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Density, viscosity and thermodynamics for viscous flow of water + 1,2-dimethoxyethane

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Densities and viscosities for the system, water (W) + 1,2-dimethoxyethane (DME), have been determined for the entire range of composition at temperatures, ranging from 303.15 to 323.15 K. Density, viscosity, enthalpy, entropy and free energy of activation for viscous flow have been plotted against the mole fraction of DME. Excess molar volume, V_m^E , excess viscosity, η^E , and excess free energy of activation, ΔG^{zE} , have also been plotted against the mole fraction of DME. Most of these properties have been fitted to appropriate polynomial equations. Results have been explained in terms of such factors as, size difference of component molecules, hydrophilic effect, hydrophobic hydration and dipole-dipole interaction.

Keywords: Density; Viscosity; Thermodynamic activation parameters; Hydrophobic hydration; Dimethoxyethane

1. Introduction

This is a part of our ongoing project on studies of volumetric and viscometric properties of aqueous solutions of organic compounds with particular reference to hydrophobic solutes. In the recent past we have reported the volumetric, viscometric and thermodynamic properties for viscous flow of aqueous solutions of hydrophobic solutes, such as, alcohols [1–3], diols [4,5], amines [6,7], diamines [8–10], amides [11] etc. It has been observed from these studies that hydrophobic hydration strongly influences 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 glycol ethers. The present study is an attempt to accomplish this interest. Recent publications on volumetric properties of aqueous DME by Douheret *et al.* [12] and Marchetti *et al.* [13], volumetric and viscometric properties by Wallace and Mathews [14] and Das *et al.* [15], viscometric properties by Ramanamurti *et al.* [16], Pal *et al.* [17] and Renard and

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Justice [18] are directly linked to our work. A few important papers [19–23] dealing with ultrasonic studies, molecular dynamics simulations and NMR spectrophotometric analysis of aqueous solutions of 1,2-dimethoxyethane are also found to be relevant in explaining our observations. In its novel approach, the article focuses particular attention to the phenomena of hydrophobic hydration and hydrophobic interaction for explaining the results of viscosity and related properties, although these phenomena were not considered seriously in the previous studies of this system. The ultimate objective of our study is to collect data on as many systems as possible and attempt to develop a model that can satisfactorily explain the volumetric and viscometric properties of aqueous solutions of both biologically and industrially important hydrophobic solutes.

2. Experimental

1,2-Dimethoxyethane (DME) was procured from Merck-Schuchardt, with quoted purity >99%. The substance was used without further purification, except that the liquid was kept over molecular sieves (4A) for at least 2 weeks prior to its use. Redistilled 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 mole fraction was accurate up to the fourth place of decimal. The density was measured by a 5 mL bicapillary pycnometer previously calibrated with doubly distilled water. An Ostwald U-tube viscometer with sufficiently long efflux time was used in viscosity measurement, so that no kinetic energy correction was necessary. 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 0.14 kg m^{-3} and $5.5 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$, respectively.

3. Results and discussion

DME is one of the simplest amphiphilic species, which is only slightly polar ($\mu = 1.17$ D) and quite miscible with water, even if very consistent hydrophobic hydration effects are present [22]. Recent studies on volumetric properties [12,13], volumetric and viscometric properties [14–16], viscometric properties [17,18], ultrasonic studies [19], computer simulations [21–23] and NMR studies [24] of the aqueous solutions of DME unambiguously indicate that DME is a hydrophobic solute. DME has its density 856.8 kg m^{-3} at 303.15 K and boiling point 85°C . All the low values of polarity, density and boiling point indicate that DME is essentially a non-associated compound.

The densities and viscosities of pure DME at different temperatures are shown in table 1. The corresponding literature values have been shown alongside our data as far as available. The agreement between the data has been found to be quite satisfactory.

Densities of the system, W + DME, have been represented in table 2, and plotted against the mole fraction of DME in figure 1, at temperatures ranging from 303.15 to 323.15 K. Densities, ρ (kg m^{-3}), viscosities, η ($\text{kg m}^{-1} \text{ s}^{-1}$) and free energies of activation

Table 1. Densities, $\rho \times 10^{-3}$ (kg m^{-3}) and viscosities, $\eta \times 10^4$ ($\text{kg m}^{-1} \text{s}^{-1}$), of pure 1,2-dimethoxyethane (DME) at different temperatures.

Temperature (K)	DME	
	ρ	η
298.15	0.8622	4.237
	(0.8621) ^a	(4.20) ^b
	(0.8626) ^b	(4.24) ⁿ
	(0.86120) ^{c,d}	(4.236) ^o
	(0.8613) ^{e,f}	(4.32) ^p
303.15	(0.86370) ^g	
	0.8568	4.031
	(0.85718) ^h	(4.21) ^c
	(0.856097) ^{i,j}	(3.94) ^m
308.15	(0.8557) ^m	
	0.8512	3.812
	(0.850680) ^{i,j}	(3.85) ⁿ
	(0.85001) ^k	(3.847) ^o
313.15	(0.85129) ⁿ	
	0.8455	3.628
	(0.84629) ^h	(3.76) ^c
	(0.845124) ⁱ	(3.55) ^m
318.15	(0.8446) ^m	
	0.8400	3.444
	(0.839575) ^{i,j}	(3.50) ⁿ
	(0.8392) ^l	(3.496) ^o
323.15	(0.84076) ⁿ	(3.38) ^m
	0.8344	3.284
	(0.83499) ^h	(3.22) ^m
	(0.833956) ^{i,j}	
	(0.833) ^m	

References ^a[30]; ^b[17]; ^c[18]; ^d[32]; ^e[33]; ^f[29]; ^g[36]; ^h[28]; ⁱ[13]; ^j[26]; ^k[35]; ^l[31]; ^m[27]; ⁿ[15]; ^o[34]; ^p[14].

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

Temperature (K)	303.15		308.15		313.15		318.15		323.15	
	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water (x_1) + 1,2-dimethoxyethane (x_2)										
0.0000	0.9957	0.000	0.9941	0.000	0.9923	0.000	0.9903	0.000	0.9881	0.000
0.0471	0.9877	-0.517	0.9852	-0.522	0.9824	-0.527	0.9791	-0.520	0.9767	-0.538
0.0951	0.9803	-1.014	0.9765	-1.008	0.9726	-1.005	0.9687	-1.000	0.9647	-0.999
0.1421	0.9709	-1.360	0.9666	-1.354	0.9623	-1.354	0.9579	-1.348	0.9534	-1.346
0.1877	0.9581	-1.511	0.9534	-1.502	0.9487	-1.500	0.9440	-1.494	0.9403	-1.491
0.2322	0.9489	-1.685	0.9442	-1.686	0.9392	-1.682	0.9344	-1.681	0.9295	-1.683
0.2770	0.9382	-1.726	0.9332	-1.726	0.9283	-1.730	0.9233	-1.727	0.9183	-1.731
0.3598	0.9212	-1.709	0.9160	-1.705	0.9108	-1.710	0.9057	-1.712	0.9007	-1.728
0.4455	0.9070	-1.612	0.9017	-1.612	0.8965	-1.626	0.8913	-1.630	0.8862	-1.650
0.5389	0.8950	-1.480	0.8897	-1.488	0.8845	-1.513	0.8793	-1.525	0.8735	-1.540
0.6952	0.8787	-1.088	0.8733	-1.098	0.8678	-1.111	0.8625	-1.124	0.8571	-1.139
0.8030	0.8694	-0.706	0.8639	-0.712	0.8583	0.718	0.8527	-0.705	0.8472	-0.713
0.9001	0.8627	-0.369	0.8573	-0.389	0.8518	-0.411	0.8462	-0.398	0.8404	-0.378
1.0000	0.8568	0.000	0.8512	0.000	0.8455	0.000	0.8400	0.000	0.8344	0.000

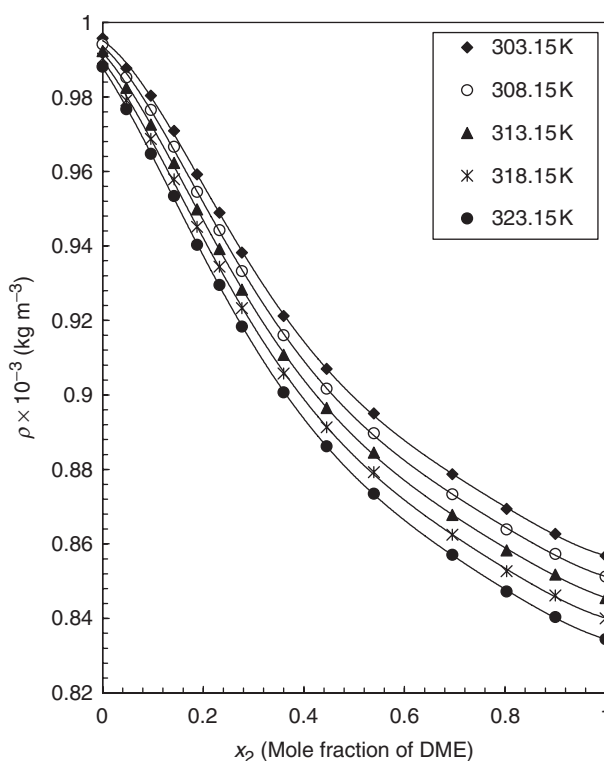


Figure 1. Variation of density, ρ , against mole fraction of DME for the system water (x_1) + DME (x_2) at different temperatures.

for viscous flow, ΔG^\ddagger (kJ mol^{-1}), have been fitted to the following polynomial equation of the form:

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

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. In all cases, extremely large values of r^2 have been found, indicating the highly satisfactory fitting of the data.

Figure 1 shows the variation of densities of the system, W + DME, for different molar ratios at different temperatures. On addition of DME to water, densities decrease quite rapidly in the water-rich region. The rate, however, decreases with increasing concentration of DME up to its pure state.

The excess molar volumes, V_m^E , have been calculated by the following equation:

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

where x_1 , M_1 and ρ_1 , respectively are the mole fraction, molar mass and density of the pure water, and x_2 , M_2 , ρ_2 are the corresponding quantities for DME. ρ is the density of

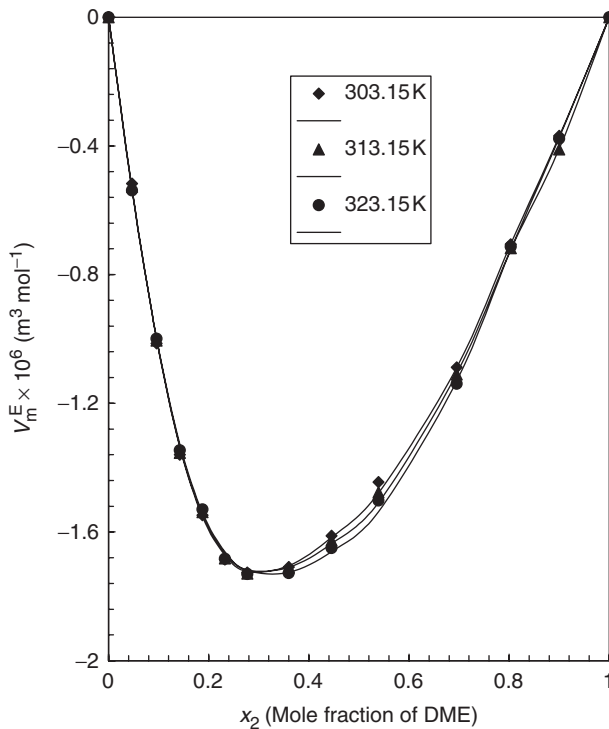


Figure 2. Variation of excess molar volume, V_m^E , against mole fraction of DME for the system water (x_1) + DME (x_2) at different temperatures.

the solution. Excess molar volumes have been plotted in figure 2 against mole fraction of DME, x_2 .

The excess properties have been fitted to a Redlich–Kister polynomial equation of the form,

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

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

An examination of figure 2 reveals that:

- (i) The excess molar volumes, V_m^E , are negative and large for the whole range of composition.
- (ii) Each of the curves shows a minimum at ~ 0.3 mol fraction of DME. The magnitude of the minimum and the composition at which it occurs correspond well with those calculated by using the density data of Das *et al.* [15].
- (iii) The effect of temperature on V_m^E is not generally significant for the whole range of composition.

The large negative values of V_m^E indicate that the factors responsible for contraction of volume on mixing of the components far outweigh the factors causing volume expansion.

Table 3. Viscosities, η , and excess viscosities, η^E in $10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$, of the system water (x_1) + 1,2-dimethoxyethane (x_2), at different temperatures.

Temperature (K)	303.15		308.15		313.15		318.15		323.15	
	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
x^2										
water (x_1) + 1,2-dimethoxyethane (x_2)										
0.0000	8.006	0.000	7.226	0.000	6.557	0.000	5.994	0.000	5.501	0.000
0.0471	13.442	5.691	11.738	4.726	10.354	3.977	9.228	3.388	8.291	2.922
0.0951	17.251	9.755	14.868	8.072	13.025	6.830	11.431	5.747	10.130	4.894
0.1421	18.372	11.110	15.826	9.228	13.766	7.738	12.080	6.540	10.704	5.592
0.1877	17.262	10.223	14.932	8.523	13.079	7.211	11.571	6.169	10.342	5.349
0.2322	15.617	8.790	13.753	7.524	12.108	6.393	10.696	5.426	9.565	4.685
0.2770	13.732	7.112	12.139	6.086	10.808	5.242	9.692	4.551	8.719	3.950
0.3598	10.927	4.672	9.800	4.365	8.860	3.561	8.048	3.137	7.336	2.767
0.4455	8.759	2.862	7.944	2.509	7.267	2.230	6.672	1.989	6.155	1.783
0.5389	7.129	1.598	6.553	1.434	6.061	1.295	5.616	1.169	5.232	1.066
0.6952	5.462	0.493	5.103	0.470	4.784	0.439	4.497	0.419	4.226	0.383
0.8030	4.759	0.144	4.480	0.156	4.217	0.140	3.986	0.145	3.769	0.134
0.9001	4.317	0.000	4.079	0.016	3.865	0.016	3.670	0.030	3.479	0.021
1.0000	4.031	0.000	3.812	0.000	3.628	0.000	3.444	0.000	3.284	0.000

For this particular system the following factors may be regarded as primarily responsible for volume contraction: (a) Hydrophilic interaction between the component molecules. (b) Geometric factors, arising out of large difference in the molar volumes (molar volumes are 18.098 and 105.182 cm^3 at 303.15 K for W and DME, respectively) and free volume of the components in the liquid state. (c) Weak physical forces, such as, dipole–dipole or dipole-induced dipole interactions and van der Waals forces. (d) Hydrophobic hydration, by virtue of which water molecules around the methyl and methylene groups of DME are so arranged as to form a cage like structure, inside which DME is lodged. This is thought to be the most important factor for volume contraction for this system.

Viscosities of the system, W + DME, are listed in table 3. Figure 3 shows the plots of viscosities against mole fraction of DME at different temperatures. The figure shows that addition of DME into water increases the viscosity rapidly, which passes through a maximum and then declines. The decline, however, continues at a slower rate up to the pure state of DME. The effect of temperature on viscosity is seen to be quite significant, particularly in the region at or around the maximum viscosity. The position of the maximum apparently remains unchanged with the variation of temperature. We observed that the maximum occurred at ~ 0.15 mole fraction of DME, which is quite in conformity with the observation of Das *et al.* [15], Ramanamurti *et al.* [16] and Pal *et al.* [17].

We wish to consider the factors (a) to (d), discussed earlier in connection with volume contraction, also as the possible reasons for the rapid increase in viscosity in water-rich region. Of these factors, we envisage that hydrophobic hydration is the most prominent one. The fairly sharp fall of viscosity following the maximum, and its continuation rather at a slower rate, can be explained by a phenomenon what is called as the hydrophobic interaction.

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

$$\eta^E = \eta - \eta_{id} \quad (4)$$

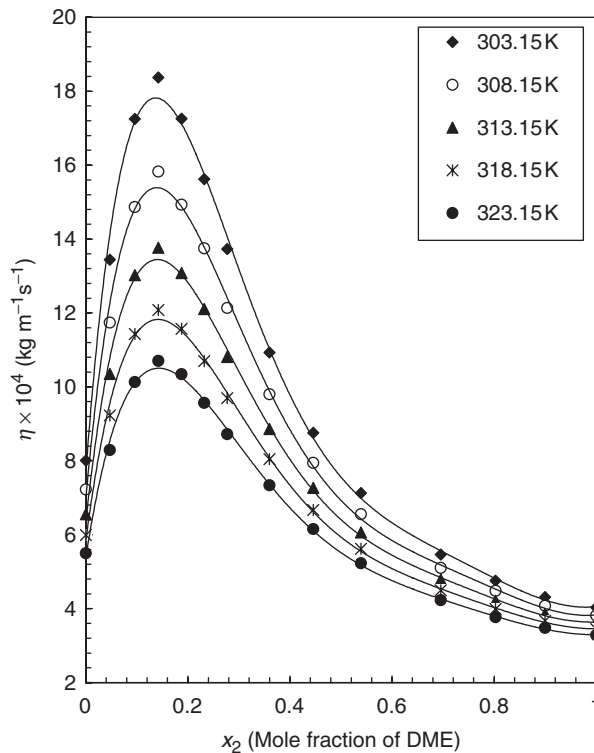


Figure 3. Variation of viscosity, η , against mole fraction of DME for the system water (x_1) + DME (x_2) at different temperatures.

Using Eyring's approach of viscosity as a rate process [25], η_{id} can be represented as,

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

where η_1 and η_2 are the viscosities of the pure components and x_1 and x_2 are the mole fractions of the corresponding components.

Putting the value of η_{id} from equation (5), equation (4) can be written as,

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2). \quad (6)$$

The η^E values have been listed in table 3 and plotted in figure 4 for the system as a function of mole fraction of DME at different temperatures.

The excess viscosities have been found to be positive and large in magnitude, indicating that the solutions are highly non-ideal at all compositions. The characteristics of the η^E curves are found to resemble closely to those of η curves, and therefore, can be explained by the same reasonings as those put forward earlier to explain the viscosity curves.

Enthalpies of activation, ΔH^\ddagger , and entropies of activation, ΔS^\ddagger , for viscous flow are related to the measured η and V_m by the following equation:

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

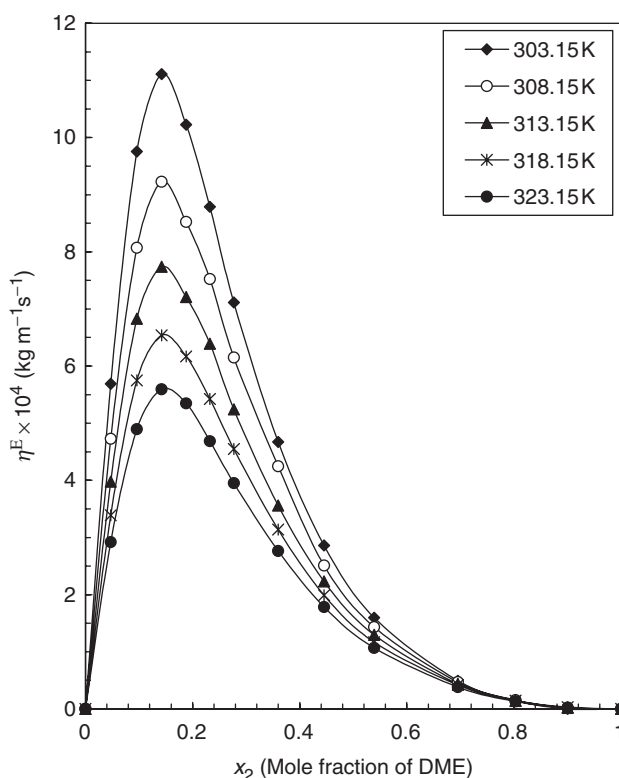


Figure 4. Variation of excess viscosity, η^E , against mole fraction of DME for the system water (x_1) + DME (x_2) at different temperatures.

From the slopes and intercepts of $\ln(\eta V_m/hN)$ versus $1/T$ obtained by the least squares method, ΔH^\ddagger and ΔS^\ddagger have been calculated.

The ΔG^\ddagger values are obtained by using the following equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger. \quad (8)$$

Excess thermodynamic quantities have been calculated by the equation,

$$Y^E = Y - (x_1 Y_1 + x_2 Y_2). \quad (9)$$

The significances of Y and Y^E have been described earlier. Y_1 and Y_2 are the properties of the pure components, W and DME, respectively.

Table 4 lists ΔH^\ddagger , $\Delta H^{\ddagger E}$, ΔS^\ddagger and $\Delta S^{\ddagger E}$ values for the system, W + DME, for different molar ratios. Figure 5 shows the plots of ΔH^\ddagger and ΔS^\ddagger as a function of mole fraction of DME. On addition of DME to water, both ΔH^\ddagger and ΔS^\ddagger rise up quite sharply, and each passes through a maximum in the water-rich region and then declines monotonously. The system shows both positive and negative ΔS^\ddagger values. The negative ΔS^\ddagger starts from ~ 0.53 mole fraction of DME and continue up to the terminal concentration.

Table 4. Enthalpies, ΔH^\ddagger (kJ mol^{-1}), excess enthalpies, $\Delta H^{\ddagger E}$ (kJ mol^{-1}), entropies, ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$), and excess entropies, $\Delta S^{\ddagger E}$ ($\text{J mol}^{-1} \text{K}^{-1}$), of activation for viscous flow for the system water (x_1) + 1,2-dimethoxyethane (x_2).

x_2	ΔH^\ddagger	$\Delta H^{\ddagger E}$	ΔS^\ddagger	$\Delta S^{\ddagger E}$	x_2	ΔH^\ddagger	$\Delta H^{\ddagger E}$	ΔS^\ddagger	$\Delta S^{\ddagger E}$
Water (x_1) + 1,2-dimethoxyethane (x_2)									
0.0000	14.967	0.000	19.532	0.000	0.3598	15.279	3.087	9.910	2.750
0.0471	19.210	4.606	27.742	9.829	0.4455	13.400	1.868	4.330	0.117
0.0951	20.985	6.757	30.186	13.952	0.5389	11.633	0.822	-0.959	-1.960
0.1421	21.273	7.402	29.492	14.846	0.6952	9.406	-0.199	-7.751	-3.378
0.1877	20.051	6.531	24.978	11.900	0.8030	8.449	-0.324	-10.753	-2.673
0.2322	19.230	6.053	22.149	10.601	0.9001	7.688	-0.337	-13.249	-1.831
0.2770	17.601	4.771	17.038	7.030	1.0000	7.254	0.000	-14.854	0.000

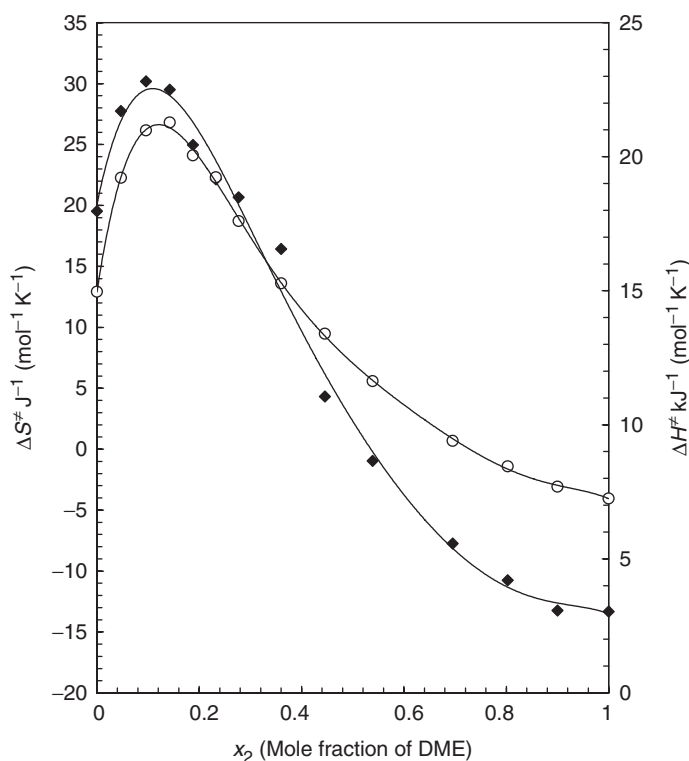


Figure 5. Variation of enthalpy, ΔH^\ddagger (\circ) and entropy, ΔS^\ddagger (\blacklozenge), of activation for viscous flow against mole fraction of DME for the system water (x_1) + DME (x_2).

Table 4 shows that the system exhibits both positive and negative values of $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$. The positive values of $\Delta S^{\ddagger E}$, predominantly in the water-rich region, indicate that the greater degree of disorder is associated with the activation process for viscous flow, while the negative values of $\Delta S^{\ddagger E}$ indicate that the species formed in the activated state are more ordered than those formed in the ground state.

Table 5 lists the ΔG^\ddagger and $\Delta G^{\ddagger E}$ values of the system, W + DME, for different molar ratios at different temperatures. Figure 6 shows the plots of ΔG^\ddagger as a function of

Table 5. Free energy of activation, ΔG^\ddagger (kJ mol^{-1}), and excess free energy of activation, $\Delta G^{\ddagger E}$ (kJ mol^{-1}), for viscous flow of the system water (x_1) + 1,2-dimethoxyethane (x_2) at different temperatures.

Temperature (K)	303.15		308.15		313.15		318.15		323.15	
	ΔG^\ddagger	$\Delta G^{\ddagger E}$	ΔG^\ddagger	$\Delta G^{\ddagger E}$	ΔG^\ddagger	$\Delta G^{\ddagger E}$	ΔG^\ddagger	$\Delta G^{\ddagger E}$	ΔG^\ddagger	$\Delta G^{\ddagger E}$
Water (x_1) + 1,2-dimethoxyethane (x_2)										
0.0000	9.046	0.000	8.948	0.000	8.851	0.000	8.753	0.000	8.655	0.000
0.0471	10.800	1.626	10.661	1.577	10.523	1.528	10.384	1.479	10.245	1.430
0.0951	11.834	2.528	11.683	2.458	11.532	2.469	11.381	2.319	11.230	2.249
0.1421	12.333	2.901	12.185	2.827	12.038	2.753	11.890	2.679	11.743	2.604
0.1877	12.479	2.924	12.354	2.864	12.229	2.805	12.104	2.745	11.979	2.686
0.2322	12.515	2.840	12.405	2.787	12.294	2.734	12.183	2.681	12.072	2.628
0.2770	12.436	2.639	12.351	2.604	12.266	2.569	12.181	2.534	12.096	2.498
0.3598	12.275	2.253	12.225	2.239	12.176	2.226	12.126	2.212	12.077	2.198
0.4455	12.087	1.833	12.065	1.832	12.044	1.832	12.022	1.831	12.000	1.830
0.5389	11.923	1.416	11.928	1.426	11.933	1.436	11.938	1.446	11.943	1.455
0.6952	11.756	0.825	11.795	0.842	11.834	0.859	11.872	0.876	11.911	0.892
0.8030	11.709	0.486	11.763	0.499	11.817	0.513	11.870	0.526	11.924	0.539
0.9001	11.705	0.218	11.771	0.227	11.837	0.236	11.904	0.246	11.970	0.254
1.0000	11.758	0.000	11.832	0.000	11.906	0.000	11.980	0.000	12.055	0.000

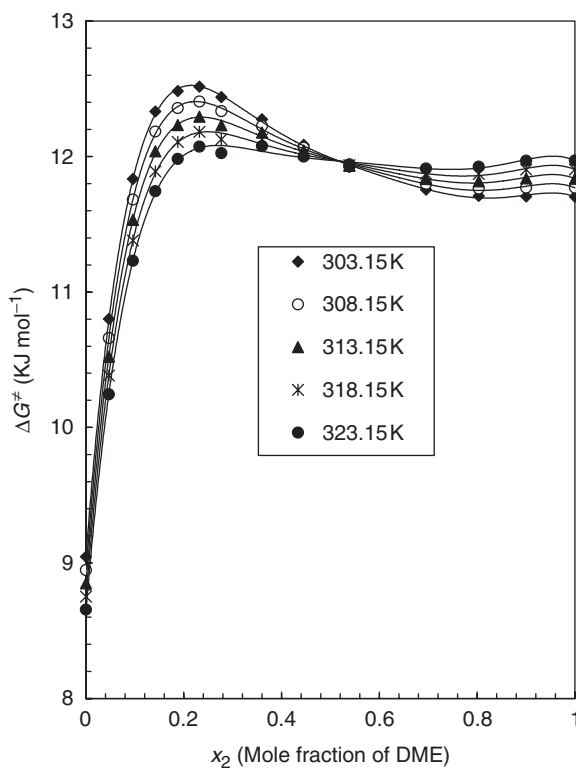
Figure 6. Variation of free energy of activation for viscous flow, ΔG^\ddagger , against mole fraction of DME for the system water (x_1) + DME (x_2) at different temperatures.

Table 6. Coefficients, A_i , of equation (1) expressing density, $\rho \times 10^{-3}$ (kg m^{-3}), coefficient of viscosity, $\eta \times 10^4$ ($\text{kg m}^{-1} \text{s}^{-1}$), free energy of activation for viscous flow, ΔG^\ddagger (kJ mol^{-1}), and the square of the regression coefficient, r^2 , for the system water + 1,2-dimethoxyethane.

Properties	Temperature (K)										r^2
	A_0	A_1	A_2	A_3	A_4	A_5	A_6				
ρ	303.15	0.9951	-0.0901	-0.9120	2.4342	-2.5617	1.1246	-0.1333			0.9999
	308.15	0.9936	-0.1200	-0.8183	2.3049	-2.5130	1.1703	-0.1661			0.9999
	313.15	0.9918	-0.1474	-0.7446	2.2649	-2.6486	1.3854	-0.2559			0.9999
	318.15	0.9898	-0.1777	-0.6094	1.9247	-2.1603	1.0138	-0.1408			0.9999
	323.15	0.9878	-0.2034	-0.5301	1.8085	-2.0898	1.0107	-0.1492			>0.9999
η	303.15	7.7167	182.67	-1101	2627	-3130.1	1846	-428.42			0.9969
	308.15	7.0042	148.96	-881.02	2058.2	-2395.7	1375.9	-309.43			0.9974
	313.15	6.3791	124.70	-734.13	1715.4	-2006.8	1163.2	-265.2			0.9977
	318.15	5.8575	104.41	-610.04	1418.9	-1657.7	962.5	-220.46			0.9981
	323.15	5.3919	88.83	-515.99	1196.4	-1396.6	811.3	-186.03			0.9984
ΔG^\ddagger	303.15	9.0469	47.458	-242.84	599.96	-794.13	539.90	-147.69			0.9998
	308.15	8.9483	46.298	-234.69	580.55	-771.24	526.57	-144.67			0.9998
	313.15	8.8497	45.134	-226.50	561.06	-748.29	513.27	-141.69			0.9997
	318.15	8.7511	43.975	-218.35	541.65	-725.40	499.94	-138.67			0.9997
	323.15	8.6526	42.811	-210.16	522.15	-702.45	486.64	-135.68			0.9995

Table 7. Coefficients, A_i , of Redlich–Kister equation, equation (3), expressing excess molar volumes, $V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$), excess viscosity, $\eta^E \times 10^4$ ($\text{kg m}^{-1} \text{s}^{-1}$), excess free energy of activation for viscous flow, $\Delta G^{\ddagger E}$ (kJ mol^{-1}), and standard deviation, σ , water + 1,2-dimethoxyethane.

Properties	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	σ
V_m^E	303.15	-6.1686	3.0092	-3.3262	6.6065	0.7292	-6.3095	0.02263
	308.15	-6.1913	2.9275	-3.1607	6.7913	-0.1475	-6.7519	0.02358
	313.15	-6.2784	2.8011	-2.6534	7.3170	-0.0535	-7.6012	0.02361
	318.15	-6.3228	2.6148	-2.4615	8.1980	0.3280	-8.3890	0.02531
	323.15	-6.3893	2.7379	-2.4648	6.8778	1.1413	-6.1985	0.02480
η^E	303.15	7.9676	-17.6119	51.2168	-120.9785	34.7690	68.2190	0.35907
	308.15	7.2456	-18.3913	43.9982	-84.9611	24.5077	42.0401	0.30224
	313.15	6.3974	-14.5625	36.2397	-76.966	21.4457	41.5531	0.21786
	318.15	5.7772	-13.2291	30.5512	-61.3447	17.4858	31.7610	0.16896
	323.15	5.2319	-11.762	25.8165	-51.3134	14.7413	26.2850	0.13511
$\Delta G^{\ddagger E}$	303.15	6.3391	-8.6143	8.9454	-10.1533	8.5078	-3.0628	0.01540
	308.15	6.3662	-8.42750	8.6317	-9.6213	8.0820	-3.0041	0.01375
	313.15	6.4030	-8.2410	8.0519	-8.8197	8.4805	-3.8942	0.03165
	318.15	6.4219	-8.0641	8.0011	-8.5051	7.2528	-2.9327	0.01147
	323.15	6.4460	-7.8880	7.7001	-7.9210	6.8015	-2.9412	0.01084

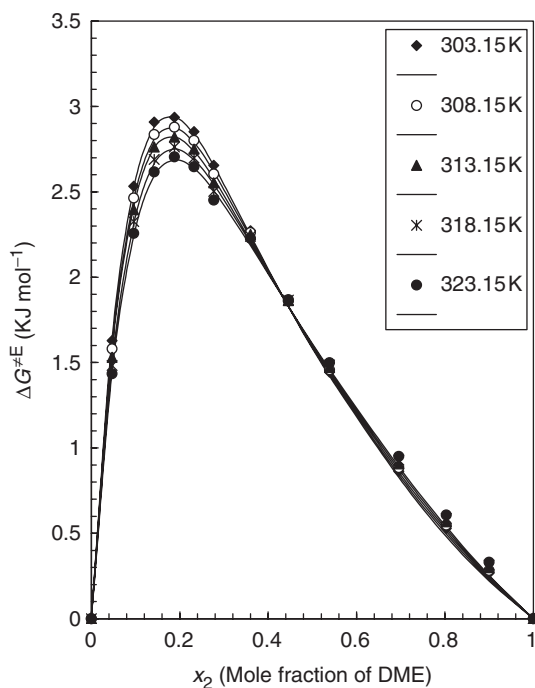


Figure 7. Variation of excess free energy of activation for viscous flow, $\Delta G^{\ddagger E}$, against mole fraction of DME for the system water (x_1) + DME (x_2) at different temperatures.

mole fraction of DME at different temperatures. Analysis of this figure shows that: (i) addition of DME to water increases the free energy quite rapidly. (ii) The system shows the maximum, fairly well-defined. (iii) The curves at all temperatures cross over at ~ 0.55 mole fraction of DME. The cross-over of the ΔG^{\ddagger} is an obvious consequence of change of sign of ΔS^{\ddagger} from positive to negative (table 4, figure 5), and the use of equation (8). The forking of the curves following the cross-over point is due to larger negative ΔS^{\ddagger} values in DME-rich region.

Figure 7 shows the variation of excess free energy of activation for viscous flow, $\Delta G^{\ddagger E}$, against mole fraction of DME at different temperatures, exhibiting the following characteristics: (i) $\Delta G^{\ddagger E}$ rises very sharply on addition of DME to water. (ii) The maxima occur at ~ 0.2 mole fraction of DME. (iii) Following the maximum in the water-rich region the values decline monotonously. (iv) The system shows positive $\Delta G^{\ddagger E}$ for the whole range of composition and the values are found to be large in magnitude. The positive $\Delta G^{\ddagger E}$ values, in effect, imply that the species formed in the activated state have to cross greater energy barrier to flow than the barrier calculated ideally.

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