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Viscosity of Mixtures of Fluoroalcohols and Water at High Pressures[1]

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Viscosities 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 falling-body viscometer. Measurements were performed at temperatures from 298 to 323 K and at pressures up to 80 MPa with an estimated uncertainty of ±2%. Viscosities obtained for these mixtures are represented by a simple empirical equation within the experimental uncertainty. The composition dependence of the viscosity is compared with that for mixtures of hydrocarbon alcohols and water.

KEY WORDS: aqueous solutions; fluoroalcohols; high pressure; hydrocarbon alcohols; nuclear magnetic resonance; viscosity.

1. INTRODUCTION

Aqueous solutions of alcohols exhibit anomalous temperature, pressure, and composition dependences in their thermophysical properties. In previous studies [1–3], the viscosity of aqueous solutions of five monohydric alcohols, methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol, and two dihydric alcohols, 1,2-ethanediol (ethylene glycol) and 1,2-propanediol (propylene glycol), has been measured in the temperature range from 283 to 348 K and at pressures up to 120 MPa. With a series of measurements, it was confirmed that each aqueous solution of monohydric alcohol has a distinct viscosity maximum near 0.3 mol fraction of alcohol, while the viscosity of dihydric solutions is slightly lower than the mole fraction average value over a whole composition range.

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[1] Paper dedicated to Professor Joseph Kestin.

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This behavior was interpreted qualitatively in terms of the complicated intermolecular interactions arising from the hydrogen bonds between water–water molecules and water–alcohol molecules.

As an extension of the previous studies, 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), has been measured at 298 and 323 K and at pressures up to 80 MPa. Although the importance of aqueous solutions of fluoroalcohols for the industrial use has been emphasized, very few experimental data for those thermophysical properties are available. An aqueous solution of 3FE has been suggested as a favorable working fluid for waste-heat recovery and as an alternative refrigerant for absorption heat pumps [4]. 5FP and its azeotropic mixture with water have a favorable cleaning ability and are possible alternatives for the restricted substance CFC-113. The viscosity has been measured with a falling-cylinder viscometer and the estimated uncertainty of the viscosity obtained is ±2%. For the mixtures of 5FP and water, the measurements were carried out in the composition range where both components dissolve completely. The densities of the sample mixtures obtained at the same temperature and pressure range with a vibrating-tube densitometer will be reported in a future publication [5].

2. EXPERIMENTS

Viscosities at high pressures were measured with a falling cylinder viscometer described in detail elsewhere [6]. The viscometer located in a high-pressure vessel consists of a colored Pyrex-glass falling cylinder and a precisely bored Pyrex-glass tube. Four small projecting lugs are attached at each end of the falling cylinder, which assure a smooth fall of the cylinder along the vertical line. A pair of optical windows is provided to the high-pressure vessel in order to observe the movement of the falling cylinder. In this study, the viscosity was obtained on a relative basis and the instrument constant has been calibrated against the recommended value of pure water [7] in the entire range of measurements. Therefore, we can determine the sample viscosity by measuring the time interval in which a He–Ne gas laser beam, which passes through the optical window, is cut off by the falling cylinder. Temperatures and pressures are measured with a strain gauge-type pressure transducer to within ±0.1 MPa and a thermistor to within ±10 mK, respectively.

3FE was obtained from Wako Pure Chemical Industries, Ltd., with a guaranteed purity better than 99% and dried over potassium carbonate for more than 24 h and distilled twice. 4FP and 5FP were obtained from Daikin Industries, Ltd., with a guaranteed purity better than 99.9% and used without any further purification. Besides the impurities of the samples, the additional uncertainty of the composition of each mixture arising from the preparation procedure should be accurate to within ±0.01 %. Judging from the precisions of the instruments, the purity of samples, and the reproducibility of measurements, we estimate the uncertainties of the viscosities obtained to be within ±2 %.

3. RESULTS

3.1. Temperature Dependence of Viscosity for Pure Alcohol

The viscosities obtained at atmospheric pressure with a falling cylinder viscometer or an Ubbelohde viscometer are shown in Fig. 1 as a function of temperature together with the corresponding hydrocarbon alcohols. The viscosities of fluoroalcohols decrease monotonously with increasing temperature in the same way as hydrocarbon alcohols but are considerably higher than each corresponding hydrocarbon alcohols, i.e., ethanol and 1-propanol. In this figure, the conspicuously high viscosity of 4FP compared to 3FE and 5FP attracts attention.

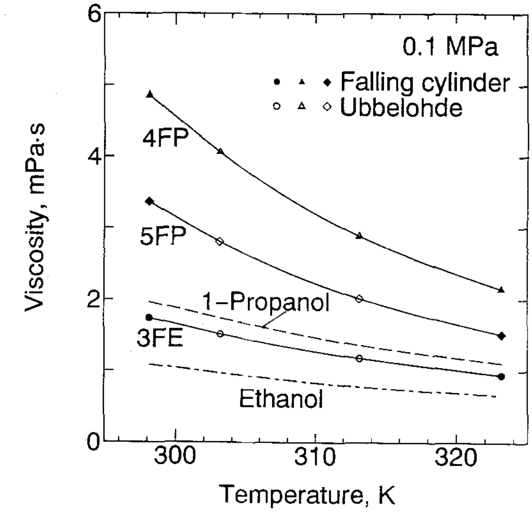

Fig. 1. Viscosity of fluoroalcohol and water mixtures at atmospheric pressure together with corresponding hydrocarbon alcohol and water mixtures.

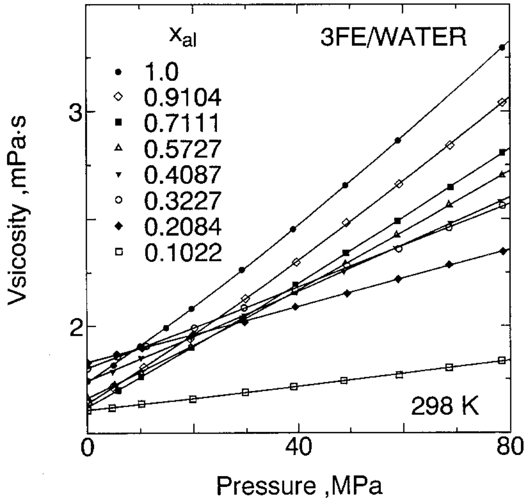

Fig. 2. Viscosity of 2,2,2-trifluoroethanol (3FE) and water mixtures at 298.15 K as a function of pressure.

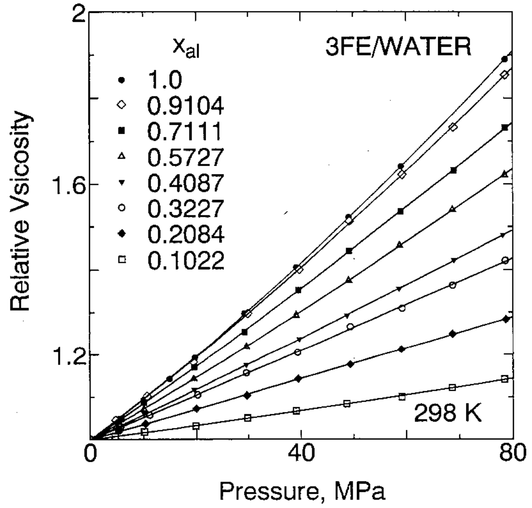

Fig. 3. Relative viscosity of 2,2,2-trifluoroethanol (3FE) and water mixtures at 298.15 K as a function of pressure.

3.2. Pressure Dependence of Viscosity

The viscosities obtained at high pressures with a falling cylinder viscometer are presented in Tables I to VI. For the 3FE aqueous mixtures, the pressure dependences of the viscosity and of the relative viscosity at 298 K, i.e., the ratio of the viscosities at high pressures to those at atmospheric pressure, are shown in Figs. 2 and 3. As shown in Fig. 2, the viscosity at each composition increases monotonously with increasing pressure and the isotherms intersects each other in the lower and middle pressure range, whereas the isotherms of relative viscosities shown in Fig. 3 are arranged according to the mole fraction and there is no intersection found. The pressure dependence of the 4FP and 5FP mixtures is similar to that of the 3FE mixture, but no intersection is observed between the isotherms in the viscosity-pressure diagrams.

In the previous studies [2, 3], we adopted a Tait-type equation to reproduce the pressure effects on the viscosity of hydrocarbon alcohol and

Table I. Viscosities of 3FE and Water Mixtures at 298.15 K

P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)
[x_{al} = 1.0]		[x_{al} = 0.9104]		[x_{al} = 0.7111]		[x_{al} = 0.5727]	
0.1	1.744	0.1	1.640	0.1	1.621	0.1	1.665
5.0	1.816	4.8	1.715	5.8	1.700	5.2	1.725
10.0	1.906	10.7	1.807	10.1	1.763	10.1	1.784
14.9	1.992	19.4	1.941	19.6	1.898	19.5	1.903
19.7	2.081	29.9	2.128	29.3	2.034	29.6	2.031
29.2	2.263	39.7	2.298	39.5	2.192	39.1	2.154
39.1	2.452	49.3	2.482	49.2	2.340	49.1	2.290
49.1	2.655	59.3	2.661	59.0	2.490	58.8	2.425
59.1	2.864	68.9	2.842	69.0	2.646	68.7	2.564
78.6	3.296	78.6	3.041	78.6	2.808	78.5	2.701
[x_{al} = 0.4087]		[x_{al} = 0.3227]		[x_{al} = 0.2084]		[x_{al} = 0.1022]	
0.1	1.743	0.1	1.802	0.1	1.828	0.1	1.608
4.8	1.786	5.7	1.856	5.6	1.868	4.7	1.619
10.1	1.850	11.2	1.906	10.4	1.896	10.2	1.637
19.6	1.947	20.2	1.991	20.0	1.961	19.9	1.659
29.6	2.050	29.6	2.085	29.7	2.017	29.8	1.689
39.7	2.157	39.4	2.173	39.5	2.089	39.1	1.716
48.8	2.253	49.4	2.282	49.4	2.151	48.7	1.743
58.7	2.362	59.2	2.360	59.1	2.218	59.2	1.769
69.0	2.480	68.7	2.458	68.7	2.285	68.6	1.803
78.2	2.581	78.6	2.562	78.7	2.347	78.4	1.835

water mixtures. But for pure water, the minimum values appears in the viscosity-pressure diagram at temperatures lower than 307 K and this anomalous behavior cannot be represented by the Tait-type equation. A Tait-type equation, therefore, cannot be applicable for dilute aqueous solutions and the following simple polynomial equation was used in the present work to correlate the experimental viscosities as a function of pressure:

$$\eta_{\mathrm{P}} = \eta_0(1 + a_1 \Delta P + a_2 \Delta P^2) \tag{1}$$

where η_{P} and η_0 are the viscosity in mPa · s at pressure P and at atmospheric pressure P_0 in MPa. In the fitting procedure, the values of η_0 were taken from Tables I to VI. The empirical coefficients a_1 and a_2 determined by the least-squares fitting were found to be correlated satisfactorily with the mole fraction of alcohol x:

Table II. Viscosities of 3FE and Water Mixtures at 323.15 K

P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)
[$x_{\mathrm{al}} = 1.0$]		[$x_{\mathrm{al}} = 0.9104$]		[$x_{\mathrm{al}} = 0.7111$]		[$x_{\mathrm{al}} = 0.5727$]	
0.1	0.948	0.1	0.935	0.1	0.912	0.1	0.911
5.1	0.999	5.4	0.987	5.0	0.946	5.1	0.945
10.0	1.048	10.1	1.025	11.2	0.995	10.1	0.977
19.5	1.141	19.5	1.103	19.5	1.059	19.7	1.041
29.4	1.240	29.9	1.195	29.4	1.135	29.5	1.105
39.1	1.340	39.2	1.281	39.4	1.210	39.4	1.168
49.3	1.446	48.8	1.373	49.1	1.287	49.0	1.236
59.1	1.551	60.5	1.481	58.8	1.366	58.9	1.302
68.8	1.658	68.6	1.562	68.5	1.442	68.8	1.370
78.7	1.763	78.8	1.666	78.9	1.523	78.6	1.432
[$x_{\mathrm{al}} = 0.4087$]		[$x_{\mathrm{al}} = 0.3227$]		[$x_{\mathrm{al}} = 0.2084$]		[$x_{\mathrm{al}} = 0.1022$]	
0.1	0.940	0.1	0.949	0.1	0.944	0.1	0.850
4.8	0.965	5.1	0.972	5.5	0.958	6.2	0.860
10.2	0.994	10.3	0.996	10.4	0.974	10.3	0.867
19.4	1.040	19.9	1.038	20.3	1.008	20.0	0.883
29.2	1.095	29.9	1.083	29.6	1.034	29.9	0.901
40.0	1.151	39.3	1.125	39.5	1.066	39.4	0.918
48.7	1.198	49.4	1.174	49.7	1.099	49.6	0.933
58.9	1.252	58.9	1.221	59.2	1.128	59.3	0.951
69.3	1.306	68.7	1.262	69.1	1.157	68.7	0.964
78.6	1.357	78.6	1.309	78.7	1.188	78.6	0.979

$$a_1 = a_{1,\mathrm{H_2O}} + \sum_{i=1}^{3} d_i x^i \tag{2}$$

$$a_2 = a_{2,\mathrm{H_2O}} + \sum_{i=1}^{2} e_i x^i \tag{3}$$

The coefficients of Eqs. (2) and (3) are given in Table VII together with the average and maximum deviations. In the determination of these coefficients, the viscosity values of pure water recommended by Sengers and Watson [7] were taken into account in order to prevent a decline of the reproducibility in lower concentration range.

3.3. Composition Dependence of Viscosity

The viscosities of sample mixtures obtained at atmospheric pressure are plotted against mole fraction in Fig. 4 together with those of the

Table III. Viscosities of 4FP and Water Mixtures at 298.15 K

P (MPa)	η (mPa·s)	P (MPa)	η (mPa·s)	P (MPa)	η (mPa·s)	P (MPa)	η (mPa·s)
$[x_{\mathrm{al}} = 1.0]$		$[x_{\mathrm{al}} = 0.8707]$		$[x_{\mathrm{al}} = 0.7598]$		$[x_{\mathrm{al}} = 0.6133]$	
0.1	4.861	0.1	4.341	0.1	3.910	0.1	3.523
6.3	5.171	5.4	4.599	5.1	4.127	5.2	3.686
9.9	5.397	10.0	4.828	10.3	4.333	10.2	3.851
19.5	5.989	19.8	5.341	19.6	4.744	19.7	4.177
29.9	6.680	29.6	5.903	29.4	5.200	29.5	4.527
39.9	7.466	39.3	6.496	39.2	5.700	39.4	4.890
50.3	8.311	49.2	7.135	49.1	6.200	48.9	5.245
59.1	9.058	58.9	7.789	58.9	6.712	59.2	5.633
68.6	9.905	68.7	8.508	68.9	7.276	69.1	6.056
78.4	10.877	78.4	9.258	78.5	7.887	78.5	6.469
$[x_{\mathrm{al}} = 0.5024]$		$[x_{\mathrm{al}} = 0.3747]$		$[x_{\mathrm{al}} = 0.2532]$		$[x_{\mathrm{al}} = 0.1237]$	
0.1	3.314	0.1	3.002	0.1	2.716	0.1	2.070
5.5	3.455	5.7	3.109	5.0	2.779	5.8	2.103
9.9	3.559	10.2	3.192	10.6	2.849	10.4	2.135
19.1	3.810	20.0	3.387	19.8	2.971	19.8	2.181
29.2	4.096	29.6	3.586	29.6	3.102	29.7	2.234
39.4	4.404	39.6	3.793	39.5	3.240	39.4	2.281
49.1	4.690	49.3	4.008	49.4	3.378	49.7	2.327
59.1	4.989	59.0	4.215	59.1	3.504	59.3	2.381
68.9	5.332	68.8	4.436	68.7	3.638	68.7	2.438
78.6	5.659	78.1	4.656	78.5	3.790	78.5	2.477

aqueous solutions of corresponding hydrocarbon alcohols. Furthermore, the composition dependence of the viscosities at elevated pressures is determined with the aid of Eqs. (1) to (3) and the typical results for the 3FE mixtures are shown in Fig. 5. For the monohydric hydrocarbon alcohol and water mixtures, it was confirmed in the previous study [2] that each isobar at low temperature and low pressures has a distinct viscosity maximum near a mole fraction of 0.3. As is evident in Fig. 4, the viscosities for 3FE mixtures and 4FP mixtures around this concentration are considerably higher than the mole fraction average values. But these departures from the average values are not so prominent as the corresponding hydrocarbon alcohol mixtures and the viscosity maximum is not observed for the 4FE mixtures. Each curvature of the isobar at higher concentration is concave, contrary to that at lower concentration. This behavior was also found for some hydrocarbon alcohol mixtures and the shallow minima were observed for the 2-propanol mixtures and 2-methyl-2-propanol

Table IV. Viscosities of 4FP and Water Mixtures at 323.15 K

P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)
[$x_{al}=1.0$]		[$x_{al}=0.8707$]		[$x_{al}=0.7598$]		[$x_{al}=0.6133$]	
0.1	2.156	0.1	1.961	0.1	1.807	0.1	1.678
4.5	2.254	6.1	2.080	5.2	1.898	5.8	1.760
9.3	2.366	10.0	2.165	10.3	1.986	10.3	1.827
19.8	2.629	20.1	2.381	19.5	2.146	19.8	1.966
29.7	2.889	29.8	2.602	29.9	2.336	29.4	2.115
39.2	3.139	39.2	2.817	39.2	2.520	39.7	2.274
48.9	3.406	49.3	3.077	49.0	2.731	49.1	2.425
58.9	3.713	59.0	3.334	58.4	2.942	58.8	2.585
68.7	4.020	68.8	3.586	69.2	3.156	68.8	2.754
78.4	4.331	78.4	3.839	79.1	3.389	78.7	2.925
[$x_{al}=0.5024$]		[$x_{al}=0.3747$]		[$x_{al}=0.2532$]		[$x_{al}=0.1237$]	
0.1	1.590	0.1	1.478	0.1	1.340	0.1	1.032
5.1	1.648	5.8	1.532	5.1	1.372	5.7	1.045
10.0	1.706	10.4	1.575	9.6	1.402	10.3	1.059
19.5	1.817	19.8	1.662	19.5	1.465	20.0	1.086
29.8	1.947	29.6	1.756	29.1	1.524	29.9	1.114
39.8	2.070	39.5	1.848	39.9	1.591	39.7	1.139
49.2	2.195	49.1	1.942	49.3	1.651	49.2	1.162
59.2	2.326	59.1	2.040	58.8	1.712	59.2	1.187
68.7	2.454	69.1	2.138	69.0	1.773	68.8	1.213
78.6	2.599	78.6	2.233	78.8	1.836	79.1	1.240

mixtures near the mole fraction of 0.9 [2]. It is also found that the anomalous composition dependence at lower concentration diminishes gradually with increasing pressure and no viscosity maximum is observed at the highest pressure of the measurement.

For the aqueous solutions of fluoroalcohols, very few viscosity data are available in the literature. As shown in Fig. 4, the present viscosities for the 3FE mixtures at 298 K and at atmospheric pressure agree quite well over and entire range of concentration with the recent data of Kaiser et al. [8], which are converted from the kinematic viscosities with the aid of our equation of state reported separately [5]. The deviations from the data of Kaiser at 323 K are a little larger than those at 298 K but still within the combined uncertainties of the experiments.

The only reference data at high pressures of Kobayashi and Nagashima [9] for the 3FE mixtures were collected at different temperatures from 273 to 453 K. But the correlation equation, which is given

Table V. Viscosities of 5FP and Water Mixtures at 298.15 K

P (MPa)	η (mPa·s)	P (MPa)	η (mPa·s)	P (MPa)	η (mPa·s)
[$x_{al} = 1.0$]		[$x_{al} = 0.8991$]		[$x_{al} = 0.7892$]	
0.1	3.367	0.1	3.069	0.1	2.774
5.3	3.646	5.4	3.318	5.6	2.989
9.8	3.905	10.1	3.538	10.2	3.195
19.5	4.496	19.2	4.004	19.8	3.591
29.5	5.167	29.6	4.573	29.5	4.018
38.5	5.822	39.6	5.148	39.2	4.491
48.1	6.586	49.3	5.753	49.0	4.982
59.3	7.473	59.4	6.448	58.8	5.522
68.6	8.292	68.9	7.122	68.9	6.092
78.6	9.358	79.2	7.942	78.7	6.698
[$x_{al} = 0.6564$]		[$x_{al} = 0.5504$]			
0.1	2.626	0.1	2.607		
5.0	2.778	5.1	2.746		
10.1	2.952	10.2	2.897		
19.5	3.258	19.7	3.175		
29.3	3.602	29.5	3.492		
39.4	3.970	39.3	3.806		
49.8	4.387	49.2	4.144		
55.4	4.610	59.0	4.541		
68.8	5.186	68.8	4.870		
78.5	5.626	78.6	5.261		

Table VI. Viscosities of 5FP and Water Mixtures at 323.15 K

P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)	P (MPa)	η (mPa · s)
$[x_{\mathrm{al}} = 1.0]$		$[x_{\mathrm{al}} = 0.8991]$		$[x_{\mathrm{al}} = 0.7892]$	
0.1	1.518	0.1	1.401	0.1	1.318
7.4	1.695	5.5	1.514	5.0	1.391
14.8	1.878	10.2	1.617	10.0	1.480
19.4	2.004	20.0	1.830	19.6	1.667
29.5	2.291	29.7	2.055	29.4	1.842
39.2	2.561	39.7	2.296	39.1	2.045
49.1	2.860	49.4	2.534	49.1	2.244
59.1	3.170	59.0	2.782	58.2	2.464
68.6	3.502	69.1	3.061	68.4	2.715
78.6	3.861	78.7	3.362	78.5	2.938
$[x_{\mathrm{al}} = 0.6564]$		$[x_{\mathrm{al}} = 0.5504]$			
0.1	1.278	0.1	1.263		
4.9	1.335	4.9	1.325		
9.8	1.404	10.3	1.396		
19.4	1.548	19.5	1.523		
29.2	1.698	29.8	1.659		
39.1	1.861	39.1	1.786		
47.6	2.005	49.4	1.934		
58.8	2.195	58.8	2.086		
68.6	2.379	68.7	2.226		
78.2	2.553	78.8	2.399		

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

$a_{1,\mathrm{H_2O}} = -2.9085 \times 10^{-4}$ (298.15 K), 3.4647×10^{-4} (323.15 K)
$a_{2,\mathrm{H_2O}} = 3.0479 \times 10^{-6}$ (298.15 K), 0.7964×10^{-6} (323.15 K)

	3FE		4FP		5FP	
	298.15 K	323.15 K	298.15 K	323.15 K	298.15 K	323.15 K
$10^2 d_1$	2.0746	1.6350	2.2432	1.8371	2.9503	2.1716
$10^2 d_2$	−1.4769	−0.9765	−1.2892	−0.8158	−2.2453	−1.2411
$10^3 d_3$	3.8387	3.1153	1.7478	−0.1544	8.7672	5.8936
$10^5 e_1$	−1.1457	−0.6846	−1.3589	−0.1931	−0.4307	2.2884
$10^5 e_2$	3.2520	1.5974	7.3435	3.4657	8.9606	2.9002
Ave. dev. (%)	0.30	0.27	0.32	0.26	0.46	0.47
Max. dev. (%)	1.08	1.09	0.98	1.18	1.27	1.37

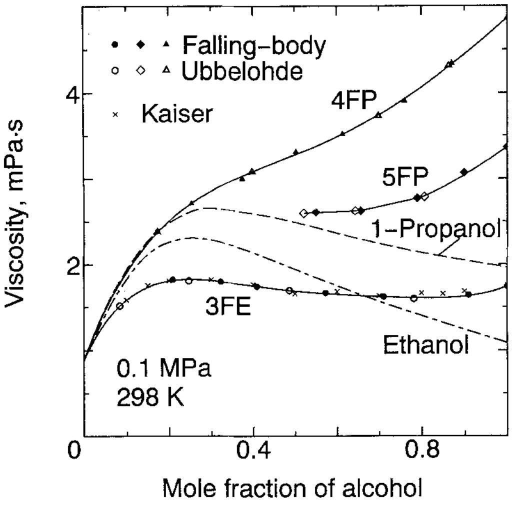

Fig. 4. Composition dependence of the viscosity of fluoroalcohol and water mixtures at atmospheric pressure together with corresponding hydrocarbon–alcohol and water mixtures.

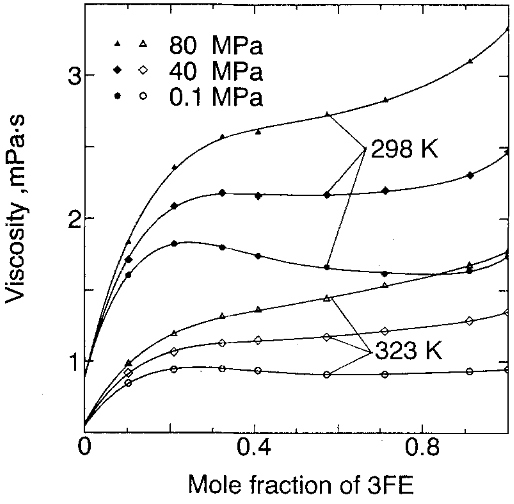

Fig. 5. Composition dependence of the viscosity of 2,2,2-trifluoroethanol (3FE) and water mixtures at various temperatures and pressures.

by Kobayashi and Nagashima in order to represent their kinematic viscosities as a function of temperature and pressure, makes it possible to compare the voscosities of 3FE mixtures. In the comparison of pure 3FE, the correlated viscosities of Kobayashi and Nagashima are systematically higher than the present data in the entire pressure range of their measurements, 0.1–40 MPa. The deviations are within 1.6% at 298 K and 2.7% at 323 K. The present viscosities for the 3FE mixtures, obtained from an interpolation as a function of the mole fraction, show considerably larger deviations from the correlation of Kobayashi and Nagashima, i.e., 4.6% for 0.85 and 6.8% for 0.60 alcohol mole fraction mixtures, respectively. But the departures are systematic and the pressure dependence of the viscosity agrees. Kaiser et al. have also undertaken the comparison of their kinematic viscosities with the correlation of Kobayashi and Nagashima and stated that the deviations are systematic and amount up to 6% in the available temperature range of the correlation. For the 4FP mixtures and 5FP mixtures, no reference data at high pressures are available.

4. DISCUSSION

4.1. Anomalies in Composition Dependence

Anomalous behaviors observed in the thermophysical properties of dilute aqueous solutions of nonpolar substances are in general explained on the basis of two concepts, hydrophobic hydration and hydrophobic interaction [10–12]. Since the hydrocarbon alcohols have hydrocarbon tails which act as hydrophobic groups in aqueous solutions, the thermophysical properties of the aqueous solutions of hydrocarbon alcohols also show unexpected temperature, pressure, and composition dependences. As illustrated in Figs. 3 and 4, the viscosities of 3FE mixtures and 4FP mixtures show a composition dependence similar to that of corresponding hydrocarbon alcohol mixtures and deviate largely from the mole fraction average values near the mole fraction of 0.3. According to the concept of hydrophobic hydration, the ice-like open-structured network of water molecules is promoted around an alkyl group of an alcohol molecule when the small amount of alcohol is added to pure water. Furthermore, there is a possibility of association of alcohol molecules by hydrophobic interaction in this lower composition range. In either case, the structure of the total system is enhanced and it results in the large increase in viscosity. At the higher concentration, the solute–solvent interaction becomes dominant and the structure of the total system is reduced. The small departure from the mole fraction average value in this higher concentration range is expected as a result of this structural breakdown.

It is of interest to compare the liquid viscosity to NMR spectroscopy data, which reflect the rotation of the molecule. No spectroscopic data are available for the present aqueous solutions of fluorocarbon alcohols, but the rotational correlation times of the alcohol molecules in the aqueous solutions of 2-propanol and its fluorine substituted compounds were determined by Mizutani et al. [13]. The composition dependence of rotational correlation time of a marked carbon atom is quite comparable to that of viscosities for fluoroalcohol mixtures obtained in this work and the definite maxima were reported at mole fractions of 0.2. With regard to these maxima, they also suggested that there is a possibility of some modification in the packing structure of the hydrophobic groups of alcohol in the micelle-like assembly, which might lead to the viscosity increasing.

4.2. Intermolecular Interaction for Fluorocarbon Alcohols

In the case of aqueous solutions of primary hydrocarbon alcohol, the viscosity increases with the molecular weight of alcohol [2]. But this rule is not satisfied for the present systems and the viscosities of 4FP mixtures are excessively higher than those of 3FE mixtures and 5FP mixtures in the entire range of the measurements. Similar anomalies have been reported in other thermophysical properties. The 4FP mixtures show very low isothermal compressibilities compared to 3FE or 5FP mixtures [5]. The isentropic compressibilities for the pure components determined by Takagi and Noguchi [14] indicate the same tendency. As shown in Table VIII, the critical temperature T_c, normal boiling point t_b, and enthalpy of vaporization ΔH_{vap} at 298 K of 4FP reported by Rochester and Symonds [15] are comparably higher than those of 3FE and 5FP. All these results seem to indicate that 4FP possesses a stronger intermolecular interaction than 3FE or 5FP, but some attention ought to be paid to the enthalpy of vaporiza-

Table VIII. Comparison of Physical Properties

	3FE	4FP	5FP
Molecular mass	100.0	132.1	150.0
b.p. (K)	347.2	382.1	353.8
T_c (K)	501.9	557.2	497.7
P_c (MPa)	5.11	4.85	5.23
$\Delta H_{vap}^{298\,K}$ (kJ · mol^{-1})	43.97	53.58	44.38
ΔE_{vis} (kJ · mol^{-1})	19.5	26.1	25.5

tion. According to Rochester and Symonds [15], the fluorocarbon alcohols have the possibility to form intramolecular hydrogen bondings in the gas phase, which leads to a decrease in the enthalpy of vaporization. And the much smaller difference of the enthalpy of vaporization between 3FE and 5FP than expected was interpreted as due to the higher energies of intramolecular hydrogen bonding of the 5FP molecule, which has a stable benzene-like nucleus structure. Both the activation energy of viscous flow and the enthalpy of vaporization are properties which reflect the intermolecular attractive force, and they are frequently compared with each other. Based on the viscosity data, given in Fig. 1, the activation energies of viscous flow at atmospheric pressure can be calculated from the Eyring equation:

$$\ln \eta = A + \frac{\Delta E_{\text{vis}}}{RT} \tag{4}$$

where ΔE_{vis} is the activation energy of viscous flow in $\text{kJ} \cdot \text{mol}^{-1}$. In contrast to ΔH_{vap}, the ΔE_{vis} of 5FP given in Table VIII is undoubtedly higher than that of 3FE. If we suppose that the intramolecular hydrogen bonding formation in the gas phase proposed by Rochester and Symonds is right, this difference between ΔH_{vap} and ΔE_{vis} can be satisfactorily explained; namely, the intramolecular hydrogen bonding in the gas phase has no effect on ΔE_{vis}. It is unknown why 4FP shows the highest values for ΔH_{vap} and ΔE_{vis}. Based on the higher values of ΔH_{vap} and t_b for partially fluorinated hydrocarbons, Rochester and Symonds [15] mentioned that the attachment of hydrogen and fluorine atoms to the same carbon atom increased the strength of the intermolecular interactions. If this supposition is correct, the anomalously higher values of the viscosity and the activation energy of viscous flow of 4FP in the present work are understood.

5. CONCLUSION

New experimental data have been presented for 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 a falling body viscometer with an estimated uncertainty of ±2%. Viscosities obtained for these mixtures were correlated with pressure by a simple empirical equation within the experimental uncertainty. For the aqueous solutions of 4FP and 5FP, a considerably larger viscosity increase was observed near an alcohol mole fraction of 0.3 than in the cases of those of hydrocarbon alcohol. The comparison between the viscosities and the spectroscopic data was discussed and similar composition dependences were observed. These results strongly support the concepts of hydrophobic hydration and hydrophobic interaction at lower alcohol concentrations.

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