

Volumetric Properties of Mixtures of Fluoroalcohols and Water at High Pressures

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Densities of aqueous solutions of 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, and 2,2,3,3,3-pentafluoropropanol have been measured with a vibrating-tube densitometer. Measurements were performed at temperatures of 298 and 323 K and at pressures up to 80 MPa with an estimated uncertainty of $\pm 0.2\%$. Molar volumes obtained for these mixtures are correlated with pressure by the Tait equation within the experimental uncertainty. Excess molar volume, isothermal compressibility, and partial molar volume of these mixtures are determined in terms of this correlation equation and compared with those of the aqueous solutions of hydrocarbon alcohols. Composition dependence of partial molar volume is discussed in comparison with that of Raman spectroscopic data.

KEY WORDS: aqueous solutions; compressibility; density; fluoroalcohols; high pressure; hydrocarbon alcohols; Raman spectroscopy.

1. INTRODUCTION

As is well-known, there exist anomalous temperature, pressure, and composition dependences in the thermophysical properties of aqueous solutions of alcohols. They are qualitatively interpreted in terms of the complicated intermolecular interactions arising from the hydrogen bonds between water-water molecules and water-alcohol molecules [1-5]. Although recent advances in computer experiments have provided great insight on this subject, accumulation of accurate experimental data on thermophysical properties over wide temperature and pressure ranges is still required to explicate these anomalies.

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In our latest publication [6], the viscosity of aqueous solutions of three fluoroalcohols, 2,2,2-trifluoroethanol (3FE), 2,2,3,3-tetrafluoropropanol (4FP), and 2,2,3,3,3-pentafluoropropanol (5FP), was measured in the temperature range from 298 to 323 K and at pressures up to 80 MPa. The temperature, pressure, and composition dependences of obtained viscosities were discussed in comparison with those of aqueous solutions of corresponding hydrocarbon alcohols previously reported [7]. Comparisons between the viscosities and the nuclear magnetic resonance (NMR) spectroscopic data were also performed and similar composition dependences were reported. Furthermore, the static dielectric constant of these aqueous solutions was measured and those temperature and pressure dependences were also discussed [8].

In the present work, the density of aqueous solutions of 3FE, 4FP, and 5FP has been measured at temperatures of 298 and 323 K and at pressures up to 80 MPa. The measurements were performed with two vibrating-tube densitometers and the estimated uncertainties of the densities obtained are $\pm 0.1\%$ for pure components and $\pm 0.2\%$ for mixtures, respectively. For the mixtures of 5FP and water, the measurements were carried out in the composition range where both components dissolve completely.

The industrial use of the aqueous solutions of fluoroalcohols has been emphasized lately, i.e., an aqueous solution of 3FE (fluorinol) appears to be a favorable working fluid for waste-heat recovery and 5FP and its azeotropic mixture with water also appear to be one of the possible alternatives for the restricted substance CFC-113 because of their favorable cleaning abilities.

2. EXPERIMENTS

Because of its advantages of a quite high precision and simplicity of handling, the vibrating-tube densitometer has become widely used. The present measurements were performed with two vibrating-tube densitometers, i.e., a commercial one, Paar DMA512, whose pressure limit is 40 MPa, and a newly constructed one for measurements in the higher pressure range. The principles of measurement for the two densitometers are basically the same and the latter one, developed in the present work, is illustrated schematically in Fig. 1. The main portion of the densitometer consists of a stainless-steel vibrating U-shaped tube (5) with a small magnet flag (4), a driving coil (1), and a couple of photocells (2 and 3) which act as a vibration detector. The length of the vibrating tube is 120 mm and its outer and inner diameters are 3.2 and 1.2 mm, respectively. Details of this densitometer are described elsewhere [9]. The natural frequency of a vibrating tube filled with a sample liquid is dependent on the

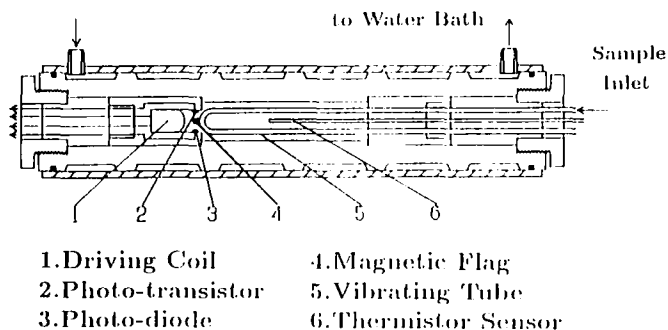


Fig. 1. Schematic diagram of the vibrating-tube densitometer.

total mass of the tube, and the density of sample liquid is given by the following equation:

$$\rho = K_1 \tau^2 + K_2 \quad (1)$$

where ρ is the sample density ($\text{kg} \cdot \text{m}^{-3}$) and τ is the natural frequency (s^{-1}). In this study, the density was obtained on a relative basis and the instrument constants K_1 and K_2 were calibrated against the recommended density values of pure water [10] and pure heavy water [11] over the entire range of measurements. The densitometer cell is jacketed and maintained isothermally at ± 10 mK by circulating water. Temperature and pressure, which are measured with a thermistor to within ± 10 mK and a digitized Bourdon gauge to within ± 0.2 MPa, respectively, are monitored by a computer together with the frequency of the vibrating tube. 3FE with a guaranteed purity better than 99% was obtained from Wako Pure Chemical Industries, Ltd., and 4FP and 5FP with a guaranteed purity better than 99.9% were obtained from Daikin Industries, Ltd. Each sample is stored over 4-Å molecular sieves for more than a week to remove water. 3FE and 5FP are distilled twice after the storage but 4FP is used without distillation. Judging from the precision of the instruments, the purity of the samples, and the reproducibility of the measurements, we estimate the uncertainties of the densities obtained to be within $\pm 0.1\%$ for the pure components. For the mixtures the uncertainty increases to $\pm 0.2\%$ because of the additional uncertainties arising from the gravimetric preparation procedure.

3. RESULTS

3.1. Molar Volume at Atmospheric Pressure

At atmospheric pressure, 30, 34, and 22 experimental densities were obtained at two temperatures for the aqueous solutions of 3FE, 4FP, and

5FP, respectively. The molar volumes obtained correlated satisfactorily with the mole fraction of alcohol, x_{al} , by the following equations within the experimental uncertainty.

$$V_0 = x_{al} V_{0,al} + (1 - x_{al}) V_{0,H_2O} + V_0^E \quad (2)$$

$$V_0^E = x_{al}(1 - x_{al}) \sum_{i=1}^5 a_i (1 - 2x_{al})^{i-1} \quad (3)$$

Here V_0 and V_0^E are the molar volume and the excess molar volume ($\text{cm}^3 \cdot \text{mol}^{-1}$) at atmospheric pressure and the subscripts al and H_2O refer to pure alcohol and pure water, respectively. The coefficients a_i in Eq. (3) are given in Table I together with the molar volume of pure components $V_{0,al}$ and V_{0,H_2O} . The excess molar volumes obtained at atmospheric pressure are also shown in Fig. 2 as a function of the mole fraction together with the corresponding hydrocarbon alcohol mixtures at 298 K. As is evident from this figure, the excess molar volumes are negative over most of the composition range and the isotherm of each mixture shifts to the positive direction with increasing temperature. But the curvatures of the isotherms are convex at higher concentrations of alcohol and a definite positive excess molar volume is observed for 5FP mixtures at 323 K. It is also found that the excess molar volumes of fluoroalcohol mixtures are less negative than those of corresponding hydrocarbon alcohol mixtures.

For the pure components of sample fluoroalcohols, a few molar volumes at atmospheric pressure are available in the literature. The present density for pure 3FE agrees with the recent reference data, Malhotra and Woolf [12], Kabata et al. [13], Kabata [14], and Nakamura et al. [15], and the deviations from those literature values are within 0.03%. But the

Table I. Coefficients in Eqs. (2) and (3)

	3FE		4FP		5FP	
	298.15 K	323.15 K	298.15 K	323.15 K	298.15 K	323.15 K
$V_{0,al}$	72.3550	74.7562	89.1862	91.7675	99.6096	103.0556
V_{0,H_2O}	18.0689	18.2334	18.0689	18.2334	18.0689	18.2334
a_1	-2.31518	-1.92323	-1.34599	-0.94896	-1.13183	-0.80389
a_2	-1.18529	-1.45430	-1.07739	-1.17370	-1.43120	-7.71051
a_3	0.05131	-0.49538	-0.07576	-0.08902	0.16755	0.01935
a_4	-2.14418	-1.48096	-1.59367	-1.26027		
a_5	-2.18436	-1.40164	-1.56471	-1.50967		
A.D. (%)	0.013	0.021	0.023	0.017	0.004	0.004
M.D. (%)	0.046	0.081	0.088	0.078	0.010	0.008

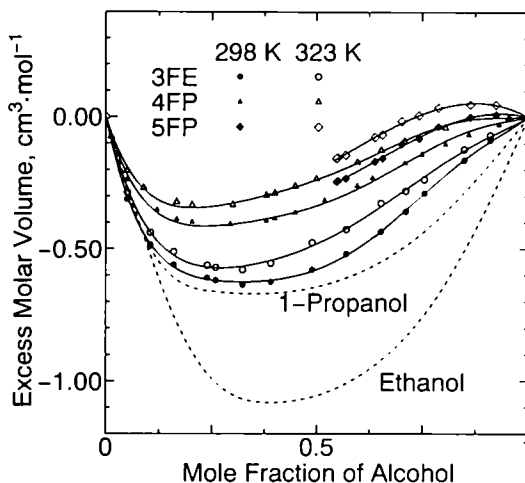


Fig. 2. Excess molar volume of the fluoroalcohol and water mixture at atmospheric pressure. Dashed lines are the aqueous solutions of ethanol and 1-propanol at 298 K.

density reported by Palepu and Clarke [16] at 298 K is 0.84% lower than the present value. For pure 4FP, very few reference data are available and the agreement with the present results is not always satisfactory, i.e., the atmospheric pressure densities at 298 K given by Noguchi [17] and Gajnos [18] are 0.09% higher and 0.32% lower than the present results, respectively. The situation is the same for pure 5FP and the atmospheric pressure density at 298 K given by Noguchi [17] is 0.25% higher than the present result.

3.2. Pressure Dependence of Molar Volume

In the previous work on a series of aqueous solutions of primary hydrocarbon alcohols [22], the following Tait equation was adopted to represent the pressure dependence of the molar volume:

$$V_P = V_0 \left(1 - C \ln \frac{B + P}{B + P_0} \right) \quad (4)$$

Here V_P and V_0 are the molar volumes ($\text{cm}^3 \cdot \text{mol}^{-1}$) at pressure P and at atmospheric pressure P_0 in MPa. In the present investigation, we adopted the Tait equation again to avoid the inferences on the derivative properties by the use of a different correlation equation. For individual mixtures in the present system, the molar volume isotherm decreases monotonously

with increasing pressure and can be satisfactorily represented by the Tait equation, as well as aqueous solutions of primary hydrocarbon alcohols. The coefficients of Eq. (4) determined by the least-squares fitting are given in Table II-V together with the average and maximum deviations. In the fitting procedure, V_0 was also determined as a fitting parameter of Eq. (4), as well as B and C . For pure 3FE, two sets of parameter, which were determined by the data collected in separate runs with the different densitometers, are given in Tables II and III. The molar volumes of pure 3FE represented by the different sets of parameters agree with each other within the combined uncertainties of the experiments. To discuss the composition dependences of volumetric properties based on the Tait equation, correlation of the empirical coefficients B and C in Eq. (4) with the mole fraction of alcohol, x_{al} , was attempted as follows. First, parameter C in Tables II-V was correlated with x_{al} by the following equation:

$$C = C_{H_2O} [1 + c_1 \{1 - \exp(c_2 x_{al})\}] \quad (5)$$

where C_{H_2O} is the parameter for pure water, which is determined to represent the recommended value of density of Kestin and Sengers [10]. Since parameter B , which was redetermined with the smoothed values of

Table II. Coefficients in Eq. (4) for 3FE and Water Mixtures at 298 K

x_{al}	V_0	B	C	Dev. (%)		Dev. (%) ^a	
				Max.	Ave.	Max.	Ave.
0.0502 ^b	20.4835	250.4733	0.11122	0.006	0.002	0.045	0.038
0.1044 ^b	23.2542	202.8278	0.10281	0.006	0.003	0.071	0.040
0.1599 ^b	26.1899	157.6333	0.09118	0.010	0.004	0.035	0.020
0.2389 ^b	30.4298	129.8135	0.08686	0.009	0.004	0.058	0.039
0.2590	31.5150	116.2744	0.08286	0.023	0.012	0.112	0.061
0.3232 ^b	34.9756	110.5905	0.08401	0.011	0.007	0.048	0.031
0.4889 ^b	44.0495	88.5944	0.08255	0.010	0.007	0.055	0.030
0.5368	46.6547	80.2500	0.07794	0.008	0.003	0.029	0.018
0.6528 ^b	53.0781	66.5894	0.07090	0.012	0.006	0.031	0.009
0.7111	56.3101	67.1808	0.07473	0.030	0.013	0.088	0.037
0.7553 ^b	58.7779	71.9388	0.08004	0.009	0.005	0.027	0.016
0.8489 ^b	63.9961	74.0710	0.08629	0.016	0.007	0.047	0.022
0.9104	67.4242	59.2054	0.07468	0.045	0.019	0.092	0.026
1.0 ^b	72.3549	67.6684	0.08429	0.016	0.007	0.040	0.019
1.0	72.3674	64.2581	0.07958	0.052	0.015	0.044	0.026

^a Deviation by smoothed Tait equation.

^b With Anton Paar 502.

Table III. Coefficients in Eq. (4) for 3FE and Water Mixtures at 323 K

x_{al}	V_0	B	C	Dev. (%)		Dev. (%) ^a	
				Max.	Ave.	Max.	Ave.
0.0502 ^b	20.7859	225.5011	0.10700	0.006	0.002	0.082	0.069
0.1044 ^b	23.6970	170.6663	0.09578	0.004	0.002	0.033	0.019
0.1599 ^b	26.7604	149.5492	0.09621	0.005	0.002	0.054	0.046
0.2389 ^b	31.1723	113.4102	0.08753	0.009	0.004	0.023	0.015
0.2590	32.3008	113.5017	0.09102	0.027	0.008	0.064	0.025
0.3232 ^b	35.9236	91.5755	0.08162	0.005	0.003	0.038	0.029
0.4889 ^b	45.3954	84.0784	0.09122	0.013	0.008	0.048	0.026
0.5368	48.1231	70.8867	0.08421	0.004	0.002	0.070	0.047
0.6528 ^b	54.8093	64.4456	0.08185	0.011	0.005	0.036	0.023
0.7111	58.1696	60.8597	0.08359	0.055	0.035	0.095	0.039
0.8489 ^b	66.0975	59.6299	0.08461	0.010	0.004	0.048	0.025
0.9104	69.6400	69.2518	0.09790	0.041	0.020	0.098	0.060
1.0 ^b	74.7549	55.1122	0.08459	0.012	0.005	0.038	0.013
1.0	74.7542	57.9177	0.08708	0.015	0.004	0.089	0.052

^a Deviation by smoothed Tait equation.

^b With Anton Paar 502.

Table IV. Coefficients in Eq. (4) for 4FP and Water Mixtures

x_{al}	V_0	B	C	Dev. (%)		Dev. (%) ^a	
				Max.	Ave.	Max.	Ave.
298 K							
0.0507	21.4365	232.5302	0.10365	0.018	0.007		
0.2028	32.0911	160.6396	0.08521	0.018	0.008	0.054	0.035
0.3996	46.1032	139.2651	0.08557	0.014	0.005	0.050	0.020
0.5969	60.2569	117.0254	0.08088	0.018	0.006	0.040	0.015
0.8052	75.2287	107.7717	0.07959	0.017	0.006	0.031	0.016
1.0	89.1913	88.5546	0.07240	0.017	0.007	0.058	0.030
323 K							
0.0507	21.7495	254.4397	0.11710	0.013	0.004		
0.2028	32.8160	145.3914	0.08874	0.017	0.008	0.053	0.019
0.3996	47.3313	118.3311	0.08826	0.035	0.009	0.042	0.016
0.5969	61.9524	97.2446	0.08518	0.024	0.009	0.137	0.073
0.8052	77.3962	92.5472	0.08520	0.012	0.004	0.027	0.015
1.0	91.7727	93.1172	0.09078	0.017	0.006	0.054	0.019

^a Deviation by smoothed Tait equation.

Table V. Coefficients in Eq. (4) for 5FP and Water Mixtures

x_{al}	V_0	B	C	Dev. (%)		Dev. (%) ^a	
				Max.	Ave.	Max.	Ave.
298 K							
0.5504	62.7086	68.6811	0.07722	0.011	0.005	0.015	0.009
0.6564	71.4325	67.9578	0.07855	0.018	0.007	0.021	0.009
0.7892	82.3887	58.6437	0.07531	0.015	0.005	0.191	0.102
1.0	99.6100	57.5264	0.07485	0.015	0.006	0.018	0.007
323 K							
0.5504	64.7621	61.4653	0.08516	0.010	0.004	0.063	0.025
0.6564	73.8478	54.5834	0.08024	0.028	0.007	0.076	0.030
0.7892	85.2166	51.6309	0.08080	0.021	0.007	0.036	0.015
1.0	103.0502	48.4428	0.08099	0.027	0.011	0.029	0.013

^a Deviation by smoothed Tait equation.

V_0 and C calculated by Eqs. (3) and (5), respectively, was found to be difficult to correlate with x_{al} by a single equation, the following two correlation equations were used according to the concentration of the mixture. For the 3FE mixtures, the following equation was introduced in the mole fraction range of alcohol higher than 0.2389:

$$B = b_1 \exp(b_{22} x_{al}^{b_2}) \quad (6)$$

In the lower concentration range, between 0 and 0.2389, the simple polynomial equation was used.

$$B = B_{H_2O} + \sum_{i=1}^4 b_i^* x_{al}^{i-1} \quad (7)$$

Here B_{H_2O} is the parameter for pure water, which is determined simultaneously with C_{H_2O} mentioned above. The coefficients b_i and b_i^* were determined by least-squares fitting, taking account of the continuity of these equations. For the 4FP mixtures and 5FP mixtures, the correlation by Eq. (6) was attempted using only the data with the mole fraction higher than 0.2028 and 0.5504, respectively. Correlation at lower concentrations for 4FP mixtures was not carried out because of the shortage of high-pressure viscosity data in this composition range. The coefficients in Eqs. (6) and (7) determined by least-squares fitting and the applicable mole fraction range of the correlation equations are given in Table VI. The average and maximum deviations of molar volume by the Tait equation

Table VI. Coefficients in Eqs. (5) to (7)

	b_1	b_2	b_3	c_1	c_2	c_{H_2O}
3FE + H ₂ O (0.2389 ≤ x_{al} ≤ 1.0)						
298 K	9.29695	1.95123	-0.203505	-0.43036	-10.6896	0.14225
323 K	0.080761	6.52835	-0.072696	-0.35504	-13.4823	0.13219
4FP + H ₂ O (0.2028 ≤ x_{al} ≤ 1.0)						
298 K	1183.915	-2.44682	112.165	-0.43551	-18.5044	0.14225
323 K	415.053	0.75914	-0.34777	-0.34483	-10.0795	0.13219
5FP + H ₂ O (0.5504 ≤ x_{al} ≤ 1.0)						
298 K	381.878	0.41774	-0.64651	-0.47257	-5.3451	0.14225
323 K	366.601	0.27306	-1.01947	-0.39461	-4.8226	0.13219
	B_{H_2O}	b_1^*	b_2^*	b_3^*	b_4^*	
3FE + H ₂ O (0 ≤ x_{al} < 0.2389)						
298 K	313.607	-932.926	-2743.53	22075.1	-33329.4	
323 K	297.928	-1655.022	5420.76	-8234.23	4140.52	

using the smoothed parameters V_0 , C , and B by Eqs. (2), (3), (5), (6), and (7) are tabulated in the seventh and eighth columns in Table II-V. Compared to the deviations of the Tait equation with the original parameters in the same tables, those with smoothed parameters become fairly large but are still within the stated experimental uncertainties of ±0.2%.

3.3. Composition Dependences of Volumetric Properties

To examine the composition dependences of volumetric properties, the excess molar volume, partial molar volume, and isothermal compressibility were determined at various pressures in terms of the smoothed parameters of the Tait equation given in Section 3.2. The excess molar volumes for 3FE mixture are shown in Fig. 3. As shown there, the excess molar volume at a constant temperature becomes less negative with increasing pressure, and at the highest pressure of the measurements, 80 MPa, the isobar at 323 K gives a slightly positive value at higher concentrations. The 4FP mixtures and 5FP mixtures show the same tendency as 3FE mixtures and the inversion to the positive value at higher concentrations is more definite than for 3FE mixtures. For some aqueous solutions, similar S-shaped curves of excess molar volumes and similar shape changes with pressure have been reported [19-21].

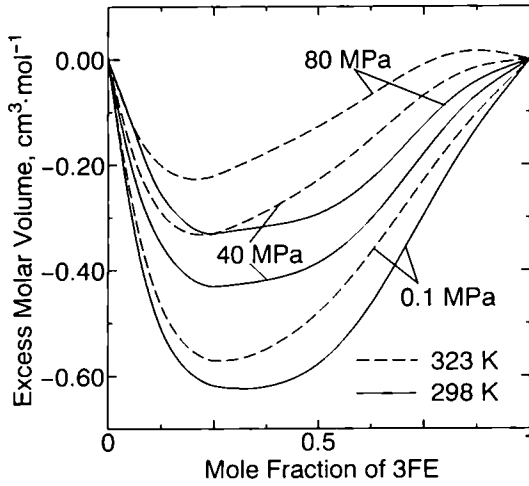


Fig. 3. Excess molar volume of 2,2,2-trifluoroethanol (3FE) and water mixtures at various pressures.

The partial molar volume of alcohol, \bar{V}_{al} , defined by the following equation is also determined by the use of the smoothed parameters of the Tait equation:

$$\bar{V}_{al} = \left[v + w_{H_2O} \left(\frac{\partial v}{\partial w_{al}} \right)_{T,P} \right] M_{al} \quad (8)$$

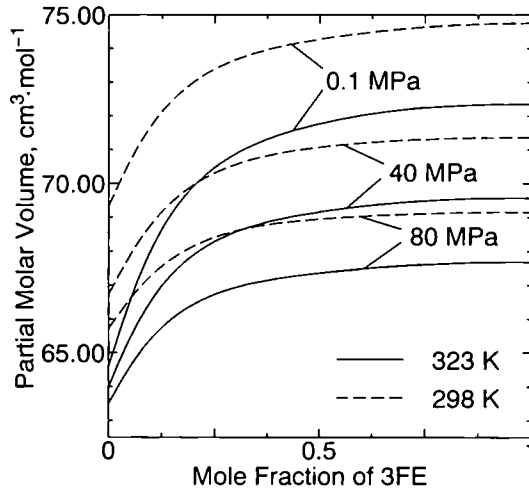


Fig. 4. Partial molar volume of 2,2,2-trifluoroethanol (3FE) at various pressures.

Here w is the mass fraction, M the molecular mass, and v the specific volume ($\text{cm}^3 \cdot \text{g}^{-1}$). Typical results for 3FE mixtures are illustrated in Fig. 4. For aqueous solutions of hydrocarbon alcohols, it is well-known that there exist sharp minima in the partial molar volume of alcohol at dilute alcohol concentrations. It has been reported previously [7] that the minimum becomes deeper and shifts to lower alcohol concentrations with an increase in the molar mass of alcohol and it shifts gradually to higher alcohol concentrations with increasing pressure. As shown in Fig. 4, the partial molar volume of 3FE indicates a marked decline at lower concentrations, but no minimum behavior was observed for this mixture. It was also confirmed that the decline in the partial molar volume becomes less remarkable as the pressure increases. For the 4FP mixtures and 5FP mixtures, the same composition dependence was observed in the mole fraction range where the smoothed parameters in Table VI are available.

The isothermal compressibilities of the present mixtures, β_T (MPa^{-1}), defined by the following equation were also determined in terms of smoothed parameters of the Tait equation.

$$\beta_T = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \left(1 - C \ln \frac{B+P}{B+0.1} \right)^{-1} \frac{C}{B+P} \quad (9)$$

The results at 298 K are given in Fig. 5. For the 4FP mixtures, the isobars at a mole fraction lower than 0.2028, where the smoothed parameters are

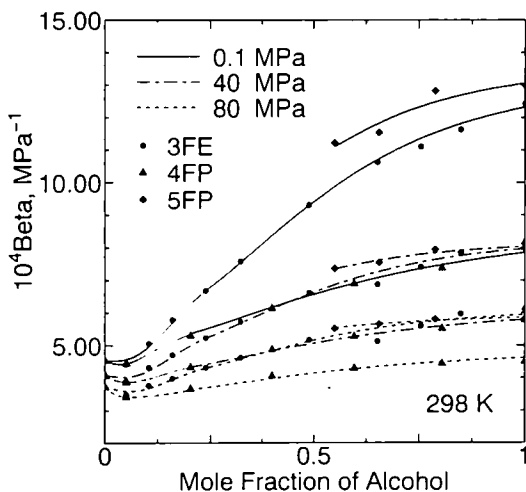


Fig. 5. Isothermal compressibilities of fluoroalcohol and water mixtures at 298 K as a function of the mole fraction of alcohol.

not available, were drawn graphically so as to pass through the experimental values. At a given temperature and pressure, the isothermal compressibility increases according to the mole fraction of alcohol. But for the 3FE mixtures and 4FP mixtures, shallow minima of isothermal compressibilities are observed at low concentrations around 0.05 mole fraction. These minima fade out gradually as the temperature and pressure increase. A similar minimum behavior was observed for a series of aqueous solutions of primary hydrocarbon alcohols in previous work [22]. Among the present fluoroalcohol mixtures, the quite low values of 4FP mixtures are conspicuous.

In comparison with the literature values, the present isothermal compressibility for pure 3FE agrees well with that of Kabata [14], and the deviation is within 1.9% over the entire temperature and pressure range in this work. The 3FE isothermal compressibility of Malhotra and Woolf [12] has a slightly different pressure dependence and the deviations from our results vary from -0.3 to 7.7% at 298 K and from -4.5 to 4.2% at 323 K with the increase in pressure. Since the measurement for 3FE by Baehr et al. [23] was performed at different temperatures, from 293 to 473 K, direct comparison cannot be made but their results have the same dependences on pressure. Takagi and Noguchi [24] determined the isentropic compressibility of pure 3FE, 4FP, and 5FP by measurements of the speed of sound. The temperature and pressure dependences of their isentropic compressibilities are similar to those of the present isothermal compressibilities and low values of 4FP were reported.

4. DISCUSSION

4.1. Comparison to Other Properties

The composition dependence of molar volume is in marked contrast to that of viscosity given in the previous work [6]. The viscosity of individual sample mixtures, namely, indicates a larger value than the mole fraction average value except at very high concentrations. And for the 3FE mixtures and 4FP mixtures, sharp viscosity maxima were observed near a mole fraction of 0.3, where those excess molar volumes deviate largely in the negative direction. According to the Eyring rate theory, viscous flow is the phenomenon that the liquid molecules which possess enough activation energy jump into a neighboring empty site one after another. Since a negative excess molar volume introduces a decrease in the empty site, which contributes to the increasing viscosity, the contrasting composition dependence between molar volume and viscosity seems understandable.

It was reported in a previous publication [6] that the viscosities of

4FP mixtures are excessively higher than those of 3FE mixtures and 5FP mixtures, which indicate an intermolecular interaction of 4FP stronger than that of 3FE or 5FP. The very low isothermal compressibilities of 4FP mixtures obtained in this study and the comparably higher values of critical temperature, normal boiling point, and enthalpy of vaporization [25] also attest to the strong intermolecular interaction of this substance.

It has also been pointed out [6] that the composition dependences of viscosities for fluoroalcohol mixtures are quite comparable to those of rotational correlation times determined from the ^{13}C NMR spin-lattice relaxation time by Mizutani et al. [26]. In the same study, Mizutani et al. also performed Raman spectrum measurement for aqueous solutions of 2-propanol (IP) and its fluorine substituted compound, 1,1,1,3,3,3-hexafluoro-2-propanol (6FIP). Their measurements were done in the C–H stretching region of sample alcohols and the frequency shift of the C–H stretching bands of alcohols upon dilution by water were determined. According to Mizutani et al., the observed frequency shift $\Delta\nu$ can be represented by the following equation as the sum of two interaction factors:

$$\Delta\nu = x_{\text{al}} \Delta\nu_{\text{al,al}} + (1 - x_{\text{al}}) \Delta\nu_{\text{al,H}_2\text{O}} \quad (10)$$

where $\Delta\nu_{\text{al,al}}$ and $\Delta\nu_{\text{al,H}_2\text{O}}$ are the homogeneous and heterogeneous interaction factors and reflect the magnitudes of interactions between alcohol–alcohol molecules and between alcohol–water molecules, respectively. Since the primary factor of frequency shift is the dispersion force, the increase and decrease in $\Delta\nu_{\text{al,al}}$ are expected to reveal the increase and decrease in the distance between the alcohol–alcohol molecules, respectively. Therefore, it is of interest to compare the composition dependence of the partial molar volume \bar{V}_{al} to that of the interaction factor $\Delta\nu_{\text{al,al}}$. The experimental results of $\Delta\nu_{\text{al,al}}$ for the aqueous solutions of 6FIP and IP given by Mizutani et al. are quite comparable to our partial molar volumes \bar{V}_{al} of fluoroalcohols and corresponding hydrocarbon alcohols. The $\Delta\nu_{\text{al,al}}$ of IP shows an abrupt decrease at lower concentrations and a sharp minimum is observed near a mole fraction of 0.1, whereas that of 6FIP decreases monotonously with a decrease in the mole fraction of alcohol and no minimum behavior is observed. These distinctive composition dependences of $\Delta\nu_{\text{al,al}}$ agree completely with those of the partial molar volumes of hydrocarbon alcohol and fluoroalcohol obtained in a series of our measurements. With regard to the decline in $\Delta\nu_{\text{al,al}}$, Mizutani et al. suggested that the possibility of a collapse of the microscopic liquid structure of alcohol and the formation of a micelle-like assembly at lower concentrations. Two similar composition dependences observed between the thermophysical properties and the

spectroscopic data, i.e., between the partial molar volume and the Raman spectrum shift and between the viscosity and the rotational correlation time, are expected to indicate the propriety of their suggestion.

5. CONCLUSION

New experimental density data are presented for the aqueous solutions of 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, and 2,2,3,3,3-pentafluoropropanol. The measurements were performed at temperatures of 298 and 323 K and at pressures up to 80 MPa with two vibrating-tube densitometers with an estimated uncertainty of $\pm 0.2\%$. Molar volumes obtained for these mixtures were correlated with pressure by the Tait equation within the experimental uncertainty, and excess molar volumes, partial molar volumes, and isothermal compressibilities of sample mixtures were determined based on this correlation equation. The composition dependences of these volumetric properties are discussed compared to those of the corresponding hydrocarbon alcohols. Comparison between the partial molar volumes and the Raman spectroscopic data was also undertaken and similar composition dependences were observed.

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