular weight but has the same temperature dependence.

1. Introduction

Diffusion coefficient measurements provide fundamental information needed in various engineering and industrial operations. For example, diffusion is important in the design of chemical reactors, liquid–liquid extractors, and absorbers, as well as distillation columns. In addition, the study of fluid-state theory, mass-transfer phenomena, and molecular interactions can be further aided by accurate determinations of diffusion coefficients.

There are many well-established methods for the determination of diffusion coefficients in liquids (*1*). The most accurate measurements of the mutual diffusion coefficients of binary liquid mixtures are performed by the interferometric method (*1*). However, this technique has been proven to be tedious and difficult to be applied to conditions far from ambient (*1,2*). Instead, the Taylor dispersion technique based on chromatographic peak broadening is used in the present work for the determination of the diffusion coefficient. This technique is direct and offers the advantage of speed and simplicity. In fact, it has been established as an absolute method for liquid diffusivity measurements (*3–5*).

Earlier studies on the poly(ethylene glycol)/water system show that, at low concentration, the diffusion coefficient depends on the polymer molecular weight and not on the concentration (*6*). However, no experimental data for diffusion coefficient as a function of temperature is available for this system. In the present paper, the infinite dilution diffusion coefficients of poly(ethylene glycol) in water at different molecular weights and at different temperatures are investigated. In addition, the infinite dilution diffusion coefficients of poly(propylene glycol) at four different temperatures are measured to study the effect of branching on diffusion.

2. Experimental Section

The ideal model of the instrument for the measurement of the diffusion coefficient by the Taylor dispersion technique consists of an infinitely long straight tube of uniform circular cross section, radius a_0, through which a fluid mixture passes in laminar flow with mean velocity, $\bar{u}_0$. A δ-function pulse of a liquid mixture is injected at a distance L from the detection point. The mutual diffusion coefficient of the liquid mixtures, D_{12}, is given by

$$D_{12} = \frac{A}{24\pi t_{id}}\left[\frac{[1 + 4\sigma_{id}^2/t_{id}^2]^{1/2} + 3}{[1 + 4\sigma_{id}^2/t_{id}^2]^{1/2} + 2\sigma_{id}^2/t_{id}^2 - 1}\right] \times [1/2 + 1/2(1 - \delta_a)^{1/2}] \quad (1)$$

where A = cross section area of the tube; t_{id} = first raw

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