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Viscosities and Volumes of Dilute Solutions of Formamide in Water + Acetonitrile and for Formamide and *N*,*N*-Dimethylformamide in Methanol + Acetonitrile Mixed Solvents: Viscosity *B*-Coefficients, Activation Free Energies for Viscous Flow, and Partial Molar Volumes

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The viscosity *B*-coefficients and partial molar volumes have been measured for *N*,*N*-dimethylformamide and formamide in methanol + acetonitrile solvent systems and for *N*,*N*-dimethylformamide in water + acetonitrile mixed solvents. These data are used to calculate the solute contribution to the activation free energy for viscous flow, $\Delta\mu^{\neq}{}_{13}$, for these systems. It is found that the $\Delta\mu^{\neq}{}_{13}$ values are simply related to the corresponding enthalpies of transfer.

Introduction

The measurement of the viscosities of solutions formed the basis of some of the earliest studies of solute−solvent interactions. Jones and Dole[1] showed that the viscosities of dilute solutions of strong electrolytes could be represented as

$$\eta_{13}/\eta_1 = \eta_r = 1 + A\sqrt{c} + Bc \qquad (1)$$

where η_{13} and η_1 are the viscosities of the solution and solvent, respectively, and c is the solute concentration. The *A*-coefficient takes account of ion−ion interactions and can be calculated[2] and the *B*-coefficient reflects the effects of solute−solvent interactions on the solution viscosity. The viscosities of dilute solutions of nonassociated nonelectrolytes can be similarly represented as

$$\eta_{13}/\eta_1 = \eta_r = 1 + Bc \qquad (2)$$

where the symbols have the obvious meanings.

B-coefficients have been measured for a wide range of electrolytes in aqueous solutions and for a smaller number of electrolytes in organic and mixed aqueous−organic solvents.[3] Nonelectrolytes have been less extensively studied although data are available for several solutes in water[4,5] and for 2-methylpropan-2-ol (*tert*-butyl alcohol) in aqueous methanol solvent systems.[6]

In the present paper we present viscosity *B*-coefficients and partial molar volumes for formamide and *N*,*N*-dimethylformamide in methanol + acetonitrile mixed solvents at 298.2 and 308.2 K and for *N*,*N*-dimethylformamide in water + acetonitrile solvents at 288.2 and 298.2 K. We also report viscosity and volume data for the solvent mixtures at these temperatures.

The values of the solute contribution to the free energy of activation for viscous flow, $\Delta\mu^{\neq}{}_{13}$, were calculated from the *B*-coefficients and molar volumes using the Feakins[6,7] relationship. It is found that the $\Delta\mu^{\neq}{}_{13}$ values are simply related to the enthalpies of transfer of the solutes in the same solvent systems.

Experimental Section

Viscosity. The viscosity measurements were made using a Schott-Gerate AVS/S measuring system and an Ubbelohde type suspended level capillary viscometer as described previously.[8]

The system was adapted to allow serial measurements to be made under computer control. The modification to the capillary viscometer involved replacing the lower reservoir by one with a volume of about 50 cm^3. The viscometer was suspended in a specially constructed double water bath, which allowed the contents of the reservoir to be stirred using a magnetic stirrer. The temperature of the inner bath was stable to ±0.001 K and was within ±0.01 K of the reported temperature.

The composition of the solution in the viscometer was altered by the addition of a stock solution, via a piston driven buret (Metrohm Dosimat 655, using a 1 cm^3 buret), through the sidearm of the viscometer. The AVS was controlled and interrogated through its RS-232 port, and the stirrer and buret were activated using reed relays under computer control.

Thus, in an experiment a known volume of solvent was placed in the viscometer and its flow time measured. Subsequently, known volumes of a stock solution were injected into the viscometer and mixed by stirring, and the flow times of the resulting solutions were measured. The weight of a 1 cm^3 injection of the stock solution was measured before and after the experiment, and the density of the final solution was measured as a check on the final solution concentration.

Typically *B*-coefficients were determined from measurements at nine solute concentrations (to 0.12 mol dm^{-3}). The precisions of the *B*-coefficients, expressed as standard errors, are listed in the tables.

Density. Densities were measured using a vibrating tube densitometer (Anton Paar DMA-60) with two cells (DMA-

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Table 1. Densities and Viscosities of Methanol (1) + Acetonitrile (2) Mixtures[a]

x_2	density/ g cm^{-3}	viscosity/ mPa s	x_2	density/ g cm^{-3}	viscosity/ mPa s
298.15 K					
0.0000	0.78663_5	0.5391	0.4383	0.78416_2	0.3604
	0.78654^{g}	0.5425^{e}			
	0.78680^{h}	0.545^{g}			
	0.78666^{i}	0.554^{i}			
0.0394	0.78694_4	0.5080	0.5393	0.78284_5	0.3460
0.0798	0.78708_5	0.4861	0.6455	0.78138_8	0.3349
0.1633	0.78689_4	0.4436	0.7574	0.77984_6	0.3285
0.2064	0.78659_2	0.4247	0.8754	0.77823_2	0.3290
0.2507	0.78623_1	0.4091	0.9368	0.77742_0	0.3334
0.3423	0.78531_8	0.3827	1.0000	0.77663_5	0.3410
				$0.77654_9{}^{b}$	0.3405^{d}
				0.77614^{c}	0.3409^{e}
				0.77645^{d}	0.345^{g}
				0.77686^{g}	0.341^{i}
				0.77690^{h}	
				0.77622^{i}	
308.15 K					
0.0000	0.77711_4	0.4506	0.5393	0.77226_6	0.3097
	0.7772^{f}	0.474^{g}			
	0.77718^{g}	0.482^{i}			
	0.77771^{i}				
0.0799	0.77732_2	0.4257	0.6451	0.77068_5	0.3010
0.1633	0.77693_4	0.3905	0.7573	0.76903_8	0.2970
0.2506	0.77617..	0.3624	0.8755	0.76734_0	0.2986
0.3423	0.77504_6	0.3400	0.9368	0.76653_1	0.3024
0.4384	0.77376_3	0.3226	1	0.76576_5	0.3087
				0.7656^{f}	0.313^{g}
				0.76564^{g}	0.306^{i}
				0.76518^{i}	

[a] Precisions are ±0.000 005 in the densities and ±0.2% in the viscosities; x_2 represents the acetonitrile mole fraction. [b] Ref 11. [c] Ref 12. [d] Ref 16. [e] Ref 18. [f] Ref 13. [g] Ref 14. [h] Ref 15. [i] Ref 17.

Table 2. Densities and Viscosities of Water (1) + Acetonitrile (2) Mixtures[a]

x_2	density/ g cm^{-3}	viscosity/ mPa s	x_2	density/ g cm^{-3}	viscosity/ mPa s
298.15 K					
0.0000	$0.997\ 04_3$	0.8904	0.3050	0.890 84	0.7520
0.0225	0.989 45	0.9457	0.3969	0.867 15	0.6535
0.0465	0.981 07	0.9759	0.5060	0.843 84	0.5503
0.0718	0.971 53	0.9808	0.6371	0.820 82	0.4572
0.0989	0.961 30	0.9687	0.7980	0.797 95	0.3811
0.1278	0.950 08	0.9453	0.8929	0.786 90	0.3537
0.1583	0.938 63	0.9165	1.0000	$0.776\ 63_5$	0.3410
0.2264	0.914 81	0.8404			
288.15 K					
0.0000	$0.999\ 10_1$	1.142	0.39695	0.876 33	0.796
0.0465	0.985 26	1.272	0.50591	0.854 37	0.655
0.09887	0.967 29	1.258	0.79795	0.808 57	0.430
0.29662	0.899 35		1.0000	0.787 65	0.376

[a] Precisions are ±0.000 02 in the densities and ±0.2% in the viscosities except for pure water, where those for the densities are ±0.000 005; x_2 represents the acetonitrile mole fraction.

601) with one, containing water, used as reference. This configuration has the advantage of minimizing the effects of variations in temperature. The system was fitted with an automatic sampler unit (Anton Paar SP-2). The apparatus was enclosed in an air thermostat kept at 0.5 K above the measuring temperature so that outgassing of samples was minimized. The temperature of the cell was controlled by circulation of water from a double water bath, the circulating bath was stable to ±0.003 K, and the measuring cell temperature was within ±0.01 K of the reported temperature.

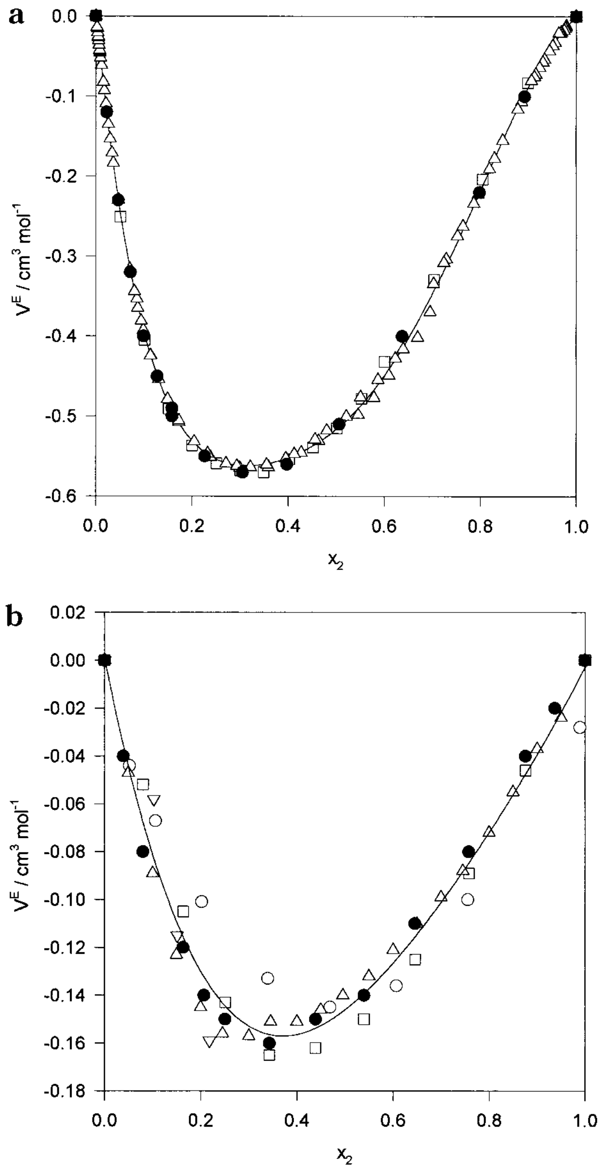

Figure 1. Excess molar volumes at 298.15 K for (a) water (1) + acetonitrile (2) mixtures [ref 11 (△), ref 12 (□), and the present results (●)] and (b) methanol (1) + acetonitrile (2) mixtures [ref 14 (△), ref 15 (○), ref 17 (□), ref 18 (▽), and the present results (●)].

Chemicals. *N*,*N*-Dimethylformamide,[9] formamide,[9] and acetonitrile[10] were purified as described previously. Water was distilled, passed through an ion exchange column, and then redistilled; the conductivity of the water was <1 × 10^{-6} S cm^2.

Results

The densities and viscosities of the mixed solvent systems are listed in Tables 1 and 2. The excess molar volumes of the mixed solvents are shown in Figure 1, and the corresponding viscosities are shown in Figure 2. Also shown in Figures 1 and 2 are comparable data taken from the literature.[11−18] In all cases the agreement among the data is excellent. We note that our viscosities for the methanol + acetonitrile system at 308.15 K are marginally but systematically lower than those of Saha et al.[14] and Nikam et al.[16]

The densities of formamide and *N*,*N*-dimethylformamide solutions in the mixed solvents followed the Root equation:[19]

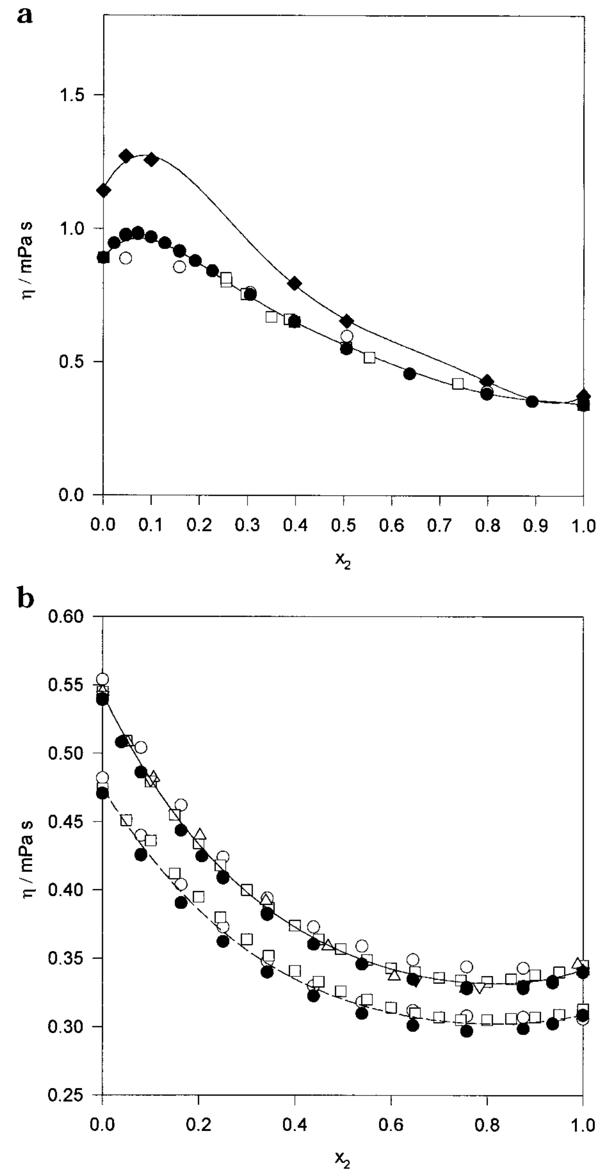

Figure 2. Solvent viscosities for (a) water (1) + acetonitrile (2) mixtures [ref 16 (○), ref 18 (□), and the present results (●) at 298.15 K and the present results (◆) at 288.15 K] and (b) methanol (1) + acetonitrile (2) mixtures at 298.15 and 308.15 K [ref 17 (○), ref 15 (△), ref 14 (□), ref 18 (▽), and the present results (●)].

$$\rho_{1,3} = \rho_1 + ac \qquad (3)$$

to within experimental error, and the partial molar volumes, V_ϕ, of the solutes were obtained from the values of α as

$$\alpha = \frac{(M_3 - \rho_1 V_\phi)}{1000} \qquad (4)$$

In eqs 3 and 4, c represents the solute concentration, $\rho_{1,3}$ and ρ_1 represent the densities of the solution and mixed solvent, and M_3 is the molecular weight of the solute.

The viscosities of the formamide and *N*,*N*-dimethylformamide solutions followed eq 2.

The partial molar volumes and *B*-coefficients for the systems studied are reported in Tables 3−5, and the *B*-coefficients are shown in Figure 3.

Eyring and co-workers[20] proposed that the free energy of activation for viscous flow of a pure liquid (1), $\Delta\mu_1^{o\neq}$, could be calculated via

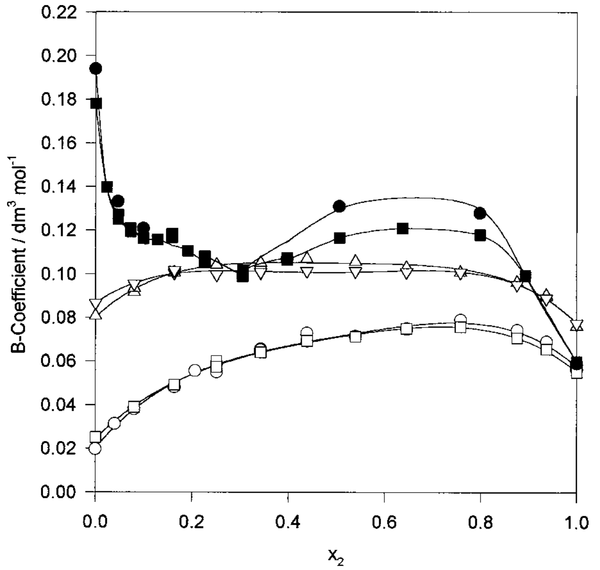

Figure 3. *B*-coefficients of formamide in methanol (1) + acetonitrile (2) mixtures at 298.15 K (△) and 308.15 K (▽), *N*,*N*-dimethylformamide in acetonitrile + methanol mixtures at 298.15 K (○) and 308.15 K (□), and *N*,*N*-dimethylformamide in water (1) + acetonitrile (2) mixtures at 288.15 K (■) and 298.15 K (●).

$$\eta_1 = \left(\frac{hN_A}{\bar{V}_1^o}\right)\exp\left(\frac{\Delta\mu_1^{o\neq}}{RT}\right) \qquad (5)$$

where N_A and h are Avogadro's number and Planck's constant and the other symbols have the obvious meanings. For a solution containing a solute (3) dissolved in a pure liquid (1) they proposed

$$\eta_{13} = \left(\frac{hN_A}{\bar{V}_{13}}\right)\exp\left(\frac{\Delta\bar{G}_{13}^{\neq}}{RT}\right) \qquad (6)$$

where $\bar{V}_{13}$ and $\Delta\bar{G}_{13}^{\neq}$ are the mean molar volume and the average Gibbs energy of activation for viscous flow. In the case of dilute solutions we write

$$\Delta\bar{G}_{13}^{\neq} = x_1\Delta\mu_1^{o\neq} + x_3\Delta\mu_3^{\neq} \qquad (7)$$

Feakins[6,7] showed that, if eqs 1 (or 2) and 7 are obeyed, then

$$B = (\nu\bar{V}_1^o - V_{\phi 3}) + \left(\frac{\bar{V}_1^o}{RT}\right)(\Delta\mu_3^{\neq} - \nu\Delta\mu_1^{o\neq}) \qquad (8)$$

where the coefficient ν is one for an undissociated solute, as in the present work, and would be, for example, 2 for a fully dissociated univalent electrolyte.

The activation free energies for the mixed solvents $\Delta\bar{G}_{1,2}^{\neq}$ were calculated from their viscosities, η_{13}, via eq 6 and are listed in Tables 6 and 7. The $\Delta\mu_{13}^{\neq}$ values calculated from the *B*-coefficients are listed in Tables 8 and 9 and are shown graphically in Figure 4.

Discussion

It is clear from Figure 4 that, with the exception of the values in pure water, the temperature variation of $\Delta\mu_{13}^{\neq}$is close to the limit of its precision. Qualitatively this corresponds to a situation where the activation entropy is small and $\Delta\mu_{13}^{\neq}$ is dominated by the enthalpy of activation.

These solute−solvent systems have been extensively studied by calorimetry[21,22] and infrared spectroscopy.[23,24]

Table 3. Limiting Partial Molar Volumes and Viscosity *B*-Coefficients for *N*,*N*-Dimethylformamide (3) in Methanol (1) + Acetonitrile (2) Mixtures[a]

x_2	V_ϕ/cm^3 mol^{-1}	B/dm^3 mol^{-1}	x_2	V_ϕ/cm^3 mol^{-1}	B/dm^3 mol^{-1}
		298.15 K			
0.0000	$74.7_1 \pm 0.06$	0.020 ± 0.0005	0.4383	$75.9_1 \pm 0.02$	0.069 ± 0.0003
				$75.9_2 \pm 0.02$	0.073 ± 0.0003
0.0395	$75.0_0 \pm 0.07$	0.031 ± 0.0007	0.5393	$76.0_8 \pm 0.04$	0.072 ± 0.0002
				$75.9_5 \pm 0.07$	0.072 ± 0.0003
0.0798	$75.3_4 \pm 0.05$	0.038 ± 0.0004	0.6455	$76.1_7 \pm 0.02$	0.075 ± 0.0002
				$76.1_2 \pm 0.05$	0.072 ± 0.0002
0.1633	$75.6_1 \pm 0.05$	0.048 ± 0.0006	0.7574	$76.2_4 \pm 0.03$	0.079 ± 0.0004
				$76.1_2 \pm 0.03$	
0.2064	$75.6_7 \pm 0.03$	0.056 ± 0.0008	0.8754	$76.4_0 \pm 0.07$	0.074 ± 0.0004
				$76.3_9 \pm 0.01$	0.073 ± 0.0003
0.2507	$75.7_0 \pm 0.03$	0.055 ± 0.0003	0.9368	$76.5_6 \pm 0.02$	0.069 ± 0.0003
		0.059 ± 0.0005			
0.3423	$75.8_3 \pm 0.04$	0.065 ± 0.0004	1.0000	$76.7_4 \pm 0.02$	0.056 ± 0.0004
		0.066 ± 0.0005			
		308.15 K			
0.0000	$75.5_5 \pm 0.03$	0.025 ± 0.0006	0.5393	$76.7_4 \pm 0.05$	0.071 ± 0.0004
0.0799	$76.0_5 \pm 0.02$	0.039 ± 0.0005	0.6451	$76.7_8 \pm 0.02$	0.075 ± 0.0003
0.1633	$76.2_3 \pm 0.02$	0.049 ± 0.0006	0.7573	$76.9_9 \pm 0.02$	0.076 ± 0.0003
0.2506	$76.4_6 \pm 0.07$	0.060 ± 0.0002	0.8755	$77.1_3 \pm 0.02$	0.071 ± 0.0003
	$74.4_4 \pm 0.04$	0.057 ± 0.0004			
0.3423	$76.6_2 \pm 0.04$	0.064 ± 0.0004	0.9368	$77.2_7 \pm 0.03$	0.066 ± 0.0004
0.4384	$76.7_1 \pm 0.02$	0.069 ± 0.0003	1.0000	$77.3_3 \pm 0.09$	0.055 ± 0.0005

[a] Precisions shown are the standard deviations; x_2 represents the acetonitrile mole fraction.

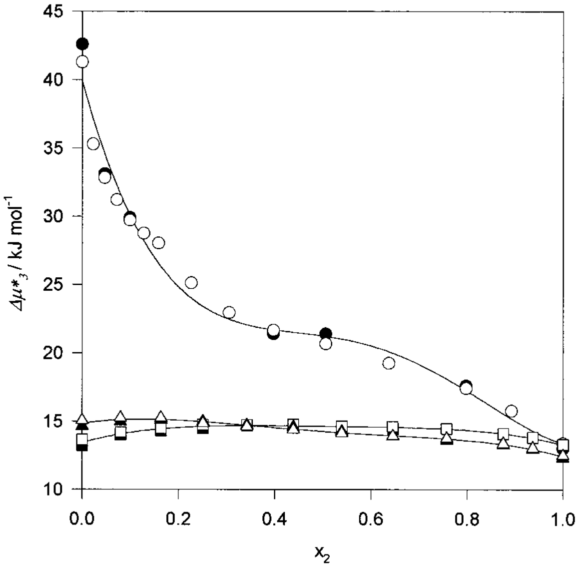

Figure 4. Solute contributions to the activation chemical potential for viscous flow, $\Delta\mu_3^{\theta\neq}$, for *N*,*N*-dimethylformamide in water (1) + acetonitrile (2) mixtures at 288.15 K (●) and 298.15 K (○) and methanol (1) + acetonitrile (2) mixtures at 298.15 K (■) and 308.15 K (□) and for formamide in methanol (1) + acetonitrile (2) mixtures at 298.15 K (▲) and 308.15 K (△).

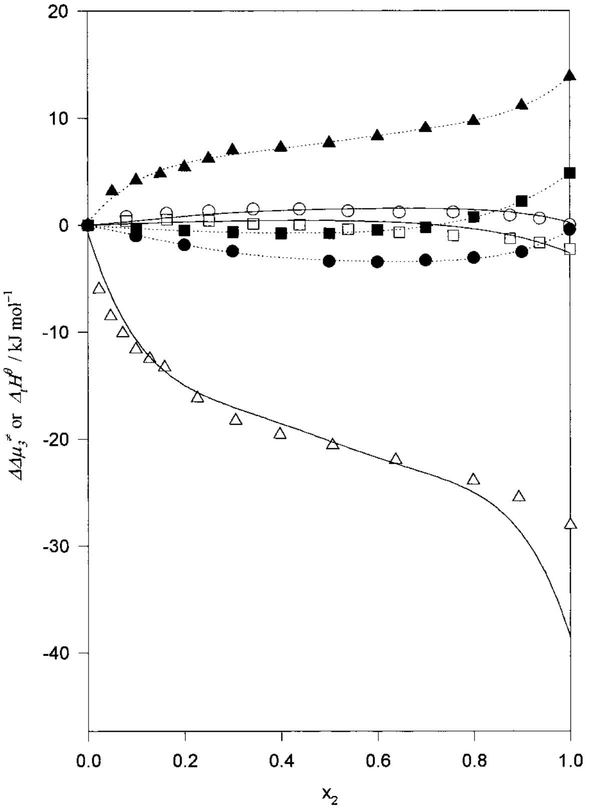

Figure 5. Variation in the solute contribution to the activation chemical potential for viscous flow, $\Delta\Delta\mu_3^{\theta\neq}$, (open symbols) and enthalpies of transfer, $\Delta_t H_3^\theta$, (filled symbols) for *N*,*N*-dimethylformamide in water (1) + acetonitrile (2) (△) and methanol (1) + acetonitrile (2) (○) mixtures and for formamide in methanol (1) + acetonitrile (2) mixtures (□); the line through the $\Delta\Delta\mu_3^{\theta\neq}$ data corresponds to eq 9 (see text).

In the present context the calorimetric studies are the more interesting.

In each of the systems considered the variation in $\Delta\mu_{13}^{\neq}$ is similar to that in the corresponding enthalpy of transfer, $\Delta_t H^\theta$, but is inverted and differs in magnitude. In effect we can write

$$\Delta\Delta\mu_3^{\theta\neq} \cong -\{A \times \Delta_t H^\theta\} \tag{9}$$

where $\Delta\Delta\mu_{13}^{\neq}$ is the change in $\Delta\mu_{13}^{\neq}$ and A is simply a proportionality constant.

This is shown in Figure 5, which shows the $\Delta_t H^\theta$ and $\Delta\Delta\mu_{13}^{\neq}$ values for the three systems reported here as a function of solvent composition. Also shown in Figure 5 are lines corresponding to eq 9. In the methanol + acetonitrile system the $\Delta\Delta\mu_{13}^{\neq}$ values conform sensibly to eq 9 over the whole range of solvent compositions, while in the aqueous acetonitrile system there is a divergence at acetonitrile mole fractions above 0.8.

Table 4. Limiting Partial Molar Volumes and Viscosity *B*-Coefficients for Formamide (3) in Methanol (1) + Acetonitrile (2) Mixtures[a]

x_2	V_ϕ/cm^3 mol^{-1}	B/dm^3 mol^{-1}	x_2	V_ϕ/cm^3 mol^{-1}	B/dm^3 mol^{-1}
298.15 K					
0.0000	$36.7_2 \pm 0.03$	0.081 ± 0.0006	0.5393	$37.3_9 \pm 0.01$	0.106 ± 0.0002
0.0798	$36.9_7 \pm 0.03$	0.092 ± 0.0007	0.6455	$37.4_4 \pm 0.02$	0.103 ± 0.0003
		0.094 ± 0.0008			
0.1633	$37.0_2 \pm 0.02$	0.101 ± 0.0007	0.7574	$37.5_5 \pm 0.03$	0.101 ± 0.0002
0.2507	$37.3_0 \pm 0.02$	0.104 ± 0.0004	0.8754	$37.5_9 \pm 0.01$	0.096 ± 0.0002
0.3422	$37.4_6 \pm 0.02$	0.105 ± 0.0005	0.9368	$37.5_9 \pm 0.03$	0.090 ± 0.0004
		0.104 ± 0.0003		$37.5_4 \pm 0.01$	0.090 ± 0.0003
0.4383	$37.4_5 \pm 0.03$	0.107 ± 0.0001	1.0000	$37.8_2 \pm 0.02$	0.076 ± 0.0004
308.15 K					
0.0000	$36.8_3 \pm 0.03$	0.087 ± 0.0010	0.5393	$37.4_7 \pm 0.02$	0.101 ± 0.0003
0.0798	$37.1_5 \pm 0.02$	0.095 ± 0.0007	0.6455	$37.5_9 \pm 0.01$	0.101 ± 0.0004
0.1633	$37.1_9 \pm 0.02$	0.102 ± 0.0006	0.7574	$37.5_4 \pm 0.02$	0.101 ± 0.0003
0.2507	$37.4_5 \pm 0.02$	0.100 ± 0.0003	0.8753	$37.6_7 \pm 0.02$	0.095 ± 0.0004
0.3422	$37.5_1 \pm 0.01$	0.101 ± 0.0004	0.9368	$37.7_6 \pm 0.02$	0.089 ± 0.0004
0.4383	$37.5_0 \pm 0.01$	0.101 ± 0.0003	1.0000	$37.9_4 \pm 0.02$	0.077 ± 0.0004

[a] Precisions shown are the standard deviations; x_2 represents the acetonitrile mole fraction.

Table 5. Limiting Partial Molar Volumes and Viscosity *B*-Coefficients for *N*,*N*-Dimethylformamide (3) in Water (1) + Acetonitrile (2) Mixtures[a]

x_2	V_ϕ/cm^3 mol^{-1}	B/dm^3 mol^{-1}	x_2	V_ϕ/cm^3 mol^{-1}	B/dm^3 mol^{-1}
288.15 K					
0	$73.6_7 \pm 0.02$	0.194 ± 0.001	0.5059		0.131 ± 0.002
0.0465		0.133 ± 0.0006	0.7979		0.128 ± 0.001
0.0989		0.121 ± 0.0001	1.0000		0.059 ± 0.001
0.3970		0.107 ± 0.001			
298.15 K					
0.0000	$74.3_4 \pm 0.02$	0.178 ± 0.0006	0.2264	$75.0_0 \pm 0.04$	0.106 ± 0.0007
					0.109 ± 0.0005
0.0225	$74.4_7 \pm 0.03$	0.139 ± 0.0004	0.3051	$75.0_8 \pm 0.02$	0.100 ± 0.0007
					0.103 ± 0.0007
0.0465		0.127 ± 0.0004	0.3969	$75.2_8 \pm 0.03$	0.109 ± 0.0010
		0.125 ± 0.0004			0.107 ± 0.0007
0.0719	$74.8_2 \pm 0.02$	0.119 ± 0.0003	0.5060	$75.3_9 \pm 0.03$	0.118 ± 0.0008
		0.122 ± 0.0004			
0.0989	$74.9_4 \pm 0.04$	0.117 ± 0.0003	0.6371	$75.9_5 \pm 0.03$	0.122 ± 0.0007
0.1278	$74.9_2 \pm 0.04$	0.116 ± 0.0003	0.7980	$76.0_8 \pm 0.03$	0.120 ± 0.0016
0.1583		0.118 ± 0.0003	0.8929	$76.4_7 \pm 0.03$	0.100 ± 0.0007
		0.117 ± 0.0005			
0.1912		0.112 ± 0.0005	1.0000	$76.7_0 \pm 0.03$	0.060 ± 0.001
308.15 K					
0.0000	$75.1_1 \pm 0.03$	0.166 ± 0.001			

[a] Precisions shown are the standard deviations; x_2 represents the acetonitrile mole fraction.

Table 6. Molar Free Energies of Activation for Viscous Flow, $\Delta\bar{G}^{\neq}_{12}$, for Methanol (1) + Acetonitrile (2) Mixtures[a]

	$\Delta\bar{G}^{\neq}_{12}$/kJ mol^{-1}	
x_2	298.15 K	308.15 K
0.0000	9.9	10.0
0.0798	9.7	9.8
0.1633	9.6	9.6
0.2064	9.5	–
0.2507	9.4	9.5
0.3423	9.3	9.4
0.4383	9.2	9.3
0.5393	9.2	9.3
0.6455	9.2	9.3
0.7574	9.2	9.3
0.8754	9.3	9.4
0.9368	9.4	9.5
1.0000	9.4	9.5

[a] Precisions are ±0.2 kJ mol^{-1}; x_2 represents the acetonitrile mole fraction.

While eq 9 represents the $\Delta\Delta\mu^{\neq}_{13}$ data for the nonelectrolyte systems reported here, its wider applicability is not clear. There are not data available for other nonelectrolyte systems against which eq 9 could be tested. There are viscosity[16] and enthalpy[25] data for several electrolyte systems including KCl and $(C_4H_9)_4NBr$ in aqueous acetonitrile mixtures and for CsCl in highly aqueous propan-1-ol + water solvents.[26] In the cases of KCl and $(C_4H_9)_4NBr$ in aqueous acetonitrile the data do not conform even approximately to eq 9 while the CsCl data in the highly aqueous propan-1-ol−water solvents are in qualitative (but not quantitative) agreement with eq 9.

In the cases reported here $\Delta\mu^{\theta\neq}_3$ is dominated by the activation enthalpy and so eq 9 may reflect an underlying relationship between the transfer and activation enthalpies. Testing this requires *B*-coefficients (and molar volumes) at two or more temperatures as well as the corresponding transfer enthalpies. There are relatively few systems where this body of data is available; however, for CsCl in highly aqueous propan-1-ol mixtures the necessary data are available[26] and show no correlation between the transfer and activation enthalpies.

It may then be that eq 9 is applicable to nonelectrolyte systems but not to those involving electrolytes, perhaps because the solvent−nonelectrolyte interactions are shorter range and significantly weaker than those with ionic solutes.

Table 7. Molar Free Energies of Activation for Viscous Flow, $\Delta\bar{G}^{\neq}_{12}$, for Water (1) + Acetonitrile (2) Mixtures at 288.15 and 298.15 K[a]

	$\Delta\bar{G}^{\neq}_{12}$/kJ mol^{-1}	
x_2	288.15 K	298.15 K
0.0000	9.4	9.2
0.0225		9.4
0.0465	9.9	9.6
0.0720		9.7
0.0989	10.0	9.8
0.1278		9.8
0.1583		9.8
0.2264		9.9
0.3051		9.8
0.3969	9.9	9.8
0.5060	9.7	9.6
0.6371		9.5
0.7980	9.3	9.4
0.8929		9.4
1.0000	9.3	9.4

[a] Precisions are ±0.2 kJ mol^{-1}; x_2 represents the acetonitrile mole fraction.

Table 8. Solute Contribution to the Free Energy of Activation for Viscous Flow, $\Delta\mu_3^{\theta\neq}$, for *N,N*-Dimethylformamide and Formamide in Methanol (1) + Acetonitrile (2) Mixtures[a]

	$\Delta\mu_3^{\theta\neq}$/kJ mol^{-1}			
	N,*N*-dimethylformamide		formamide	
x_2	298.15 K	308.15 K	298.15 K	308.15 K
0	13.2	13.6	14.6	15.1
0.0798	14.0	14.2	15.0	15.2
0.1633	14.3	14.5	15.1	15.2
0.2507	14.5	14.7	15.0	14.9
0.3423	14.7	14.8	14.7	14.6
0.4383	14.7	14.8	14.6	14.4
0.5393	14.5	14.6	14.2	14.1
0.6455	14.4	14.6	13.9	13.9
0.7574	14.4	14.5	13.6	13.7
0.8754	14.1	14.1	13.3	13.4
0.9368	13.8	13.8	12.9	13.0
1.0000	13.2	13.3	12.3	12.5

[a] Precisions are ±0.2 kJ mol^{-1}; x_2 represents the acetonitrile mole fraction.

Table 9. Solute Contribution to the Free Energy of Activation for Viscous Flow, $\Delta\mu_3^{\theta\neq}$, for *N,N*-Dimethylformamide in Water (1) + Acetonitrile (2) Mixtures[a]

	$\Delta\mu_3^{\theta\neq}$/kJ mol^{-1}	
x_2	288.15 K	298.15 K
0.0000	42.6	41.3
0.0225		35.3
0.0465	33.1	32.8
0.0720		31.2
0.0989	29.9	29.7
0.1278		28.8
0.1583		28.0
0.2264		25.1
0.3051		23.0
0.3969	21.4	21.7
0.5060	21.4	20.7
0.6371		19.3
0.7980	17.6	17.4
0.8929		15.8
1.0000	13.0	13.2

[a] Precisions are ±0.2 kJ mol^{-1}; x_2 represents the acetonitrile mole fraction.

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