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Excess Volume, Isothermal Compressibility, and Excess Enthalpy of the Binary Liquid System Trichlorofluoromethane + 2,2,4-Trimethylpentane

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Molar excess volumes of the binary liquid mixtures of trichlorofluoromethane + 2,2,4-trimethylpentane (isooctane) have been determined from density measurements at atmospheric pressure, the isothermal compressibilities have been determined from density measurements from 0.1 to 10 MPa, and the molar excess enthalpies have been measured by means of a Picker calorimeter at atmospheric pressure, all at 293.15 K.

Introduction

The excess properties of liquid mixtures of trichlorofluoromethane (R11) + 2,2,4-trimethylpentane (ISO) were measured to support the search for suitable substitutes with similar properties as fluorocarbons, which will be phased out in the near future. Also, the data were needed for theoretical studies of a recently developed equation of state that incorporates information on molecular shape (*1*).

Experimental Section

R11 (Hoechst, West Germany) with a checked purity of 99.7% by GLC was dried by storing over molecular sieve 4A (Union Carbide, USA) in contact with the gas phase. ISO (Baker Analyzed Reagent, J. T. Baker Chemicals, Holland) with a purity of 99.94% as determined by GLC was dried by storage over Na–Pb alloy (p.a., Merck, West Germany). The substances were used without further purification but carefully outgassed by several pump–thaw cycles immediately before each measurement. The measured densities at 293.15 K of R11 and ISO, 1.487 23 and 0.691 92 g cm^{-3}, respectively, are in accordance with the literature values, 1.488 (*2*) and 0.691 93 g cm^{-3} (*3*). The relative atomic masses used were A_r(H) = 1.007 94, A_r(C) = 12.011, A_r(Cl) = 35.4527, and A_r(F) = 18.9984, according to IUPAC (1987) (*4*).

Molar excess volumes V^E were calculated from precise density measurements of the liquids by means of a vibrating glass tube densimeter (Model DMA 02 D, Paar, Austria) at 293.15 K and atmospheric pressure, with a precision in the densities of 3 × 10^{-6} g cm^{-3} and an accuracy of 5 × 10^{-5} g cm^{-3}. V^E and the mole fraction x_i were accurate to respectively 0.003 cm^3 mol^{-1}, at the maximum value, and 3 × 10^{-5} (*5*).

Mmolar volumes V and isothermal compressibilities κ of mixtures of constant composition, at 0.1, 2, 4, 6, 8, and 10 MPa and 293.15 K, were determined from densities measured in a vibrating steel capillary densimeter (Model DMA 512, Paar) with a precision of 7 × 10^{-6} g cm^{-3} over the entire pressure range. Isothermal compressibilities, κ°, at p° = 0.1 MPa, could be determined by a fit of V to a modified Tait equation

$$V = V^\circ[1 + n\kappa^\circ(p - p^\circ)]^{-1/n} \tag{1}$$

(where V° is the molar volume at p°) with a relative error of 0.01 (*5*). The accuracy of the mole fraction is the same as above.

Table I. Molar Excess Volumes V^E of the Liquid System R11 (1) + ISO (2) at 293.15 K and Atmospheric Pressure, Coefficients A_i, Maximum δ_{max} and Standard Deviations σ,[a] Equations 2–4

x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
0.100 73	0.084	0.652 23	0.313
0.104 44	0.094	0.690 97	0.302
0.204 26	0.162	0.739 33	0.279
0.207 87	0.165	0.748 06	0.273
0.299 74	0.234	0.792 85	0.249
0.321 23	0.243	0.817 12	0.229
0.404 30	0.283	0.844 05	0.206
0.470 12	0.312	0.850 37	0.200
0.528 39	0.323	0.894 66	0.151
0.542 64	0.325	0.948 10	0.079
0.570 74	0.326		

[a] A_0 = 1.266; A_1 = 0.413; A_2 = −0.002; δ_{max}/(cm^3 mol^{-1}) = 0.006; σ/(cm^3 mol^{-1}) = 0.003.

Measurement of molar excess enthalpies H^E by means of a dynamic flow microcalorimeter of Picker type (Setaram, France) at 293.15 K and atmospheric pressure has been described in detail elsewhere (*6*). The separators and the tubing through which the liquids were pushed into the calorimeter had to be cooled by an ice/water mixture to avoid the formation of bubbles in the flow system due to the proximity of R11 to its boiling point (296.83 K). This seems to be the first case that such a system was measured in a Picker calorimeter. Still, the mole fractions had an accuracy of 1 × 10^{-4} and the enthalpies were measured with relative errors of 0.025 at the maximum value.

Results and Discussion

In Table I, the molar excess volumes at 293.15 K and atmospheric pressure are presented. The molar volumes measured at various pressures and the calculated isothermal compressibilities at 0.1 MPa are shown in Table II. The measured molar excess enthalpies are given in Table III.

The V^E and H^E data have been fitted to Redlich–Kister-type polynomials

$$Z^E = x_1x_2\left[\sum_{i=0}^{k} A_i(x_1 - x_2)^i\right] \tag{2}$$

where Z^E is either V^E/(cm^3 mol^{-1}) or H^E/(J mol^{-1}). The coefficients A_i are summarized in Tables II and III together with the standard deviation σ defined as

$$\sigma^2 = \sum_N [Z_m - Z_f]^2/(N - m) \tag{3}$$

(with Z_m being the measured value and Z_f the fitted value, N the number of data points, and m the number of coefficients) and the maximum deviation δ_{max}

$$\delta_{max} = \max|Z_m - Z_f| \tag{4}$$

Equation 1 represents the experimental V values with an overall standard deviation σ = 0.002 cm^3 mol^{-1} and a maximum de-

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Table II. Measured Molar Volumes V of the Liquid System R11 (1) + ISO (2) at Pressures p (MPA) of 0.1, 2, 4, 6, 8, and 10 MPa and 293.15 K and Isothermal Compressibilities κ° at 0.1 MPa Calculated with the Modified Tait Equation (Equation 1, n = 10.2)

	$V/(\mathrm{cm^3\ mol^{-1}})$						
x_1	p = 0.1	p = 2	p = 4	p = 6	p = 8	p = 10	$10^{12}\kappa^\circ/\mathrm{Pa^{-1}}$
0.000 00	165.092	165.636	164.173	164.724	163.289	162.871	1468
0.163 94	153.290	152.859	152.420	151.997	151.588	151.192	1494
0.287 64	144.379	143.965	143.543	143.136	142.744	142.363	1527
0.381 19	135.789	135.392	134.989	134.603	134.229	133.866	1550
0.441 41	133.282	132.890	132.494	132.110	131.742	131.381	1561
0.493 23	129.503	129.118	128.730	128.354	127.994	127.641	1575
0.526 61	127.091	126.712	126.328	125.959	125.601	125.255	1584
0.572 70	123.735	123.364	122.987	122.624	122.275	121.935	1596
0.622 54	120.110	119.746	119.376	119.020	118.677	118.343	1616
0.636 36	119.116	118.755	118.387	118.033	117.693	117.364	1617
0.689 90	115.220	114.866	114.506	114.160	113.827	113.504	1637
0.734 37	111.954	111.608	111.257	110.919	110.592	110.278	1648
0.789 05	107.945	107.609	107.268	106.938	106.620	106.313	1665
0.897 48	99.964	99.645	99.324	99.013	98.711	98.424	1701
1.000 00	92.355	92.056	91.753	91.461	91.180	90.908	1731

Table III. Molar Excess Enthalpies H^E of the Liquid System R11 (1) + ISO (2) at 293.15 K and Atmospheric Pressure, Coefficients A_i, Maximum δ_{max} and Standard Deviations σ,[a] equations 2–4

x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$
0.1612	76	0.7194	179
0.1828	84	0.7591	169
0.2892	129	0.7755	163
0.3100	135	0.7972	153
0.3772	157	0.8279	137
0.4250	171	0.8440	130
0.5008	188	0.8652	116
0.5746	196	0.8968	96
0.6027	195	0.9067	89
0.6299	194	0.9248	73
0.6681	191	0.9486	53
0.6868	186	0.9669	36

[a] $A_0 = 747$; $A_1 = 310$; $A_2 = 46$; $A_3 = 13$; $\delta_{max}/(\mathrm{J\ mol^{-1}}) = 2$; $\sigma/(\mathrm{J\ mol^{-1}}) = 1$.

viation $\delta_{max} < 0.003\ \mathrm{cm^3\ mol^{-1}}$.

V^E has a maximum of ~0.33 $\mathrm{cm^3\ mol^{-1}}$ at a mole fraction of R11 of $x_1 = 0.58$. H^E has a maximum of 195 J $\mathrm{mol^{-1}}$ around $x_1 \sim 0.59$. The related system, carbon tetrachloride + ISO, exhibits a maximum H^E of 415 J $\mathrm{mol^{-1}}$ at $x_1 \sim 0.56$ and 298.15 K (*7*), which shows the influence on this excess property, if one chlorine atom in CCl_4 is replaced by fluorine in R11. At the same time, the increase of the equimolar V^E is of about 0.2% only (*8*).

Glossary

A_i	coefficients in eq 2
H^E	molar excess enthalpy, J $\mathrm{mol^{-1}}$
ISO	2,2,4-trimethylpentane (isooctane)
m	number of coefficients in eq 2
N	number of measured data points
n	Tait constant, eq 1
p	pressure, MPa
R11	trichlorofluoromethane
V	molar volume, $\mathrm{cm^3\ mol^{-1}}$
V^E	molar excess volume, $\mathrm{cm^3\ mol^{-1}}$
x_i	mole fraction of component i
Z^E	general excess data

Greek Letters

δ_{max}	maximum deviation in units of fitted data
κ	isothermal compressibility, $\mathrm{TPa^{-1}}$
σ	standard deviation in units of fitted data

Subscripts

m, f	measured or fitted values

Superscripts

°	values at p° = 0.1 MPa

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