

VISCOSITIES AND DENSITIES OF 2,2,2-TRIFLUOROETHANOL + WATER AT VARIOUS TEMPERATURES

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ABSTRACT

The densities and viscosities at 298, 303, 308 and 313 K for 2,2,2-trifluoroethanol + water were determined. From experimental results, the excess viscosity and excess molar free energy of activation of flow were computed and are presented as a function of the mole fraction of 2,2,2-trifluoroethanol. The deviation from additivity in the values of the excess parameters is discussed in terms of the strength of the interaction between the components of the mixture.

INTRODUCTION

Viscosities of liquid mixtures are required for the solutions of many problems concerning heat transport, mass transport and fluid flow. Recently, organic fluorocarbons and their water mixtures have been identified and proposed for use in Rankin engines for various terrestrial and space applications [1]. Pure trifluoroethanol and its mixtures have been subjected to extensive dynamic testing for thermal stability [2]. Excess molar enthalpies and vapour–liquid equilibrium data for the 2,2,2-trifluoroethanol + water system have been reported [3,4]. The present work deals with the measurements of viscosities and densities of binary mixtures of 2,2,2-trifluoroethanol (TFE) with water (H₂O) at different temperatures. From the measured experimental values, excess viscosity (η^E) and excess molar Gibbs free energy for activation flow (G^{*E}) were calculated

EXPERIMENTAL

2,2,2-Trifluoroethanol (Aldrich Chemical Co. Ltd.) of stated purity > 99 mol%, was dried over molecular sieves. Freshly deionized water was degassed before use. All the solutions were prepared by mixing weighed amounts of pure liquids.

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TABLE 1

Density and viscosity data for the trifluoroethanol–water system

x^a	Density (g ml^{-1})				Viscosity (cP)			
	298 K	303 K	308 K	313 K	298 K	303 K	308 K	313 K
0.0000	0.9970	0.9956	0.9940	0.9922	0.890	0.789	0.719	0.653
0.0260	1.0431	1.0398	1.0368	1.0340	1.152	0.999	0.887	0.791
0.0503	1.0778	1.0746	1.0676	1.0627	1.358	1.163	1.017	0.899
0.0750	1.1110	1.1071	1.1028	1.0987	1.528	1.312	1.138	1.002
0.0984	1.1359	1.1312	1.1252	1.1197	1.634	1.395	1.214	1.065
0.1984	1.2205	1.2146	1.2092	1.2020	1.882	1.588	1.398	1.223
0.3016	1.2641	1.2572	1.2502	1.2433	1.876	1.609	1.406	1.235
0.4012	1.2956	1.2878	1.2814	1.2739	1.819	1.566	1.375	1.211
0.5015	1.3210	1.3102	1.3055	1.2979	1.757	1.523	1.338	1.179
0.5993	1.3382	1.3279	1.3217	1.3137	1.713	1.492	1.305	1.159
0.6501	1.3473	1.3391	1.3308	1.3233	1.656	1.450	1.284	1.145
0.8029	1.3641	1.3557	1.3461	1.3368	1.651	1.444	1.278	1.362
0.9024	1.3724	1.3641	1.3545	1.3463	1.673	1.468	1.296	1.152
1.0000	1.3711	1.3623	1.3553	1.3545	1.737	1.357	1.201	1.054

^a Mole fraction of trifluoroethanol.

Densities were determined with an Anton Paar densimeter DMA 45 with an estimated precision of $1 \times 10^{-4} \text{ g ml}^{-1}$. The densimeter was calibrated with water and air. The temperature of the thermostated water measured from the output of the densimeter remained constant within $\pm 0.001 \text{ K}$. The viscosity measurements were carried out in modified Ostwald viscometers. The temperatures of the thermostated bath remained constant within $\pm 0.02 \text{ K}$. Viscosities were expressed in units of cP equal to $10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$. The reproducibility of the viscosities was estimated to be $\pm 0.005 \text{ cP}$. The density of the 2,2,2-trifluoroethanol agrees very well with the available data [3]. Excess viscosities (η^E) and free energy of activation flow G^{*E} were calculated using the following equations and the experimental data (Table 1) at different temperatures

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \quad (1)$$

$$G^{*E} = RT[\ln \eta v - (x_1 \ln \eta_1 v_1 + x_2 \ln \eta_2 v_2)] \quad (2)$$

where η and v are the viscosity and molar volume of the mixtures respectively and η_1 , η_2 , v_1 and v_2 are the viscosities and densities of the pure components. The values of η^E and G^{*E} were fitted by the method of least-squares to the equation

$$A^E = x(1-x) \sum_{j=1}^n a_j (1-2x)^{j-1} \quad (3)$$

TABLE 2

Values of coefficients for eqn. (3) determined by the method of least-squares

γ^E ^a	T(K)	a_1	a_2	a_3	a_4	a_5	a_6	S ^b
η^E	298	1.763	2.922	2.321	2.870	1.474	-0.661	0.012
	303	1.792	1.975	1.702	2.351	2.669	-2.068	0.010
	308	1.504	1.663	1.723	2.085	1.733	-2.081	0.005
	313	1.155	1.836	5.627	-6.873	-4.524	9.667	0.035
G^{*E}	298	5514	6128	3106	1928	6516	6180	20
	303	6026	5171	2691	2146	8581	2669	18
	308	5928	5041	3358	2400	7082	1635	9.1
	313	5640	5824	12250	-16630	-5878	26590	37

^a Units: η^E (cP) and G^{*E} ($J mol^{-1}$).^b S , Standard deviation.

where A^E represents the excess property, a_j is the polynomial coefficient and n is the polynomial degree.

RESULTS AND DISCUSSION

The experimental densities, ρ , and viscosities, η , are given in Table 1. The values of the coefficients for eqn. (3) are given in Table 2. Figures 1 and 2 show the values of η^E and G^{*E} as a function of the mole fraction of

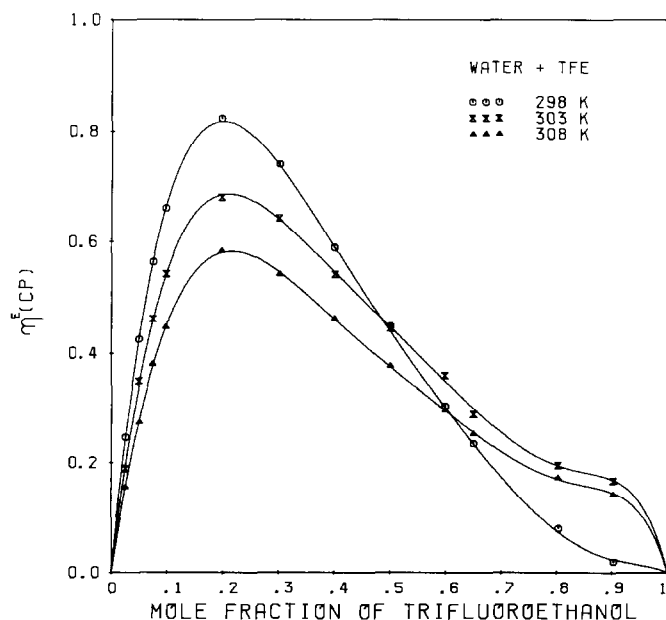


Fig. 1 Composition dependence of excess viscosity at 298, 303 and 308 K.

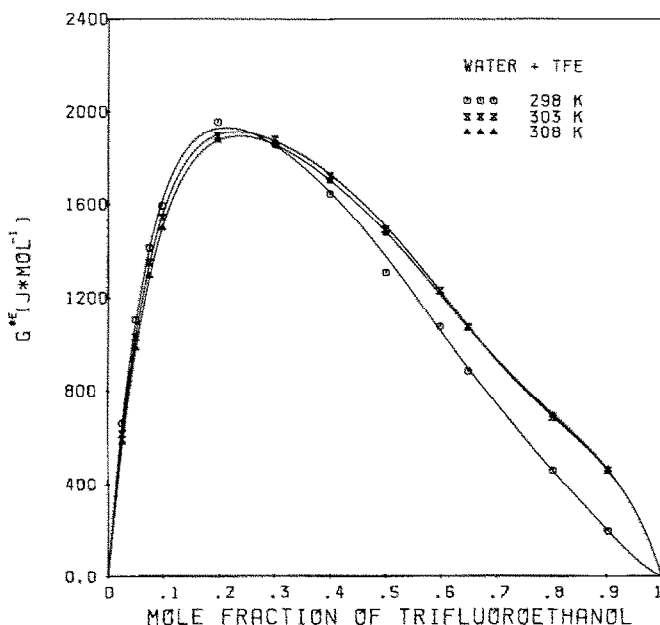


Fig. 2. Composition dependence of excess Gibbs free energy of activation of flow at 298, 303 and 308 K.

2,2,2-trifluoroethanol. Continuous curves were obtained with the aid of the coefficients of eqn. (3). Plots at 313 K were not included in the diagrams to avoid overlapping. The results indicate that the water and 2,2,2-trifluoroethanol mixtures result in a liquid structure where the flow is slightly more viscous than would be expected on the basis of the viscosities of the pure components. This suggests that strong specific interaction between the two components is predominant: this behaviour is usually characterized by distinct maxima in the viscosity versus composition curves, by positive excess viscosities and by positive values of G^{*E} [5-9]. The unsymmetrical nature of these curves indicates that the breaking energy of hydrogen bonding in water, when mixed with 2,2,2-trifluoroethanol, is not compensated for by the formation of weak hydrogen bonds between the alcohol and water molecules. The variations of η^E and G^{*E} with temperature indicate a decrease in the strength of interaction with a rise in temperature.

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