Viscometric and Density Study of Binary Mixtures of 2,2,2-Trifluoroethanol with Anilines

Ramamurthy Palepu[a]; Joseph H. Macneil[b]; Paul Wiseman[a]

[a] Department of Chemistry, University College of Cape Breton, Sydney, N.S., Canada [b] Department of Chemistry, Queen's University, Kingston, Ontario, Canada

PLEASE SCROLL DOWN FOR ARTICLE

VISCOMETRIC AND DENSITY STUDY OF BINARY MIXTURES OF 2,2,2-TRIFLUOROETHANOL WITH ANILINES

RAMAMURTHY PALEPU*, JOSEPH H. MACNEIL[1] and PAUL WISEMAN

Department of Chemistry, University College of Cape Breton, Sydney, N.S., Canada B1P 6L2.

Viscosity coefficients and densities of binary mixtures of 2,2,2-trifluoroethanol with aniline and N-alkylanilines have been measured at five temperatures over the entire composition range. From the experimental data, excess volumes, viscosities and free energies of activation values were calculated and discussed in terms of intermolecular interactions between the components in the binary mixtures. Semiempirical equations of McAllister and Heric were employed to fit the experimental viscosity of the binary mixtures.

KEY WORDS: Viscosities, densities, binary mixtures, excess free energy of activation flow.

1 INTRODUCTION

A knowledge of the interaction of the amino group with other organic groups may be of potential use for the extension of group models to systems of interest in biochemical studies. Previously we have reported the viscosities and densities of binary mixtures of anilines with phenols and alcohols.[1-5] This work presents the viscosity and density of binary mixtures of 2,2,2-trifluoroethanol (TFE) with aniline (ANL), N-methylaniline (MEA), N-ethylaniline (EAN), N,N-dimethylaniline (DMA) and N,N-diethylaniline (DEA). From the experimental densities and viscosities, the excess volume (V^E), excess viscosity (η^E) and the excess free energy of activation of flow (ΔG^{*E}) have been computed. The experimental viscosity values of the binary mixtures were analysed in terms of semitheoretical equations of McAllister[6] and Heric[7,8] in order to examine the closeness of the fit between each of the above relations and the experimental values.

2 EXPERIMENTAL SECTION

Anilines and N-alkylanilines used in the present investigation were the same as our earlier studies.[1-5] 2,2,2-trifluoroethanol (Aldrich Chemical Co. Ltd.) of stated purity

---

* To whom the correspondence should be addressed.
[1] Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

>99 mole percent, was dried over molecular sieves. Densities were determined with an Anton Paar densimeter DMA 45 with an estimated precision of 1×10^{-4} 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 ± 0.001 K. The viscosity measurement were carried out in an Ostwald viscometer. Temperatures of the thermostated bath remained constant within ± 0.02 K. Viscosities were expressed in units of cP equal to 10^{-3} Kg m^{-1} s^{-1}. The reproducibility of the viscosities was estimated to be ± 0.005 cP. The density and the viscosity values of the pure compounds agree very well with the available data in the literature.[9,10]

3 THEORETICAL ASPECTS

Excess properties were calculated from the experimental viscosity and density values and the following equations

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \tag{1}$$

$$V^E = V - (x_1 V_1 + x_2 V_2) \tag{2}$$

$$\Delta G^{*E} = RT[\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \tag{3}$$

where η, η_1 and η_2 are the viscosities of the mixture and of the pure components V, V_1 and V_2 are the molar volumes of the mixture and of the pure components. The molar volume V of the mixture is defined as

$$V = (x_1 M_1 + x_2 M_2)\rho^{-1} \tag{4}$$

where M_1 and M_2 are the molecular masses of the components, ρ is the density of the mixture and x_i is the mole fraction of the component i in the solution. The values of ΔG^{*E} and V^E were fitted at each temperature to a polynomial equation by the methods of least squares:

$$Y^E = x(1 - x) \sum_{j=1}^{n} A_j(1 - 2x)^{j-1} \tag{5}$$

where A_j is the polynomial coefficients and n is the polynomial degree.[11] The values of coefficients at 298 K along with the standard deviation (σ) calculated according to Eq. (6) are shown in Table 1.

$$\sigma = \left[\frac{\sum (Y^E_{expt} - Y^E_{cal})^2}{n_{expt} - n} \right]^{1/2} \tag{6}$$

Excess viscosity (η^E) values were found to be very small for all the systems in the present study, therefore no attempts were made to fit excess η^E into the equation (5).

Viscosity data for the liquid mixtures were also analysed in light of the various theories of liquid mixtures viscosity. The various approaches for accurate estimation of viscosity mixtures have been discussed by Reid et al.[12] One approach for the estimation of liquid mixtures viscosity is due to McAllister[6], who has adopted the

Table 1 Coefficients A_j and standard deviations for representation of V^E(cm³/mol) and ΔG^{*E}(J/mol) calculated by Eq. (5) at 298 K.

System		A_1	A_2	A_3	A_4	A_5	A_6	σ
TFE + ANL	V^E	-0.238	-0.007	-0.002	0.018			0.0031
	ΔG^{*E}	744.8	88.88	-1196	-71.3	1253		16
TFE + MEA	V^E	1.186	-0.298	-0.210	2.610	1.038	-2.921	0.0050
	ΔG^{*E}	537.2	-426.8	441.3				10
TFE + EAN	V^E	1.945	0.992	-0.586				0.0016
	ΔG^{*E}	443.4	-2.9	-22.5	-105.3			5
TFE + DMA	V^E	3.416	2.585	-0.036	-0.168			0.0048
	ΔG^{*E}	352.8	-556.7	1954	304.9	-2161		8
TFE + DEA	V^E	3.177	-0.685	-5.191	9.906	9.054	-7.757	0.1000
	ΔG^{*E}	788.0	759.7	200.1	-273.1			30

Eyring approach,[13,14] and has considered the interaction between layers of molecules as if the molecules were undergoing a chemical reaction and have to overcome a potential barrier of this process. For a binary mixture of A and B in which case molecular interactions of 1-1-1, 2-2-2, 1-2-1, 2-1-2, 1-1-2 and 1-2-2 types can be visualized, and McAllister's approach for a three body interaction yields the equation:

$$\ln = x_1^3 \ln v_1 + 3x_1^2 x_1 \ln v_{12} + 3x_1 x_2^2 \ln v_{21} + x_2^3 \ln v_2$$

$$+ \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 3x_1^2 x_2\left[\ln \tfrac{2}{3} + \frac{M_2}{3M_1}\right] \tag{7}$$

$$+ 3x_1 x_2^2\left[\ln \tfrac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3\left[\ln \frac{M_1}{M_2}\right]$$

In Eq. (7) v_1, v_2 and v refer to the kinematic viscosities of the pure components 1, 2 and the mixture respectively. The interaction parameters v_{12} and v_{21} were determined by the methods of least squares from the viscosity data for the various systems, as described by Reid et al.[12]. Since our data extended over a wide temperature range, the temperature functionality for the interaction parameters was obtained by the assumption of an Andrade[6] form

$$v_{12} = A_{12} \exp\left[\frac{B_{12}}{T}\right], \qquad v_{21} = A_{21} \exp\left[\frac{B_{21}}{T}\right] \tag{8}$$

Table 2 shows the values of A and B for the various systems of the current study. In comparison of the experimentally determined data with the values obtained by McAllister's method, the average percent error was found to be less than 1.0%. The following relation was proposed by Heric[7,8] to correlate viscosities of binary mixtures.

$$\log v = x_1 \log v_1 + x_2 \log v_2 + x_1 \log M_1 + x_2 \log M_2$$
$$- \log(x_1 M_1 + x_2 M_2) + \Delta_{12} \tag{9}$$

where Δ_{12} is a deviation function

$$\Delta_{12} = x_1 x_2[\beta'_{12} + \beta''_{21}(x_1 - x_2)] \tag{10}$$

Table 2 Andrade coefficients for the temperature functionality of McAllister constants for binary mixtures.

System	v_{12}		v_{21}	
	A_{12}	B_{12}	A_{21}	B_{21}
TFE + ANL	6.97×10^{-4}	2463.2	2.97×10^{-3}	1947.6
TFE + MAN	8.85×10^{-4}	2256.8	6.01×10^{-3}	1690.0
TFE + EAN	9.16×10^{-4}	2259.0	5.32×10^{-4}	2372.2
TFE + DMA	3.68×10^{-3}	1746.9	5.76×10^{-3}	1625.3
TFE + DEA	1.87×10^{-3}	2039.7	4.27×10^{-3}	1805.6

Table 3 Values of adjustable parameters of Heric's equation.

System	$T(K)$	β'_{12}	β''_{21}	Average % error
TFE + ANL	298	0.2587	−0.0292	0.58
	303	0.5740	−0.2605	1.12
	308	0.5485	−0.2488	1.17
	313	0.6080	−0.2662	1.13
	318	0.6267	−0.2287	1.26
TFE + MAN	298	0.2435	−0.1599	0.43
	303	0.4992	−0.4496	1.58
	308	0.4862	−0.4080	1.54
	313	0.5785	−0.4854	1.78
	318	0.5269	−0.4462	1.81
TFE + EAN	298	0.1777	−0.0165	0.10
	303	0.1770	−0.0095	0.06
	308	0.1816	−0.0454	0.12
	313	0.1937	−0.0439	0.21
	318	0.1998	−0.0473	0.31
TFE + DMA	298	−0.0694	−0.1895	0.87
	303	0.1403	−0.1224	0.37
	308	0.2325	−0.0624	0.71
	313	0.2974	−0.3265	1.60
	318	0.2051	−0.0287	0.08
TFE + DEA	298	0.3293	−0.3379	0.60
	303	0.5941	−0.4282	0.51
	308	0.5691	−0.3442	0.42
	313	0.5776	−0.4032	0.80
	318	0.6139	−0.5586	1.12

The two adjustable parameters β'_{12} and β''_{12} were determined from a nonlinear least-squares methods and are presented in Table 3.

4   RESULTS AND DISCUSSION

Analysis of the adjustable parameters together with average percentage error indicate that both McAllister and Heric with two adjustable parameters are found to be effective in fitting our experimental data. The selection of a cubic equation (McAllister) is justified, since for each solution in this work the ratio of radius

$$\frac{r_2}{r_1} = \left[\frac{V_2^0}{V_1^0}\right]^{1/3}$$

is found to be less than 1.5. The values of excess volumes (V^E) and excess free energies of activation flow (ΔG^{*E}) at 298 K are graphically represented in Figures 1 and 2
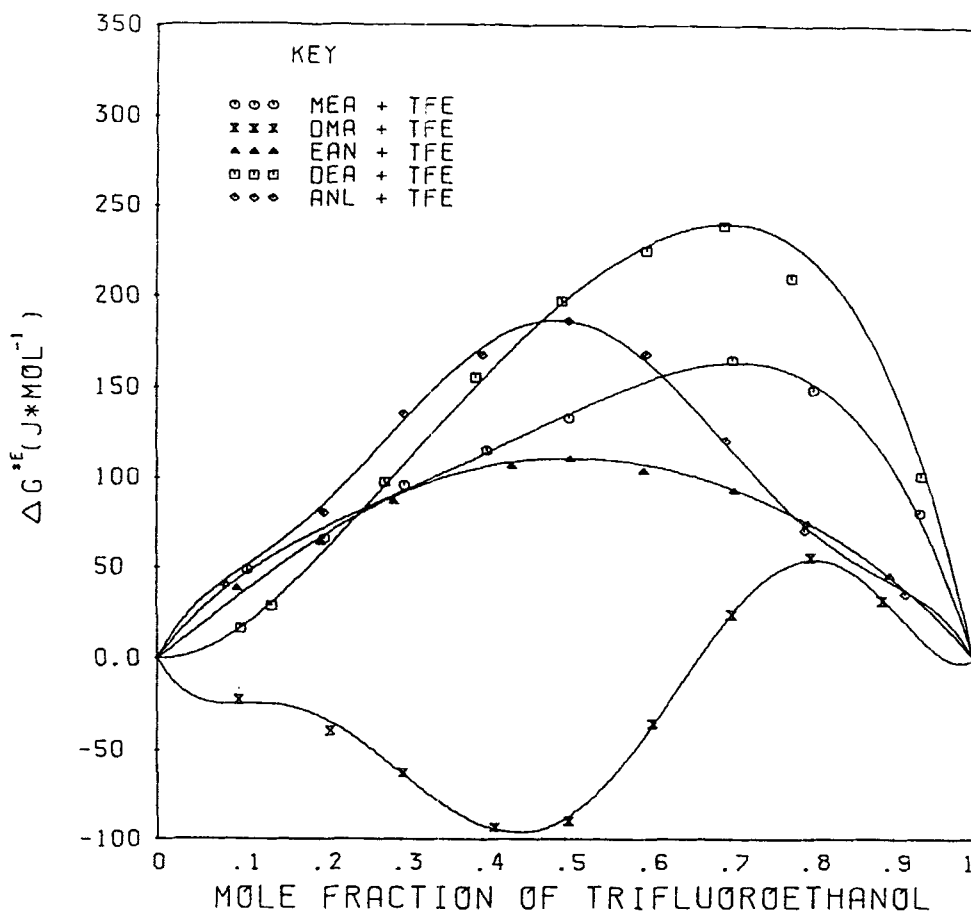
R. PALEPU, J. H. MACNEIL AND P. WISEMAN

Figure 1 Plot of excess volume against mole fraction of trifluoroethanol at 298 K.

respectively, as a function of mole fraction of trifluoroethanol. The continuous curves were generated with the aid of the coefficients of Eq. 5.

Positive values of excess volumes have been attributed to a looser liquid structure which may be due to the breaking of the hydrogen bonds in the pure components.[15] The negative values of V^E for ANL + TFE are explained in terms of different sizes of the molecules or dipole–dipole interaction between them.[16] Excess viscosities and values of ΔG^{*E} suggest that the specific interactions significant enough to cause notable changes in the degree of association are not present in the mixtures.[17-20] One can conclude from these results that the specific interactions between TFE and anilines are mainly due to dispersion forces and may also be due to the weak hydrogen bonding of the type N—H---O and O—H---N.
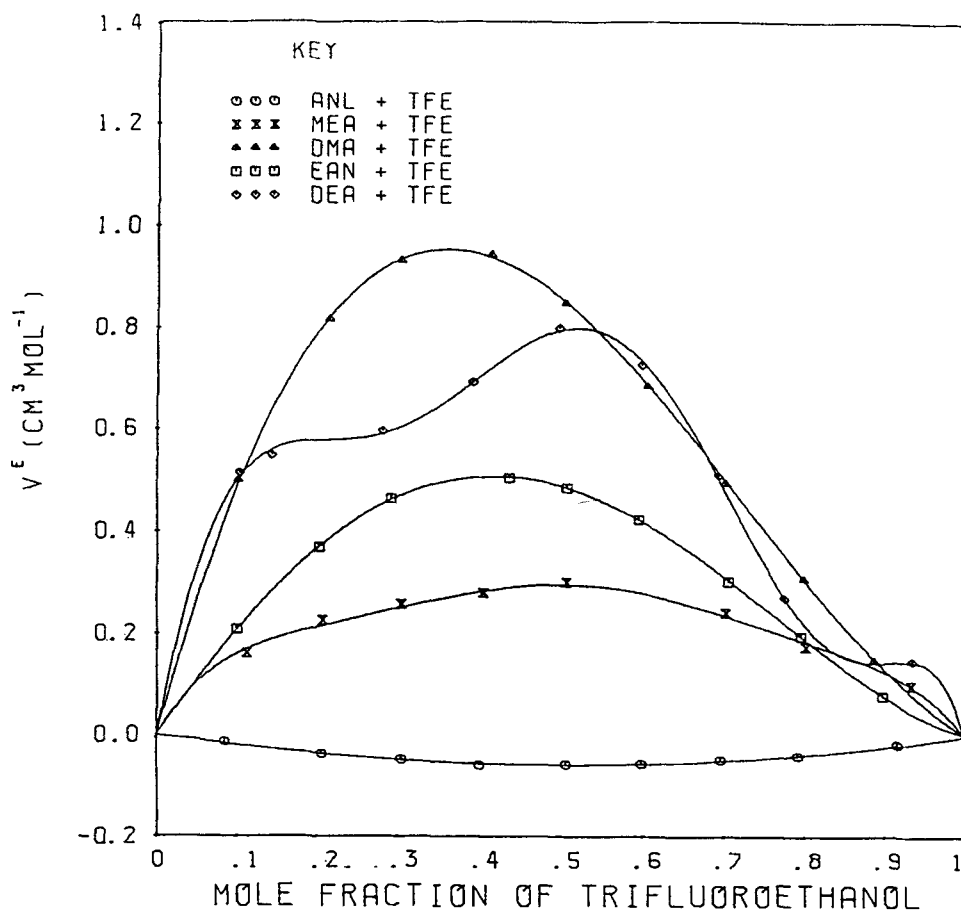
Figure 2 Plot of excess Gibbs free energy of activation of flow against mole fraction of trifluoroethanol
at 298 K.

References

1. R. Palepu, J. Oliver and B. MacKinnon, *Can. J. Chem.*, **63**, 1024 (1985).
2. R. Palepu, J. Oliver and D. Campbell, *J. Chem. Eng. Data*, **30**, 355 (1985).
3. D. J. G. Irwin, R. Johnson and R. Palepu, *Thermochimica Acta*, **82**, 277 (1984).
4. R. Palepu and J. H. MacNeil, *Australian J. Chem.*, **41**, 791 (1988).
5. R. Palepu and J. H. MacNeil, *Thermochimica Acta*, **149**, 275 (1989).
6. R. A. McAllister, *AIChE. J.*, **6**, 427 (1960).

7. E. L. Heric, *J. Chem. Eng. Data*, **11**, 66 (1966).
8. E. L. Heric and J. G. Brewer, *J. Chem. Eng. Data*, **12**, 1574 (1967).
9. M. C. S. Subha and S. B. Rao, *J. Chem. Eng. Data*, **33**, 104 (1988).
10. A. Coney and K. W. Morcom, *J. Chem. Thermodynamics*, **20**, 736 (1988).
11. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
12. R. C. Reid, J. M. Prausnitz and J. K. Sherwood, The Properties of Gases and Liquids, McGraw-Hill, New York (1977).
13. V. A. Bloomfield and R. K. Dewan, *J. Phys. Chem.*, **75**, 3113 (1971).
14. S. Glasston, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York (1941).
15. M. V. P. Rao, and P. R. Naidu, *Can. J. Chem.*, **52**, 788 (1974).
16. I. Prigogine, The Molecular Theory of Solution, Amsterdam (1957).
17. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).
18. Y. Fialkov, *Russ. J. Phys.*, **41**, 398 (1967).
19. T. M. Reed and T. E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959).
20. R. Meyers, M. Meyers, J. Metzger and A. Peneloux, *J. Chem. Phys.*, **62**, 405 (1971).