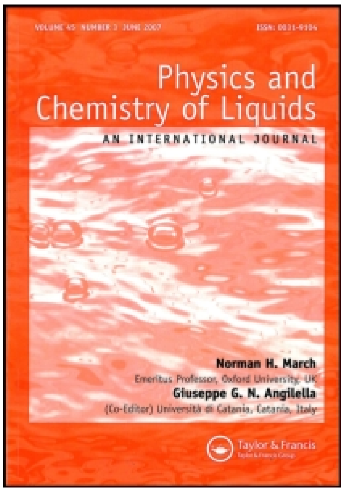

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Density, viscosity and thermodynamic activation of viscous flow of water acetonitrile

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Density, viscosity and thermodynamic activation of viscous flow of water + acetonitrile

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Densities and viscosities for the system, water + acetonitrile, have been determined for the entire range of composition at temperatures ranging from 303.15 to 323.15 K. Density, excess molar volume, viscosity, thermodynamic activation parameters for viscous flow and some of their excess values have been plotted against the mole fraction of acetonitrile and fitted to appropriate polynomial equations. Results have been explained in terms of hydrophilic effect, hydrophobic hydration, hydrophobic interaction and dipole-dipole interaction.

Keywords: Acetonitrile; Density; Excess molar volume; Hydrophobic hydration; Viscosity

1. Introduction

This is a part of our ongoing project on the volumetric and viscometric properties of aqueous solutions of organic compounds with particular reference to hydrophobic solutes. In the recent past, we reported the volumetric, viscometric and thermodynamic properties of aqueous solutions of hydrophobic solutes, such as, alcohols [1–3], diols [4] and amines [5–9]. It was seen that hydrophobic hydration influences strongly the volumetric and viscometric properties of these systems, particularly in the water-rich region. We are now interested to extend our work to aqueous systems of small organic molecules, as we believe that the knowledge on physicochemical properties of aqueous solutions of small hydrophobic molecules can be useful to understand the properties of aqueous solutions of large hydrophobic molecules which are of biological and industrial interest. This particular piece of study involving the volumetric, viscometric as well as thermodynamic activation parameters for viscous flow of aqueous solutions of acetonitrile is an attempt to accomplish this purpose.

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Recent publications on volumetric properties of aqueous acetonitrile by Tamura *et al.* [10], Benson *et al.* [11, 12], Sakurai [13], Van Mears and Sumsen [14] and Acostal *et al.* [15], volumetric and viscometric properties by Cunningham *et al.* [16] and viscometric properties by Douheret and Moreau [17] and thermodynamic studies on this system by Nikolova [18] are worth mentioning in relation to our work.

2. Experimental

Acetonitrile was procured from Aldrich, with quoted purity, 99.9%. The substance was used without further purification, except that the liquid was kept over molecular sieves (4A) for at least two weeks prior to its use. Twice distilled water was used in the preparation of the solutions. An analytical balance of accuracy ±0.0001 g was used in density measurement. The solutions were prepared by weighing the masses of the components by the same balance. The density was measured by a 5 ml bicapillary pycnometer previously calibrated with redistilled water. An Ostwald U-tube viscometer with sufficiently long efflux time was used in viscosity measurement. The flow time was recorded by an electronic timer accurate up to ±0.01 s. For every measurement, a thermostatic water bath controlled to ±0.05 K was used. The average uncertainty in the measured density and viscosity was not more than $1.4 \times 10^{-1}\,\mathrm{kg\,m^{-3}}$ and $5.5 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively.

3. Results and discussion

The densities and viscosities of pure acetonitrile at different temperatures are listed in table 1 together with available literature values, for comparison, in which the agreement between the measured and literature values has been found to be quite satisfactory.

Densities and excess molar volumes of the system water + acetonitrile at temperatures, 303.15, 308.15, 313.15, 318.15 and 323.15 K, have been shown in table 2. The densities have been plotted against mole fraction of acetonitrile, x_2, in figure 1. The density decreases rather rapidly in the initial stage. However, the decrement still

Table 1. Densities, $\rho \times 10^{-3}$ ($\mathrm{kg\,m^{-3}}$), and viscosities, $\eta \times 10^{4}$ ($\mathrm{kg\,m^{-1}\,s^{-1}}$), of pure acetonitrile at different temperatures.

		Temperatures				
Compound	Properties	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
Acetonitrile	ρ	0.7716 (0.7715)[a,b] (0.771146)[c] (0.7725)[d]	0.7661 (0.7660)[b] (0.7681)[d]	0.7607 (0.7601)[a] (0.7626)[d]	0.7552	0.7496 (0.7495)[a] (0.7491)[f]
	η	3.322 (3.33)[b] (3.485)[d] (3.25)[e]	3.171 (3.19)[b] (3.285)[d]	3.042 (3.102)[d]	2.918	2.799 (2.729)[f]

[a] Reference [1027], [b] Reference [28], [c] Reference [26], [d] Reference [29], [e] Reference [30], [f] Reference [31].

Table 2. Densities, $\rho \times 10^{-3}$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$(m^3 mol^{-1}), of the system, water (x_1) + acetonitrile (x_2), at different temperatures.

T (K)	303.15		308.15		313.15		318.15		323.15	
x_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water (x_1) + acetonitrile (x_2)										
0.0000	0.9957	0.000	0.9941	0.000	0.9923	0.000	0.9903	0.000	0.9881	0.000
0.0498	0.9779	−0.246	0.9755	−0.244	0.9729	−0.242	0.9703	−0.244	0.9675	−0.245
0.0650	0.9729	−0.319	0.9702	−0.315	0.9675	−0.315	0.9648	−0.318	0.9620	−0.323
0.0840	0.9642	−0.351	0.9613	−0.347	0.9582	−0.342	0.9550	−0.339	0.9517	−0.338
0.1498	0.9386	−0.482	0.9350	−0.476	0.9314	−0.472	0.9278	−0.473	0.9241	−0.475
0.2534	0.9024	−0.557	0.8984	−0.558	0.8943	−0.557	0.8901	−0.558	0.8858	−0.561
0.3831	0.8663	−0.560	0.8618	−0.562	0.8573	−0.558	0.8527	−0.569	0.8478	−0.568
0.5071	0.8389	−0.497	0.8339	−0.493	0.8290	−0.491	0.8240	−0.491	0.8189	−0.493
0.6075	0.8205	−0.409	0.8155	−0.414	0.8105	−0.416	0.8054	−0.419	0.8001	−0.418
0.7039	0.8052	−0.295	0.8000	−0.296	0.7949	−0.299	0.7896	−0.297	0.7842	−0.297
0.8042	0.7922	−0.202	0.7869	−0.205	0.7815	−0.196	0.7761	−0.194	0.7706	−0.192
0.8940	0.7820	−0.108	0.7766	−0.110	0.7713	−0.111	0.7659	−0.114	0.7603	−0.110
1.0000	0.7716	0.000	0.7661	0.000	0.7607	0.000	0.7552	0.000	0.7496	0.000

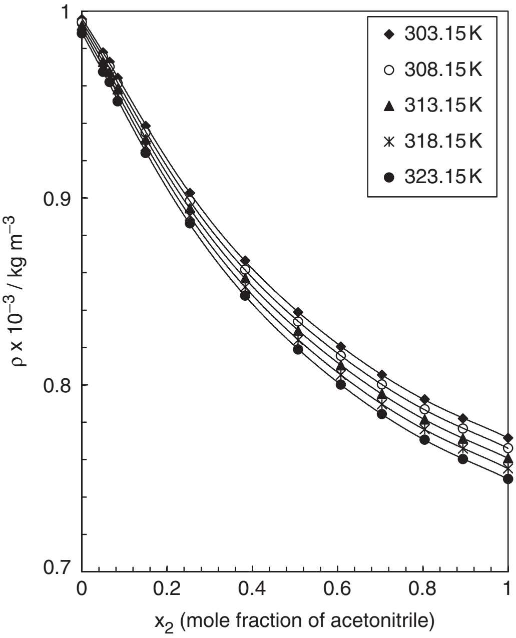

Figure 1. Variation of density, ρ, against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

continues until the pure state of acetonitrile is reached, but at a slower rate. Densities, ρ kg^{-1} m^{-3}, viscosities, η kg^{-1} m^{-1} s^{-1} and free energies of activation for viscous flow, $\Delta G^{\neq}$ kJ^{-1} mol^{-1}, have been fitted to the following polynomial equation of the form,

$$Y = \sum_{i=0}^{n} A_i x_2^i \qquad (1)$$

where, Y stands for each of the above properties. The coefficients, A_i, and the squares of the regression coefficients, r^2, are shown in table 6. The excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, have been calculated by the following equation,

$$V_{\mathrm{m}}^{\mathrm{E}} = \left[\frac{(x_1 M_1 + x_2 M_2)}{\rho} - \left\{\frac{(x_1 M_1)}{\rho_1} + \frac{(x_2 M_2)}{\rho_2}\right\}\right] \tag{2}$$

where, x_1, M_1 and ρ_1 are the mole fraction, molar mass and density, respectively, of pure water, x_2, M_2 and ρ_2 are the corresponding quantities for acetonitrile, and ρ is the density of the solution. Excess molar volumes have been plotted in figure 2 against mole fraction of acetonitrile, x_2. All the excess properties have been fitted to a Redlich–Kister polynomial equation of the form,

$$Y^{\mathrm{E}} = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{3}$$

where, Y^{E} stands for $V_{\mathrm{m}}^{\mathrm{E}}$, η^{E} and $\Delta G^{\neq \mathrm{E}}$. The coefficients of the equation, A_i, for each property and their standard deviations, σ, are listed in table 7.

An examination of $V_{\mathrm{m}}^{\mathrm{E}}$ *versus* x_2 curves shows that:

(a) $V_{\mathrm{m}}^{\mathrm{E}}$ values are negative for the whole range of composition showing minima at ~0.3 mole fraction of acetonitrile, the magnitude of which is reasonably large. Tamura *et al.* [10] determined the excess molar volume for this system at 30°C and

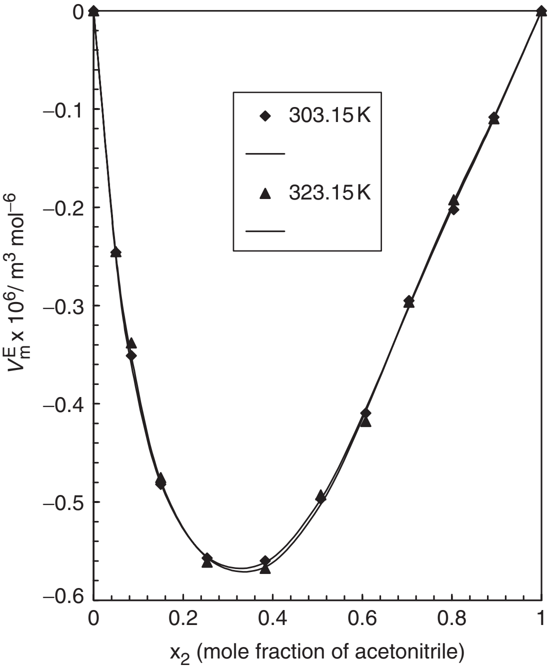

Figure 2. Variation of excess molar volume, $V_{\mathrm{m}}^{\mathrm{E}}$, against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

observed the minimum which corresponds almost quantitatively to ours in respect of magnitude and composition.

(b) The effect of temperature on V_m^E is found to be quite significant.

The negative V_m^E indicates that the factors responsible for contraction of volume on mixing of the components somehow outweigh the factors, if any, causing volume expansion. In this particular system the following factors may be regarded to be primarily responsible for volume contraction: (a) Specific interaction between the component molecules. (b) Hydrophobic hydration. (c) Weak physical forces, such as, dipole-dipole or dipole-induced dipole interaction, van der Waals forces, *etc*.

Viscosities and excess viscosities of the system, water + acetonitrile, are listed in table 3. Figure 3 shows the plots of viscosities against mole fraction of acetonitrile at different temperatures. Examination of this figure shows that, on addition of acetonitrile to water, η increases rapidly, which passes through a maximum at $x_2 = \sim 0.1$ and then declines quite rapidly, followed by a slower rate until the pure state of acetonitrile is reached. The effect of temperature on viscosity is seen to be quite significant particularly in the region at or around the maxima. However, the position of the maxima apparently remains unchanged irrespective of temperature. Our observed maximum at ~0.1 mole fraction of acetonitrile, is found to correspond well to that of Douheret and Moreau [17].

The rapid initial increase of viscosity can also be attributed to the three possible factors as discussed earlier to explain the negative V_m^E. Of these, the effect due to the hydrophobic hydration is thought to be the most prominent one for the rapid rise of viscosity. The phenomenon of hydrophobic hydration assumes that as acetonitrile is added to water, more and more clustered water is formed around acetonitrile in the form of cages, with its simultaneous destruction in a complex manner depending upon the concentrations of water cages, water and acetonitrile. As long as the rate of growth of these cages is larger than its rate of destruction, viscosity rises. At a composition where these two rates balance, the maximum occurs. Following the maximum, hydrophobic interaction becomes prominent. The interaction is supposed

Table 3. Experimental viscosities, η, and excess viscosities, η^E in $10^{-4}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, of the system, water ($x_1$) + acetonitrile ($x_2$), at different temperatures.

T (K)	303.15		308.15		313.15		318.15		323.15	
x_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
Water (x_1) + acetonitrile (x_2)										
0.0000	8.006	0.000	7.226	0.000	6.557	0.000	5.994	0.000	5.501	0.000
0.0498	8.684	1.021	7.729	0.793	6.998	0.687	6.350	0.567	5.802	0.483
0.0650	8.736	1.175	7.826	0.977	7.058	0.820	6.402	0.682	5.847	0.582
0.0840	8.728	1.292	7.812	1.069	7.062	0.915	6.409	0.767	5.863	0.666
0.1498	8.314	1.296	7.485	1.098	6.782	0.938	6.185	0.804	5.689	0.718
0.2534	7.376	0.970	6.700	0.835	6.120	0.723	5.635	0.640	5.199	0.564
0.3831	6.065	0.347	5.596	0.323	5.157	0.269	4.801	0.250	4.458	0.210
0.5071	5.088	−0.037	4.711	−0.048	4.410	−0.032	4.101	−0.060	3.857	−0.048
0.6075	4.532	−0.160	4.236	−0.145	3.978	−0.134	3.754	−0.117	3.550	−0.099
0.7039	4.039	−0.271	3.804	−0.243	3.598	−0.221	3.408	−0.203	3.239	−0.180
0.8042	3.676	−0.270	3.486	−0.240	3.318	−0.218	3.161	−0.199	3.012	−0.183
0.8940	3.442	−0.205	3.278	−0.168	3.132	−0.168	2.996	−0.153	2.870	−0.137
1.000	3.322	0.000	3.171	0.000	3.042	0.000	2.918	0.000	2.799	0.000

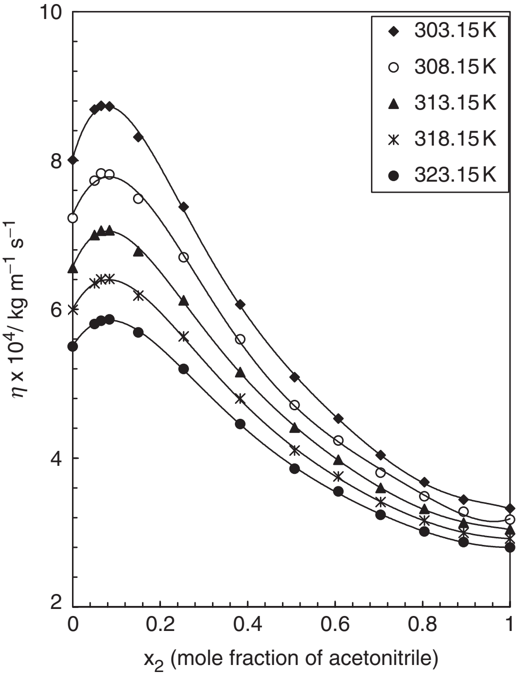

Figure 3. Variation of viscosity, η, against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

to occur by the overlap of the hydrate co-spheres, with the consequent release of water molecules from these co-spheres to the bulk. The process continues until the pure state of acetonitrile is reached. This approach appears to be satisfactory to explain viscosity behavior of aqueous acetonitrile (figures 3 and 4) and the post – maximum region.

There are convincing evidence to show that the compound acetonitrile is a hydrophobic solute. X-ray diffraction and infrared spectrum studies on acetonitrile – water mixtures by Takamuku *et al.* [19], Jarmoz *et al.* [20] and Bretie and Lan [21] suggested the presence of: (i) dipole-dipole interaction and formation of weak hydrogen bonds between acetonitrile and water molecules in the range, $0.2 < x_2 < 0.8$, and (ii) hydrogen bond net work of water stabilized by acetonitrile molecules at $x_2 < 0.2$. Wakisaka *et al.* [22–24] confirmed the formation of clusters in the acetonitrile + water mixtures by mass spectroscopy. The authors also claimed that the following types of acetonitrile-hydrate clusters, $H^+(CH_3CN)_1(H_2O)_{16\text{–}26}$, $H^+(CH_3CN)_2(H_2O)_{14\text{–}16}$ and $H^+(CH_3CN)_3(H_2O)_{12\text{–}22}$, are formed in the aqueous solutions of acetonitrile. All these studies above provide unambiguous support of hydrophobic hydration of acetonitrile molecule in the water-rich region. Also, large positive excess enthalpy, *i.e.*, an endothermic mixing of acetonitrile with water suggests weak hydrophilic bond interaction of acetonitrile [25].

Excess viscosity, η^E, defined as the difference between the measured viscosity, η, and the ideal viscosity, η_{id}, of the solutions, can be expressed as,

$$\eta^E = \eta - \eta_{id} \tag{4}$$

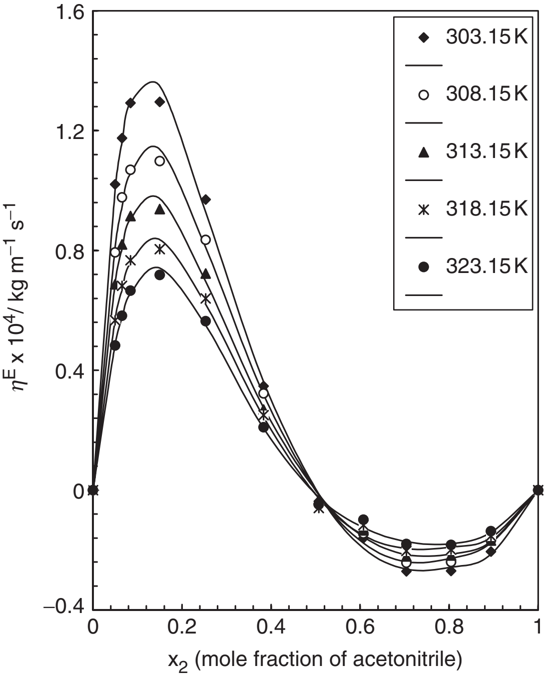

Figure 4. Variation of excess viscosity, η^E, against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

Using Eyring's approach of viscosity as a rate process [32], η_{id} can be represented as,

$$\eta_{id} = \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{5}$$

By putting the value of η_{id} from equation (5) to equation (4),

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{6}$$

Figure 4 represents the variation of excess viscosities of the system, water + acetonitrile as a function of mole fraction of acetonitrile at different temperatures. Examination of the curves shows that, the addition of acetonitrile to water increases the excess viscosity sharply, which passes through a maximum and then declines quite rapidly up to about 0.4 mole fraction of acetonitrile. Following this composition the rate of decrease becomes smaller and smaller, exhibiting minima at ~0.7 mole fraction of acetonitrile. It is interesting to notice that both positive and negative excess viscosities, η^E, are observed for this system, although the magnitude of the positive excess viscosities is far more greater than that of the negative values. The deviations of the observed viscosities from their ideal values, which are large in magnitude, especially in the water-rich region, indicate that the system is highly non-ideal. The large excess viscosities in the water-rich region may be accounted for by the effects, such as, (i) hydrophilic, (ii) hydrophobic and (iii) dipolar interactions, as discussed in connection with V_m^E and viscosity behaviour of this system. We observed similar type of negative η^E for aqueous systems of 2-propanol and *t*-butanol in the solute-rich region [2].

The negative excess viscosities in this region may be due to the formation of species having such structural features that render them to flow more easily.

Enthalpies of activation, $\Delta H^{\neq}$, and entropies of activation, $\Delta S^{\neq}$, for viscous flow have been determined by using the following equation,

$$\ln\left(\frac{\eta V_m}{hN}\right) = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R} \tag{7}$$

From the slopes and intercepts of the above equation, obtained by the least squares method, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are calculated.

The $\Delta G^{\neq}$ values are obtained by using the equation,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{8}$$

Excess thermodynamic properties have been calculated by the following equation,

$$Y^{\mathrm{E}} = Y - (x_1 Y_1 + x_2 Y_2) \tag{9}$$

where, all the terms have their usual significances.

Table 4 lists $\Delta H^{\neq}$, $\Delta H^{\neq \mathrm{E}}$, $\Delta S^{\neq}$ and $\Delta S^{\neq \mathrm{E}}$ values for the system, water + acetonitrile, for different molar ratios. Figure 5 shows the plots of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as a function of mole fraction of acetonitrile. The curves show that, on addition of acetonitrile to water, both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ rise up sharply, pass through maxima in the water-rich region and then decline monotonously. However, the system shows both positive and negative $\Delta S^{\neq}$ values.

Table 4 shows both positive and negative values of $\Delta H^{\neq \mathrm{E}}$ and $\Delta S^{\neq \mathrm{E}}$ for the system. The negative values of $\Delta H^{\neq \mathrm{E}}$ persist over a region of $0.5 < x_2 < 1$, but, negative $\Delta S^{\neq \mathrm{E}}$ extend over a large region of composition. The clustered structures of water are assumed to be thermally much less stable than the normal water structure [33, 34]. So, in the activation process for viscous flow these structures are more easily broken down resulting in an increase of the overall degree of disorder. This explains positive $\Delta S^{\neq \mathrm{E}}$ values in water-rich region, where clustered water is predominantly formed. The negative values of $\Delta S^{\neq \mathrm{E}}$ indicate that the species formed in the activated state are more ordered than what is to be expected.

Table 5 lists the $\Delta G^{\neq}$ and $\Delta G^{\neq \mathrm{E}}$ values of the system for different molar ratios at different temperatures. Figure 6 represents the plots of $\Delta G^{\neq}$ as a function of mole fraction of acetonitrile at different temperatures. The figure shows that: (i) addition of

Table 4. Enthalpies, $\Delta H^{\neq}$ (kJ mol^{-1}), excess enthalpies, $\Delta H^{\neq \mathrm{E}}$ (kJ mol^{-1}), entropies, $\Delta S^{\neq}$ (J mol^{-1} K^{-1}), and excess entropies, $\Delta S^{\neq \mathrm{E}}$ (J mol^{-1} K^{-1}) of activation for viscous flow for the system, water (x_1) + acetonitrile (x_2).

x_2	$\Delta H^{\neq}$	$\Delta H^{\neq \mathrm{E}}$	$\Delta S^{\neq}$	$\Delta S^{\neq \mathrm{E}}$	x_2	$\Delta H^{\neq}$	$\Delta H^{\neq \mathrm{E}}$	$\Delta S^{\neq}$	$\Delta S^{\neq \mathrm{E}}$
Water (x_1) + acetonitrile (x_2)									
0.0000	14.967	0.000	19.532	0.000	0.5071	10.307	−0.008	2.342	−0.944
0.0498	15.916	1.408	21.349	3.412	0.6075	8.907	−0.468	−2.118	−2.188
0.0650	15.904	1.535	21.042	3.592	0.7039	7.912	−0.575	−5.116	−2.147
0.0840	15.665	1.471	20.010	3.168	0.8042	6.961	−0.603	−8.206	−1.974
0.1498	14.846	1.258	16.877	2.144	0.8940	6.246	−0.491	−10.580	−1.471
0.2534	13.467	0.833	12.116	0.702	1.0000	5.761	0.000	−12.505	0.000
0.3831	11.653	0.210	6.419	−0.844					

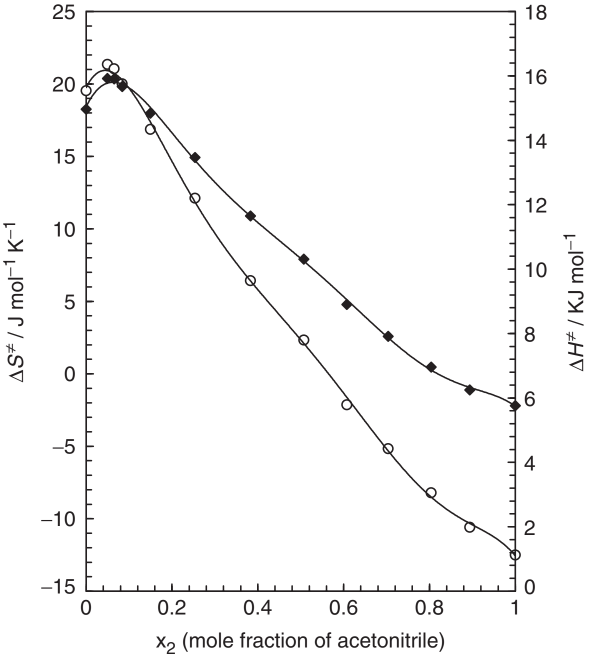

Figure 5. Variation of enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, of activation for viscous flow against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

Table 5. Free energy of activation, $\Delta G^{\neq}$ (kJ mol^{-1}), and excess free energy of activation, $\Delta G^{\neq}$(kJ mol^{-1}), for viscous flow of the system, water (x_1) + acetonitrile (x_2) at different temperatures.

T (K)	303.15		308.15		313.15		318.15		323.15	
x_2	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$
water (x_1) + acetonitrile (x_2)										
0.0000	9.046	0.000	8.948	0.000	8.851	0.000	8.753	0.000	8.655	0.000
0.0498	9.444	0.373	9.338	0.356	9.231	0.339	9.124	0.322	9.017	0.305
0.0650	9.525	0.446	9.420	0.428	9.315	0.410	9.210	0.392	9.104	0.374
0.0840	9.599	0.511	9.499	0.495	9.399	0.479	9.299	0.463	9.199	0.447
0.1498	9.729	0.608	9.645	0.597	9.561	0.586	9.476	0.575	9.392	0.565
0.2534	9.794	0.620	9.733	0.616	9.672	0.612	9.612	0.609	9.552	0.606
0.3831	9.707	0.465	9.675	0.470	9.643	0.474	9.611	0.479	9.579	0.483
0.5071	9.597	0.294	9.586	0.300	9.574	0.304	9.562	0.309	9.550	0.314
0.6075	9.549	0.196	9.560	0.207	9.570	0.217	9.581	0.228	9.591	0.239
0.7039	9.478	0.076	9.504	0.086	9.523	0.097	9.555	0.108	9.581	0.118
0.8042	9.448	−0.005	9.489	0.005	9.530	0.015	9.571	0.025	9.612	0.034
0.8940	9.453	−0.045	9.506	−0.038	9.559	−0.031	9.612	−0.023	9.665	−0.016
1.000	9.552	0.000	9.615	0.000	9.677	0.000	9.740	0.000	9.802	0.000

acetonitrile to water increases the free energy quite rapidly; (ii) the presence of maximum with some degree of distinction at lower temperatures and (iii) the curves at all temperatures cross over at ~0.55 mole fraction of acetonitrile.

Figure 7 shows the variation of excess free energy of activation for viscous flow, $\Delta G^{\neq E}$, against the mole fraction acetonitrile at different temperatures.

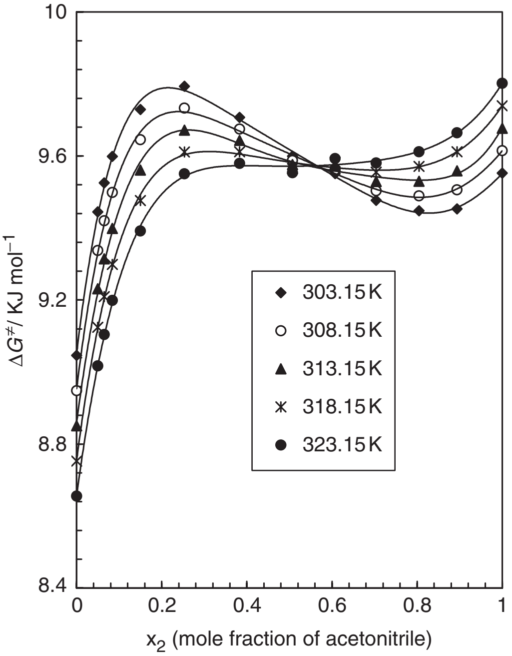

Figure 6. Variation of free energy of activation for viscous flow, $\Delta G^{\neq}$, against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

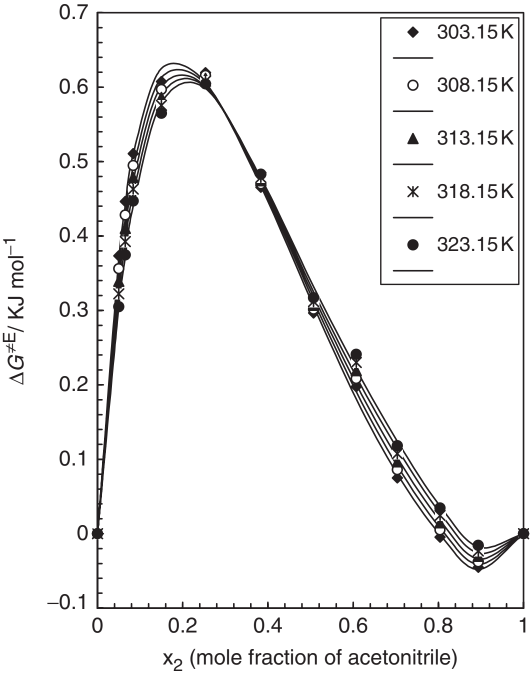

Figure 7. Variation of excess free energy of activation for viscous flow, $\Delta G^{\neq E}$, against mole fraction of acetonitrile for the system, water (x_1) + acetonitrile (x_2).

Table 6. Coefficients, A_i, of equation (1) expressing density, $\rho \times 10^{-3}$ (kg m^{-3}), coefficients of viscosity, $\eta \times 10^{4}$ (kg m^{-1} s^{-1}), free energy of activation, $\Delta G^{\neq}$ (kJ mol^{-1}) and the squares of the regression coefficients, r^2, for the system, water + acetonitrile.

Properties	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
ρ	303.15	0.9960	−0.3434	−0.5696	2.8383	−4.6940	3.6350	−1.0908	>0.9999
	308.15	0.9944	−0.3611	−0.5355	2.8144	−4.6865	3.6183	−1.0779	>0.9999
	313.15	0.9926	−0.3824	−0.4355	2.5049	−4.1719	3.2001	−0.9471	>0.9999
	318.15	0.9906	−0.3996	−0.3682	2.3176	−3.8934	3.0034	−0.8952	>0.9999
	323.15	0.9885	−0.4160	−0.2995	2.1066	−3.5373	2.7074	−0.8001	>0.9999
η	303.15	8.0290	20.211	−179.07	495.52	−689.93	482.06	−133.51	0.9998
	308.15	7.2720	13.52	−106.14	221.51	−201.21	68.233	–	0.9995
	313.15	6.5681	13.637	−117.37	310.45	−416.09	218.88	−76.041	0.9999
	318.15	6.0036	10.811	−89.565	220.34	−273.38	171.75	−43.053	0.9998
	323.15	5.5042	9.3835	−76.105	181.79	−217.09	130.10	−30.79	0.9999
$\Delta G^{\neq}$	303.15	9.0526	9.8791	−49.402	119.35	−156.92	105.79	−28.19	0.9968
	308.15	8.9537	9.5931	−45.34	105.45	−133.95	87.509	−22.604	0.9976
	313.15	8.8614	8.8394	−35.226	64.144	−56.069	19.129	–	0.9976
	318.15	8.7561	9.0211	−37.215	77.652	−88	50.957	−11.431	0.9989
	323.15	8.6573	8.7351	−33.152	63.753	−65.027	32.68	−5.8441	0.9992

Table 7. Coefficients, A_i of Redlich–Kister equation, equation (3), expressing excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}} \times 10^{6}$(m^3 mol^{-1}) excess viscosity $\eta^{\mathrm{E}} \times 10^{-4}$ (kg m^{-1} s^{-1}), excess free energy of activation, $\Delta G^{\neq \mathrm{E}}$ (kJ mol^{-1}) and standard deviation, σ, for the system, water + acetonitrile.

Properties	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	σ
$V_{\mathrm{m}}^{\mathrm{E}}$	303.15	−2.0104	1.4909	−0.1543	0.2336	−1.6657	0.9801	0.00900
	308.15	−2.0108	1.5093	−0.2135	0.0329	−1.5186	1.1735	0.00962
	313.15	−2.0100	1.4171	−0.1170	0.5721	−1.6485	0.5070	0.01058
	318.15	−2.0313	1.5104	−0.0101	0.2177	−1.7817	0.8056	0.01319
	323.15	−2.0307	1.5109	−0.0362	0.2674	−1.7229	0.8328	0.01470
η^{E}	303.15	0.0177	−4.8554	5.3618	−4.5686	7.0972	−7.4989	0.03974
	308.15	−0.0039	−4.3311	4.9342	−4.2343	5.1484	−4.6509	0.03400
	313.15	−0.0089	−3.7727	4.2083	−3.6737	4.1142	−4.0753	0.02509
	318.15	−0.0593	−3.4678	4.2878	−2.9797	2.2350	−3.1417	0.02889
	323.15	−0.0563	−2.8063	3.7952	−4.4428	1.8772	−0.4045	0.02128
$\Delta G^{\neq \mathrm{E}}$	303.15	1.2614	−2.6156	1.5201	−1.1609	1.3797	−2.0183	0.01390
	308.15	1.2890	−2.5498	1.5603	−1.2484	1.1188	−1.6358	0.01354
	313.15	1.3098	−2.4793	1.6505	−1.3358	0.7923	−1.2722	0.01348
	318.15	1.3354	−2.4116	1.7189	−1.4400	0.5032	−0.8594	0.01387
	323.15	1.3597	−2.3316	1.7801	−1.6468	0.2245	−0.3361	0.01426

Examination of the figure at a particular temperature shows that: (i) positive $\Delta G^{\neq \mathrm{E}}$ values are observed in the water-rich region which are moderately large, (ii) the presence of well-defined maximum in water-rich region and very small negative $\Delta G^{\neq \mathrm{E}}$ values in the highly rich region of acetonitrile with minimum at ~0.9 mole fraction of acetonitrile. The positive $\Delta G^{\neq \mathrm{E}}$ implies that the species formed in the region in question have to surmount a larger energy barrier than that of ideal solutions for the activation of viscous flow, and hence, encounter a large resistance to flow. On the other hand, negative $\Delta G^{\neq \mathrm{E}}$ indicates the opposite effect, and hence, the species encounter less resistance to flow in the specified concentration range.

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References

[1] M.A. Saleh, S. Akhtar, M. Nessa, M.S. Uddin, M.M.H. Bhuiyan. *Phys. Chem. Liq.*, **36**, 53 (1998).
[2] S. Akhtar, M.A. Saleh, M.M.H. Bhuiyan, M.S. Uddin, B. Sultana, M. Nessa. *Phys. Chem. Liq.*, **37**, 215 (1999).
[3] S. Akhtar, M.A. Saleh, M. Shamsuddin Ahmed, M.M.H. Bhuiyan, M.S. Uddin, B. Sultana, M. Nessa. *Phys. Chem. Liq.*, **41**, 475 (2003).
[4] M.A. Saleh, S. Begum, S.K. Begum, B.A. Begum. *Phys. Chem. Liq.*, **37**, 785 (1999).
[5] M.A. Saleh, S. Akhtar, A.R. Khan. *Phys. Chem. Liq.*, **38**, 137 (2000).
[6] M.A. Saleh, S. Akhtar, A.R. Khan. *Phys. Chem. Liq.*, **39**, 85 (2001).
[7] M.A. Saleh, M. Shamsuddin Ahmed, M.S. Islam. *Phys. Chem. Liq.*, **40**, 477 (2002).
[8] M.A. Saleh, S. Akhtar, M. Shamsuddin Ahmed. *Phys. Chem. Liq.*, **42**, 103 (2004).
[9] M.A. Saleh, S. Akhtar, M. Shamsuddin Ahmed. *J. Mol. Liq.*, **116**, 147 (2005).
[10] K. Tamura, M. Nakamura, S. Murakami. *J. Solution Chem.*, **26**, 1199 (1997).
[11] G.C. Benson, Y.P. Handa. *J. Solution Chem.*, **10**, 291 (1981).
[12] G.C. Benson, P.J. D'Arcy, Y.P. Handa. *Thermochim. Acta.*, **46**, 295 (1981).
[13] M. Sakurai. *J. Chem. Eng. Data*, **37**, 358 (1992).
[14] N. Van Mears, G. Sumsen. *J. Solution Chem.*, **22**, 427 (1993).
[15] J. Acostal, Al. Alberto, R. Eva, S. Ana. *Fluid Phase Equilib.*, **201**, 102 (2002).
[16] G.P. Cunnigham, G.A. Vidulich, R.L. Kay. *J. Chem. Eng. Data*, **12**, 336 (1967).
[17] G. Douheret, C. Moreau. *Thermochim. Acta*, **13**, 385 (1975).
[18] P.V. Nikolova, S.J.B. Duff, P. Westh, C.A. Haynes, Y. Kasahara, K. Nishikawa, Y. Koga. *Can. J. Chem.*, **78**, 1553 (2000).
[19] T. Takamuku, M. Tabata, A. Yamaguchi, J. Nishimoto, M. Kumamoto, H. Wakita, T. Yamaguchi. *J. Phys. Chem. B*, **102**, 8880 (1998).
[20] D. Jarmoz, J. Stangret, J. Lingdren. *J. Am. Chem. Soc.*, **115**, 6165 (1993).
[21] J. Bretie, Z. Lan. *J. Phys. Chem. B.*, **101**, 4111 (1997).
[22] A. Wakisaka, H. Abdoul-Carime, Y. Yamamoto, Y. Kiyozumi. *J. Chem. Soc. Faraday Trans.*, **94**, 369 (1998).
[23] A. Wakisaka, Y. Shimuzu, N. Nishi, K. Tokumaru, H. Sakuragi. *J. Chem. Soc. Faraday Trans.*, **88**, 1129 (1992).
[24] A. Wakisaka, S. Takahashi, N. Nishi. *J. Chem. Soc. Faraday Trans.*, **91**, 4063 (1995).
[25] K.W. Morcom, R.W. Smith. *J. Chem. Thermodyn.*, **1**, 503 (1969).
[26] M.I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi. *J. Chem. Eng. Data*, **41**, 1307 (1996).
[27] L. Jannelli, M. Panshini, R. Jalenti. *J. Chem. Eng. Data*, **29**, 263 (1984).
[28] R. Abraham, M. Abdulkhadar, C.V. Ashokan. *J. Chem. Thermodyn.*, **32**, 1 (2000).
[29] S. Paez, M. Contreas. *J. Chem. Eng. Data*, **34**, 455 (1989).
[30] G. Ritzoulis. *Can. J. Chem.*, **67**, 1105 (1989).
[31] G.S. Gokavi, J.R. Raju, T.M. Aminabhavi, R.H. Balundgi, M.V. Muddapur. *J. Chem. Eng. Data*, **31**, 15 (1986).
[32] S. Glasstone, K.J. Laidler, H. Eyring. *The Theory of Rate Process*, p. 477, McGraw-Hill Book Company, Inc., New York (1941).
[33] F. Franks. *Water*, p. 41, The Royal Society of Chemistry, London (1985).
[34] A.K. Covington, P. Jones. *Hydrogen-Bonded Solvent Systems*, p. 221, Taylor and Francis Ltd., London (1968).