the alkanols. For ethanol and the solutes having more than two hydroxyl groups, the quantity $D\eta/T$ is essentially temperature-independent. This is in contrast to results obtained for nonpolar solutes in organic solvents where $D\eta/T$ tends to increase with increasing viscosity of the solvent or with decreasing temperature (*18*, *20–22*). In view of the smaller variation of $D\eta/T$ in water, the diffusion coefficients of nonelectrolytes in water may be estimated with greater certainty than in organic solvents.

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Excess Volume, Isothermal Compressibility, and Excess Enthalpy of the Binary Liquid System 2,2,2-Trifluoroethanol + 2,5,8,11,14-Pentaoxapentadecane

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Molar excess volumes of the binary liquid mixtures of 2,2,2-trifluoroethanol + 2,5,8,11,14-pentaoxapentadecane (tetraethylene glycol dimethyl ether) have been determined from density measurements at atmospheric pressure and 293.15 and 313.15 K, the isothermal compressibilities were determined from density measurements at 0.1–10 MPa and 293.15 K, and the molar excess enthalpy has been measured by a Picker calorimeter at atmospheric pressure and 293.15 K. The data were needed for a possible application of the mixture as the working fluid in heat transformers.

Introduction

Thermodynamic property data on 2,2,2-trifluoroethanol (TFE) + 2,5,8,11,14-pentaoxapentadecane (E 181) mixtures are scarce, although these mixtures have been suggested as working fluids in heat transformers (*1*). In this paper we report excess enthalpy data that are especially needed in the design of transformers providing heat at high temperatures (*2*). Additionally, we measured the excess volumes necessary to calculate the molar excess enthalpy data obtained by means of a Picker flow calorimeter. Also, isothermal compressibilities were determined for future theoretical studies of a recently developed equation of state that incorporates information on molecular shape (*3*).

Experimental Section

TFE (p. synth.; Merck, West Germany; stated purity 98%), with a purity of 99.8% checked by GLC, was not further purified. It was degassed by several pump–thaw cycles until the density remained constant and was stored over molecular sieve 3A in contact with the gas phase. E 181 (p. synth.; Merck, West Germany; stated purity 98%), with a purity of 99.5% determined by GLC, was treated similarly. However, degassing to constant density had to be performed by continuous pumping of the hot liquid to reduce its viscosity, which otherwise would have impeded the diffusion of gases.

Table I. Measured Densities ρ and Calculated Molar Excess Volumes V^E of the Liquid System TFE (1) + E 181 (2) at 293.15 or 313.15 K and Atmospheric Pressure

	T = 293.15 K		T = 313.15 K	
x_1	$\rho/(\mathrm{g\ cm^{-3}})$	$V^E/(\mathrm{cm^3\ mol^{-1}})$	$\rho/(\mathrm{g\ cm^{-3}})$	$V^E/(\mathrm{cm^3\ mol^{-1}})$
0.000 00	1.011 26	0.000	0.992 74	0.000
0.025 80	1.014 54	0.002		
0.057 61	1.018 73	0.000	0.999 97	−0.004
0.093 85			1.004 84	−0.015
0.143 16	1.030 99	−0.004		
0.181 66	1.037 02	−0.003	1.017 66	−0.021
0.293 35	1.056 74	−0.007	1.036 72	−0.035
0.395 49	1.078 28	−0.006	1.057 52	−0.042
0.487 05	1.101 32	−0.007	1.079 77	−0.055
0.588 18	1.132 27	−0.009	1.109 61	−0.065
0.692 38	1.172 50	−0.020	1.148 36	−0.083
0.801 49	1.228 13	−0.061	1.201 82	−0.130
0.851 42	1.260 08	−0.088	1.232 40	−0.151
0.900 85	1.297 41	−0.134	1.267 96	−0.185
0.919 90	1.313 38	−0.141	1.283 15	−0.186
0.949 43	1.340 13	−0.136		
0.950 67			1.309 68	−0.172
0.970 74	1.360 70	−0.098	1.328 12	−0.130
1.000 00	1.390 99	0.000	1.356 45	0.000

The densities of the pure compounds at atmospheric pressure can be found in Table I. Recently, molar volumes of TFE of 72.25 (*4*) and 72.4 $\mathrm{cm^3\ mol^{-1}}$ (*5*) and a density of E 181 of 1.006 51 $\mathrm{g\ cm^{-3}}$ (*6*), all at 298.15 K, have been published. The

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Table II. Measured Molar Volumes V of the Liquid System TFE (1) + E 181 (2) at Pressures p and 293.15 K, Calculated Isothermal Compressibilities $\kappa°$ at 0.1 MPa, and Constant n for the Modified Tait Equation

	$V/(\mathrm{cm^3\ mol^{-1}})$							
x_1	0.1 MPa	2 MPa	4 MPa	6 MPa	8 MPa	10 MPa	$10^{12}\kappa°/\mathrm{Pa^{-1}}$	n
0.000 00	219.84	219.58	219.31	219.04	218.78	218.52	627	9.75
0.055 21	211.89	211.64	211.37	211.12	210.86	210.60	634	9.75
0.151 12	197.69	197.45	197.20	196.95	196.71	196.46	649	9.75
0.239 08	184.66	184.43	184.19	183.95	183.72	183.49	663	9.95
0.302 44	175.27	175.05	174.82	174.59	174.37	174.14	673	9.75
0.439 59	154.96	154.76	154.54	154.33	154.12	153.92	706	9.95
0.544 88	139.36	139.17	138.96	138.76	138.57	138.37	746	9.95
0.648 60	123.98	123.80	123.61	123.42	123.24	123.05	789	9.95
0.755 28	108.15	107.98	107.80	107.62	107.45	107.28	851	9.95
0.854 00	93.46	93.30	93.13	92.96	92.79	92.63	947	10.15
0.951 25	79.01	78.85	78.69	78.53	78.37	78.22	1069	10.15
1.000 00	71.91	71.75	71.59	71.43	71.28	71.13	1164	10.15

Table III. Measured Molar Excess Enthalpies H^E of the Liquid System TFE (1) + E 181 (2) at 293.15 K and Atmospheric Pressure

x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$
0.1603	-1357	0.7884	-3288
0.2229	-1717	0.8063	-3168
0.3710	-2510	0.8122	-3126
0.4208	-2733	0.8365	-2956
0.4605	-2878	0.8676	-2645
0.5165	-3117	0.8786	-2479
0.5546	-3259	0.8840	-2455
0.6263	-3433	0.9158	-2007
0.6585	-3490	0.9245	-1897
0.7098	-3495	0.9304	-1756
0.7369	-3460	0.9718	-960
0.7539	-3433	0.9772	-848

corresponding values at 298.15 K obtained by linear interpolation from the data at 293.15 and 313.15 K reported in this work (72.37 and 1.006 63, respectively) agree very well with these literature data.

Relative molar masses according to IUPAC (1984) were used, i.e., M_r(TFE) = 100.040 4296 and M_r(E 181) = 222.281 68.

***Excess Volumes*.** Molar excess volumes were calculated from density measurements by means of a vibrating glass tube densimeter (DMA 02 D, A. Paar, Austria) at 293.15 or 313.15 K and atmospheric pressure. The temperature was controlled to within 0.002 K with a precision temperature controller (Model PTC 40, Tronac, Orem, UT). It was measured by a calibrated platinum resistance thermometer (IPTS-68) and an ac double bridge (Automatic Systems Laboratory, England). This thermometer was positioned upstream in the circulating fluid of the thermostat (NBD 8/17 and cryostat UK 30D, Lauda, West Germany) very closely to the vibrating tube. The temperature is believed to be accurate to within 0.005 K. It was checked regularly by a thermocouple, which could be dipped into the liquid filled into the vibrating tube for the density measurement and allowed to measure the actual temperature of this liquid in the tube. The instrument was calibrated with tridistilled water (*7*) and air (*8*). The measurements were reproducible to 3×10^{-6} g cm^{-3}. Absolute errors of 5×10^{-5} g cm^{-3} were found in the density range between 0.7 and 1.5 g cm^{-3} at 293.15 K by comparison with pycnometric measurements that allowed accuracies better than 1×10^{-5} g cm^{-3} (*9*). At 313.15 K the absolute errors in the densities were about 1×10^{-4} g cm^{-3}.

The mixtures were prepared from carefully degassed pure liquids. The less volatile substance was introduced under high vacuum into a glass sample tube (volume about 9 cm^3; capped with a Teflon tap) and its mass determined by weight. Then, the sample was frozen and the volatile liquid added under vacuum in such an amount that after both liquids were warmed and mixed, only a minute vapor space appeared in the filled sample tube, which was weighed again. Correction for vapor space was performed but had only a small influence on the final mole fraction for which uncertainties of 3×10^{-5} were estimated. Thus, the excess molar volume is accurate to 0.003 cm^3 mol^{-1} at the maximum value. The mixtures were pressed into the densimeter without losses by evaporation or contact to air.

***Isothermal Compressibilities*.** Molar volumes and isothermal compressibilities of mixtures of constant composition, at pressures of 0.1, 2, 4, 6, 8, and 10 MPa and at 293.15 K, were determined from densities measured in a steel capillary vibrating tube densimeter (DMA 512, Paar). The liquid was pressurized by nitrogen through a capillary system long enough to prevent diffusion of the gas into the sample. The pressure was measured by means of a quartz pressure transducer (4073 A 100, Kistler Instrumente, Switzerland), calibrated against a deadweight gauge and a digital voltmeter (191, Keithly, West Germany). The relative error in pressure, $\Delta p/p$, was estimated to be 1×10^{-4}. The temperature was kept constant (Thermostat N3, Haake, West Germany) to 0.011 K, measured, and checked as described above. The densimeter was calibrated with benzene and carbon tetrachloride, the pressure dependence of their densities being known with good accuracy (*10*). The measurements were reproducible to 5×10^{-6} g cm^{-3} over the entire pressure range. Mole fractions are of the same accuracy as above.

The molar volumes at the different pressures were fitted by nonlinear regression to a modified Tait equation (*11*)

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

leading to the two parameters n and $\kappa°$, where $\kappa°$ is the isothermal compressibility at the pressure $p° = 0.1$ MPa. Values of κ at other pressures can be calculated from

$$\kappa^{-1} = (\kappa°)^{-1} + n(p - p°) \qquad (2)$$

Relative errors of $\Delta\kappa°/\kappa°$ were found to be 0.01.

***Excess Enthalpy*.** Measurement of molar excess enthalpies by a dynamic flow microcalorimeter of Picker type (Setaram, France) at 293.15 K and atmospheric pressure has been described in detail previously (*12*). Here, the mole fraction had an accuracy of 1×10^{-4}, and the enthalpies were measured with relative errors better than 0.025 at the minimum value.

Results and Discussion

In Table I are presented the measured densities and the molar excess volumes calculated from them. 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.

Density data have been fitted to polynomials

$$\rho/(\mathrm{g\ cm^{-3}}) = \sum_{i=0}^{5} A_i x_1^{\,i} \qquad (3)$$

Table IV. Coefficients of Fits to Measured Data, Maximum $\delta_{\max}$, and Standard Deviations σ for the Liquid System TFE (1) + E 181 (2)

Density at Atmospheric Pressure, Equation 3

T/K	A_0	A_1	A_2	A_3	A_4	A_5	$\delta_{\max}$/(g cm^{-3})	σ/(g cm^{-3})
293.15	1.011 26	0.125 90	0.056 41	0.209 39	−0.293 93	0.282 28	0.000 34	0.000 21
313.15	0.992 72	0.120 52	0.070 62	0.141 92	−0.195 99	0.227 07	0.000 40	0.000 25

Molar Excess Volume at Atmospheric Pressure, Equation 4

T/K	B_0	B_1	B_2	C_1	C_2	$\delta_{\max}$/(cm^3 mol^{-1})	σ/(cm^3 mol^{-1})
293.15	−0.026	0.012	−0.125	−1.982	1.018	0.003	0.002
313.15	−0.215	0.181	−0.147	−1.867	0.898	0.004	0.003

Molar Excess Enthalpy at Atmospheric Pressure, Equation 5

T/K	D_0	D_1	D_2	D_3	D_4	D_5	D_6	$\delta_{\max}$/(J mol^{-1})	σ/(J mol^{-1})
293.15	−12 124	−7341	−12 087	−6280	25 035	8726	−35 280	78	31

molar excess volume data to equations recommended for strongly skewed curves

$$V^{\mathrm{E}}/(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = x_1x_2\left[\sum_{i=0}^{2} B_i(x_1 - x_2)^i\right]\Big/\left[1 + \sum_{i=1}^{2} C_i(x_1 - x_2)^i\right] \quad (4)$$

and molar excess enthalpies to Redlich–Kister-type polynomials

$$H^{\mathrm{E}}/(\mathrm{J\ mol}^{-1}) = x_1x_2\sum_{i=0}^{6} D_i(x_1 - x_2)^i \quad (5)$$

The coefficients are summarized in Table IV together with the standard deviation σ defined as

$$\sigma^2 = \sum_{N} [Z_{\mathrm{m}} - Z_{\mathrm{f}}]^2/(N - m) \quad (6)$$

(where Z_{m} is the measured value, Z_{f} the fitted value, N the number of data points, and m the number of coefficients) and the maximum deviation $\delta_{\max}$

$$\delta_{\max} = \max|Z_{\mathrm{m}} - Z_{\mathrm{f}}| \quad (7)$$

Equation 1 represents the experimental V values with an overall standard deviation of $\sigma = 0.003$ cm^3 mol^{-1} and maximum deviation of $\delta_{\max} < 0.006$ cm^3 mol^{-1}. For the fit of eq 3, six coefficients were necessary to reach a standard deviation compatible with the quality of the density data. Especially at high densities, the ρ vs x_1 curve becomes almost straight. However, it was not intended to look for a better functional representation of that data. Also, at least seven Redlich–Kister coefficients had to be used to fit the rather asymmetrical H^{E} curve properly.

The large exothermic excess enthalpy, −3.5 kJ mol^{-1} at $x_1 \sim 0.7$, and the strongly peaked excess volume with minima of −0.14 cm^3 mol^{-1} (293.15 K) and −0.185 cm^3 mol^{-1} (313.15 K) at $x_1 \sim 0.9$ indicate complex formation between the fluoroalcohol and the polyether. Fluoroalcohols are less self-associated than ordinary alcohols, because the fluorine group reduces the ability of the oxygen atom to act as potential acceptor for hydrogen bonding (*5*). This leads to a more pronounced interaction in mixtures between the OH hydrogen of the fluoroalcohol and the oxygen atoms of the ether.

Glossary

A_i	coefficients in eq 3
B_i,C_i	coefficients in eq 4
D_i	coefficients in eq 5
E 181	2,5,8,11,14-pentaoxapentadecane
H^{E}	molar excess enthalpy, J mol^{-1}
m	number of coefficients in eq 3–5
N	number of measured data points
n	Tait constant
p	pressure, MPa
T	temperature, K
TFE	2,2,2-trifluoroethanol
V	molar volume, cm^3 mol^{-1}
V^{E}	molar excess volume, cm^3 mol^{-1}
x_i	mole fraction of component i

Greek Letters

Δ	range of errors
$\delta_{\max}$	maximal deviation in units of fitted data
κ	isothermal compressibility, TPa^{-1}
ρ	density, g cm^{-3}
σ	standard deviation in units of fitted data

Subscripts

m,f	measured or fitted values

Superscripts

o	values at $p^\circ = 0.1$ MPa

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