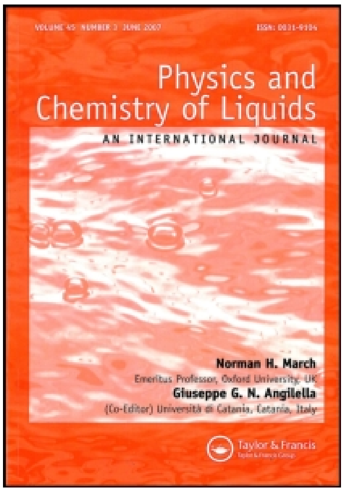

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Thermodynamic activation parameters for viscous flow of dilute aqueous solutions of ethylenediamine, trimethylenediamine and *N*,*N*-dimethyltrimethylenediamine

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The density and the viscosity data have been used to determine the thermodynamic activation parameters, free energies ($\Delta G^{\ddagger}$), enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$), for viscous flow of the systems; water (W) + ethylenediamine (ED), W + trimethylenediamine (TMD) and W + *N*,*N*-dimethyltrimethylenediamine (DMTMD) in the temperature range of 303.15–323.15 K over the composition range of $0 \leq X_2 \leq 0.45$, where X_2 is the mole fraction of diamines. On addition of diamines to water, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values increase sharply, pass through a maximum and then decline. The heights of maximum in the $\Delta G^{\ddagger}$ *versus* X_2 curve vary as, W + DMTMD > W + TMD > W + ED. For all systems, the excess properties, $\Delta G^{\ddagger E}$, $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ are positive. The observed increase in thermodynamic values may be due to combined effect of hydrophobic hydration of diamines and water–diamine interaction as a result of hydrophilic effect.

Keywords: excess thermodynamic properties; density; viscosity; aqueous diamines; hydrophobic hydration; hydrophilic effect

1. Introduction

Thermodynamic and transport properties of binary liquid mixtures help in understanding the nature of molecular interactions taking place in solutions. These data are also very useful in chemical or process industries and to develop new theoretical models. Aqueous solutions of hydrophobic solutes are one of the particular areas of interest. Advancement in experimental techniques as well as theoretical methods has provided a better insight into the structural aspect of water around hydrophobic solutes [1–15]. The structure and the interaction for small spherical type solutes whose sizes are comparable with the water molecule have been studied extensively [7–10]. The feature of the water structure is described as the so-called clathrate-like geometry. Very large spheres or planar walls have also been investigated in detail to mimic extended hydrophobic surfaces [11–14]. The structures and the interactions in these two extreme cases have been found to be quite different. Kinoshita [15] studied the structure of water around hydrophobic solutes of varying size and concluded that the structure exhibits drastic change with the solute size.

There are a limited number of studies on the thermodynamics of aqueous solutions of hydrophobic solutes. This prompted us to undertake the present studies with the hope

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of collecting new data hitherto not known. Moreover, we wished to see how the thermodynamic properties are influenced by the structural differences of the diamines in these systems. Recently, we reported the viscometric and volumetric properties of the aqueous systems of ethylenediamine (ED), trimethylenediamine (TMD) and *N*,*N*-dimethyltrimethylenediamine (DMTMD) [16–18]. We observed large volume contraction and a large increase of viscosity in the water-rich region for these systems. The thermodynamic parameters are also thought to be effected more in the water-rich region and therefore we restricted the compositions of the systems within this region (0–0.45 mole fraction of diamines). A large amount of data has been collected at closely spaced compositions, so that the variation of these properties as a function of solute concentration could be observed more precisely. Recent publications by Batalin *et al.* [19] on adiabatic compressibility, Kapadi *et al.* [20] on the temperature dependence of excess molar volumes, Ivanova *et al.* [21] on the density and viscosity, and Sasaki *et al.* [22] on the ultrasonic velocity of the ethylenediamine and water system are worth mentioning in relation to our work.

2. Experimental

The diamines under investigation were procured from the manufacturers with quoted purities: ethylenediamine (Beijing Chemical Works, 99%), trimethylenediamine (Merck-Schuchardt, 98%) and *N*,*N*-dimethyltrimethylenediamine (Merck-Schuchardt, 98%). As measures of purity check, the densities and viscosities of pure liquids were compared with the available literature values [20,23,24]. Our measured values of densities and viscosities of pure liquids have been found to be very satisfactory with literature (Table 1). These were used without further purification except that each of the diamines was kept over molecular sieves (4A) for at least 2 weeks prior to its use. Thrice distilled water was used in the preparation of all the diamine solutions. An Ostwald U-tube viscometer of the British Standard Institution with sufficiently long efflux time was used, so that no kinetic energy

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 liquids at different temperatures.

		Temperature (K)						
Compounds	Property	293.15	298.15	303.15	308.15	313.15	318.15	323.15
ED	ρ	0.8997 0.8997[a] 0.8995[b] 0.8994[c]	0.8952	0.8908 0.890325[a]	0.8861 0.885616[a]	0.8814 0.880896[a]	0.8767 0.876153[a]	0.8716
	η	16.03	14.35 15.4[c]	12.99 12.90[a]	11.91 11.67[a]	10.80 10.60[a]	9.86 9.67[a]	9.04
TMD	ρ		0.8846 0.884[b]	0.8801	0.8756	0.8711	0.8667	0.8622
	η		18.00	15.94	14.23	12.97	11.81	10.70
DMTMD	ρ	0.8210	0.8170	0.8123	0.8080	0.8035	0.7990	0.7946
	η	11.52	10.49	9.41	8.62	7.93	7.31	6.78

Note: [a][20], [b][23], [c][24].

correction was necessary in viscosity measurement. The density was measured by a 25 mL specific gravity bottle. An analytical balance of accuracy ±0.0001 g was used in density measurement. The solutions were prepared by mixing known masses of the components determined by the same balance. Mole fractions were accurate up to the fourth place of decimal. For every measurement, a thermostatic water bath controlled to ±0.05 K was used. The density bottle was calibrated with deionised and doubly distilled water at 303.15, 308.15, 313.15, 318.15 and 323.15 K. The densities (ρ) and viscosities (η) of the systems, water (W) + ED, W + TMD and W + DMTMD, over the composition range, $0 \leq X_2 \leq 0.45$, (where X_2 represents mole fraction of diamines) and at temperatures ranging from 303.15 to 323.15 K were reported in our previous studies [16,17,25]. However, the density and viscosity data used to calculate the thermodynamic properties are listed in Table 2. The average uncertainty in the measured viscosity and density was found to be no more than $5.5 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ and $1.4 \times 10^{-1}\,\mathrm{kg\,m^{-3}}$, respectively.

Eyring equation of the following form was used to calculate the enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation for the viscous flow:

$$\ln(\eta V_m/hN) = \Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R, \tag{1}$$

where the terms have their usual significances. From the slopes and intercepts of the above equation, obtained by the least squares method, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are calculated.

The $\Delta G^{\ddagger}$ values are obtained by using the simple thermodynamic relation,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}. \tag{2}$$

The thermodynamic activation parameters for the viscous flow were represented by a common polynomial equation of the form,

$$Y = \sum_{i=0}^{n} A_i X_2^i, \tag{3}$$

where A_i is the i-th coefficient, Y stands for $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and X_2 for the mole fraction of diamines.

The excess thermodynamic properties (Y^E) i.e. $\Delta G^{\ddagger E}$, $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ have been calculated by the following equation,

$$Y^E = Y - (X_1 Y_1 + X_2 Y_2), \tag{4}$$

where the subscripts 1 and 2 represent the pure components of the mixture i.e. water and diamine, respectively.

Each of the experimentally obtained excess properties were fitted to a Redlich–Kister polynomial equation of the type,

$$Y^E = X_1 X_2 \sum_{i=0}^{n} A_i (1 - 2X_1)^i. \tag{5}$$

3. Results and discussion

Enthalpies ($\Delta \mathrm{H}^{\ddagger}$), excess enthalpies ($\Delta H^{\ddagger E}$), entropies ($\Delta S^{\ddagger}$) and excess entropies ($\Delta S^{\ddagger E}$) for all the systems are listed in Table 3. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values have been expressed

Table 2. Experimental densities, $\rho \times 10^{-3}$ (kg m^{-3}), and viscosities, $\eta \times 10^{4}$ (kg m^{-1} s^{-1}), of the systems, W + ED, W + TMD and W + DMTMD, at different temperatures.[a]

T/K	303.15		308.15		313.15		318.15		323.15	
X_2	ρ	η	ρ	η	ρ	η	ρ	η	ρ	η
W (X_1) + ED (X_2)										
0.0000	0.9957	8.00	0.9941	7.22	0.9922	6.56	0.9903	5.98	0.9881	5.49
0.0500	0.9917	13.68	0.9897	12.08	0.9874	10.75	0.9851	9.64	0.9826	8.70
0.0999	0.9916	22.91	0.9891	19.71	0.9863	17.17	0.9835	15.15	0.9805	13.34
0.1500	0.9928	36.35	0.9896	30.59	0.9863	26.02	0.9831	22.43	0.9797	19.50
0.1998	0.9931	52.92	0.9894	43.47	0.9857	36.18	0.9819	30.48	0.9781	26.02
0.2488	0.9913	67.97	0.9873	54.84	0.9832	44.89	0.9791	37.33	0.9750	31.44
0.2749	0.9894	73.72	0.9853	59.20	0.9810	48.25	0.9769	39.93	0.9726	33.47
0.2997	0.9870	76.78	0.9827	61.33	0.9784	49.97	0.9741	41.14	0.9697	34.39
0.3246	0.9840	77.67	0.9796	62.13	0.9752	50.42	0.9708	41.54	0.9665	34.76
0.3488	0.9807	76.70	0.9763	61.33	0.9718	49.87	0.9674	41.17	0.9629	34.40
0.3739	0.9769	73.84	0.9724	59.18	0.9679	48.26	0.9634	39.91	0.9588	33.46
0.3944	0.9738	70.20	0.9693	56.43	0.9648	46.21	0.9603	38.40	0.9556	32.34
0.4542	0.9635	59.65	0.9596	48.71	0.9549	40.32	0.9504	33.85	0.9457	28.75
1.0000	0.8908	12.99	0.8861	11.91	0.8814	10.80	0.8767	9.86	0.8716	9.04
W (X_1) + TMD (X_2)										
0.0518	0.9894	16.37	0.9871	14.37	0.9847	12.67	0.9821	11.27	0.9794	10.08
0.1000	0.9885	29.91	0.9855	25.34	0.9823	21.74	0.9791	18.87	0.9757	16.50
0.1498	0.9877	48.82	0.9840	40.12	0.9802	33.45	0.9765	28.27	0.9725	24.17
0.2004	0.9845	67.62	0.9805	54.46	0.9763	44.67	0.9721	37.14	0.9684	31.32
0.2498	0.9790	78.72	0.9747	63.09	0.9703	51.28	0.9660	42.36	0.9617	35.48
0.2734	0.9756	80.88	0.9712	64.73	0.9669	52.68	0.9625	43.51	0.9584	36.46
0.2984	0.9717	81.08	0.9674	65.02	0.9634	52.97	0.9585	43.79	0.9544	36.62
0.3248	0.9672	79.18	0.9628	63.64	0.9584	51.99	0.9539	43.07	0.9494	36.19
0.3502	0.9628	76.14	0.9583	61.55	0.9537	50.27	0.9493	41.89	0.9447	35.18
0.3766	0.9576	71.21	0.9534	57.74	0.9493	47.54	0.9448	39.72	0.9403	33.54
0.4041	0.9532	66.81	0.9486	54.64	0.9441	45.09	0.9396	37.87	0.9351	32.11
0.4467	0.9453	59.11	0.9409	48.71	0.9364	40.68	0.9319	34.45	0.9275	29.35
1.0000	0.8801	15.94	0.8756	14.23	0.8711	12.97	0.8667	11.81	0.8622	10.70
W (X_1) + DMTMD (X_2)										
0.0488	0.9773	23.76	0.9745	20.23	0.9716	17.41	0.9687	15.20	0.9656	13.36
0.0999	0.9639	50.10	0.9600	40.70	0.9561	33.59	0.9522	28.16	0.9482	23.93
0.1470	0.9497	71.75	0.9455	57.21	0.9413	46.35	0.9370	38.21	0.9328	32.06
0.1743	0.9413	79.60	0.9370	63.15	0.9327	50.89	0.9285	41.76	0.9242	34.85
0.1999	0.9334	83.48	0.9293	66.16	0.9249	53.16	0.9206	43.62	0.9161	36.18
0.2247	0.9262	83.78	0.9219	66.43	0.9175	53.56	0.9131	43.87	0.9087	36.35
0.2497	0.9190	81.94	0.9147	64.99	0.9103	52.48	0.9060	43.01	0.9015	35.72
0.2744	0.9122	77.87	0.9078	62.16	0.9035	50.23	0.8994	41.32	0.8947	34.44
0.2998	0.9054	72.75	0.9011	58.12	0.8966	47.23	0.8923	39.04	0.8880	32.65
0.3238	0.8993	67.28	0.8950	54.16	0.8906	44.23	0.8863	36.72	0.8819	30.81
0.3744	0.8874	55.64	0.8834	45.40	0.8790	37.57	0.8746	31.55	0.8702	26.73
0.3988	0.8826	50.44	0.8782	41.43	0.8738	34.48	0.8694	29.05	0.8650	24.75
0.4365	0.8750	43.26	0.8706	35.86	0.8661	30.13	0.8618	25.66	0.8574	22.05
1.0000	0.8123	9.41	0.8080	8.62	0.8035	7.93	0.7990	7.31	0.7946	6.78

Note: [a]From [16], [17] and [25].

Table 3. Enthalpies, $\Delta H^{\ddagger}$ (kJ mol^{-1}), excess enthalpies, $\Delta H^{\ddagger E}$ (kJ mol^{-1}), entropies, $\Delta S^{\ddagger}$ (J mol^{-1} K^{-1}), and excess entropies, $\Delta S^{\ddagger E}$ (J mol^{-1} K^{-1}), of activation for viscous flow of the systems, W + ED, W + TMD and W + DMTMD.

X_2	$\Delta H^{\ddagger}$	$\Delta H^{\ddagger E}$	$\Delta S^{\ddagger}$	$\Delta S^{\ddagger E}$	X_2	$\Delta H^{\ddagger}$	$\Delta H^{\ddagger E}$	$\Delta S^{\ddagger}$	$\Delta S^{\ddagger E}$
W (X_1) + ED (X_2)					W (X_1) + TMD (X_2)				
0.0000	15.02	0.00	19.72	0.00	0.0000	15.02	0.00	19.72	0.00
0.0500	18.03	3.06	24.24	5.45	0.0518	19.33	4.31	26.69	7.94
0.0999	21.44	6.53	30.40	12.55	0.1000	23.66	8.64	34.98	17.13
0.1500	24.80	9.95	36.92	20.01	0.1498	27.99	12.97	44.25	27.32
0.1998	28.30	13.50	44.64	28.66	0.2004	30.63	15.61	49.40	33.42
0.2488	30.73	15.99	49.95	34.89	0.2498	31.74	16.73	51.00	35.95
0.2749	31.45	16.74	51.33	36.76	0.2734	31.72	16.71	50.35	35.74
0.2997	31.96	17.28	52.38	38.27	0.2984	31.60	16.58	49.53	35.39
0.3246	32.04	17.38	52.21	38.57	0.3248	31.12	16.11	47.78	34.13
0.3488	31.88	17.26	51.52	38.34	0.3502	30.66	15.65	46.21	33.04
0.3739	31.46	16.86	50.13	37.42	0.3766	29.86	14.85	43.78	31.10
0.3944	30.77	16.20	48.06	35.74	0.4041	29.07	14.04	41.32	29.15
0.4542	28.96	14.46	42.76	31.55	0.4467	27.68	12.67	37.20	25.82
1.0000	13.87	0.00	0.96	0.00	1.0000	14.98	0.00	1.02	0.00
W (X_1) + DMTMD (X_2)									
0.0000	15.02	0.000	19.72	0.000	0.2744	32.46	18.13	50.78	38.17
0.0488	22.93	8.036	34.94	16.48	0.2998	31.81	17.55	48.73	36.78
0.0999	29.42	14.65	48.57	31.43	0.3238	30.99	16.79	46.23	34.90
0.1470	32.10	17.45	53.16	37.24	0.3744	29.02	14.95	40.45	30.43
0.1743	32.92	18.34	54.30	39.10	0.3988	28.17	14.16	38.07	28.68
0.1999	33.28	18.76	54.49	40.10	0.4365	26.59	12.68	33.56	25.15
0.2247	33.20	18.75	53.64	39.74	1.0000	12.46	0.00	−6.19	0.00
0.2497	33.00	18.62	52.66	39.41					

Table 4. Coefficients, A_i, of Equation (3) expressing enthalpy, $\triangle H^{\ddagger}$ (kJ mol^{-1}), and entropy, $\triangle S^{\ddagger}$ (J mol^{-1} K^{-1}), of activation for viscous flow and the square of the regression coefficients, r^2, for viscous flow of the systems, W + ED, W + TMD and W + DMTMD.

Systems	Properties	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
W + ED	$\Delta H^{\ddagger}$	15.022	61.537	−86.812	1835.4	−9096.1	14831	−7706.3	0.9999
	$\Delta S^{\ddagger}$	19.711	92.590	−233.68	5859.3	−27408	43669	−22494	0.9997
W + TMD	$\Delta H^{\ddagger}$	15.038	64.431	450.47	−2330.2	761.08	8600.3	−10270	0.9998
	$\Delta S^{\ddagger}$	19.761	70.503	1460.7	−6213.9	−301.54	29287	−32797	0.9995
W + DMTMD	$\Delta H^{\ddagger}$	15.008	168.87	191.63	−7207.4	31807	−59554	41897	0.9996
	$\Delta S^{\ddagger}$	19.667	296.88	1381.9	−23335	98130	−182150	128063	0.9991

satisfactorily by Equation (3), the coefficients of which are shown in Table 4 together with the values of r^2. The plots of $\Delta H^{\ddagger}$ against the mole fraction of diamines are shown in Figure 1. The plots of $\Delta S^{\ddagger}$ *versus* X_2 are not shown here, since they are found to follow a similar trend. All the systems show rapid increase in $\Delta H^{\ddagger}$ values, pass through

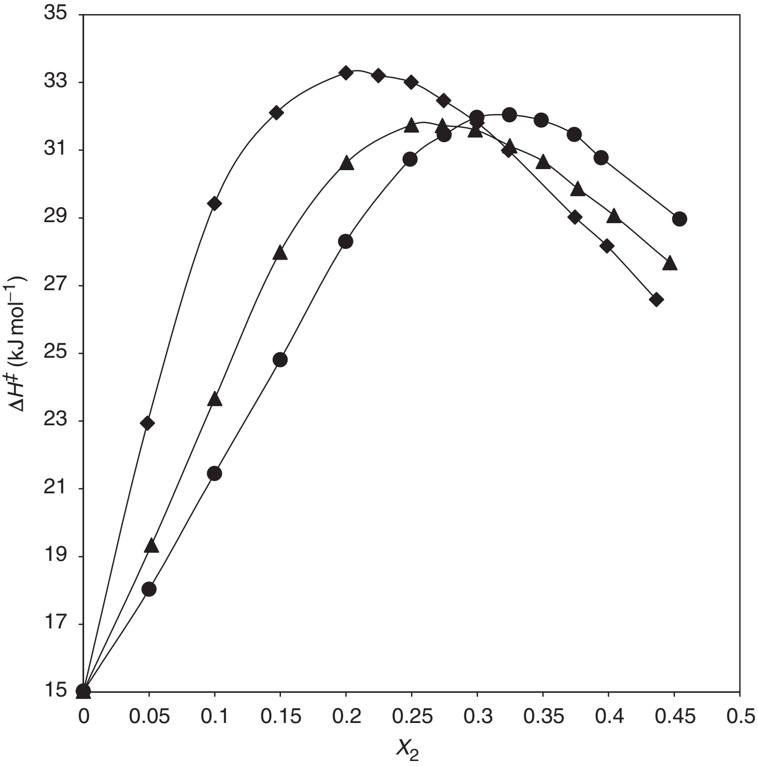

Figure 1. Comparison of enthalpy ($\Delta H^{\ddagger}$) curves of the systems, W + ED (●), W + TMD (▲) and W + DMTMD (◆), against mole fraction of diamines (X_2).

Table 5. Coefficients, A_i, of Redlich–Kister equation, Equation (5), expressing excess enthalpy, $\Delta H^{\ddagger E}$ (kJ mol^{-1}), and excess entropy, $\Delta S^{\ddagger E}$ (J mol^{-1} K^{-1}), of activation for viscous flow and standard deviation, σ, of the systems, W + ED, W + TMD and W + DMTMD.

Systems	Properties	A_0	A_1	A_2	A_3	σ
W + ED	$\Delta H^{\ddagger E}$	48.412	−104.76	−14.959	98.070	0.2017
	$\Delta S^{\ddagger E}$	101.64	−275.12	−106.87	223.97	0.5915
W + TMD	$\Delta H^{\ddagger E}$	48.338	−2.1396	301.37	283.43	0.1334
	$\Delta S^{\ddagger E}$	100.00	24.114	807.89	784.58	0.4090
W + DMTMD	$\Delta H^{\ddagger E}$	44.413	−38.897	162.88	40.972	0.1993
	$\Delta S^{\ddagger E}$	88.640	−60.053	460.99	185.23	0.6083

a maxima and then gradually decrease as the concentration of solute increases. W + ED, W + TMD and W + DMTMD systems exhibit distinct maxima near $X_2 = 0.325$, 0.25 and 0.2, respectively, in their $\Delta H^{\ddagger}$ *versus* X_2 as well as $\Delta S^{\ddagger}$ *versus* X_2 curves. The $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ values are also fitted to the Redlich–Kister polynomial Equation (5) and the coefficients of the equation and the standard deviations are shown in Table 5. Figures 2 and 3 are the comparative diagrams of $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ for aqueous diamines. The excess functions $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ for W + ED, W + TMD and W + DMTMD systems

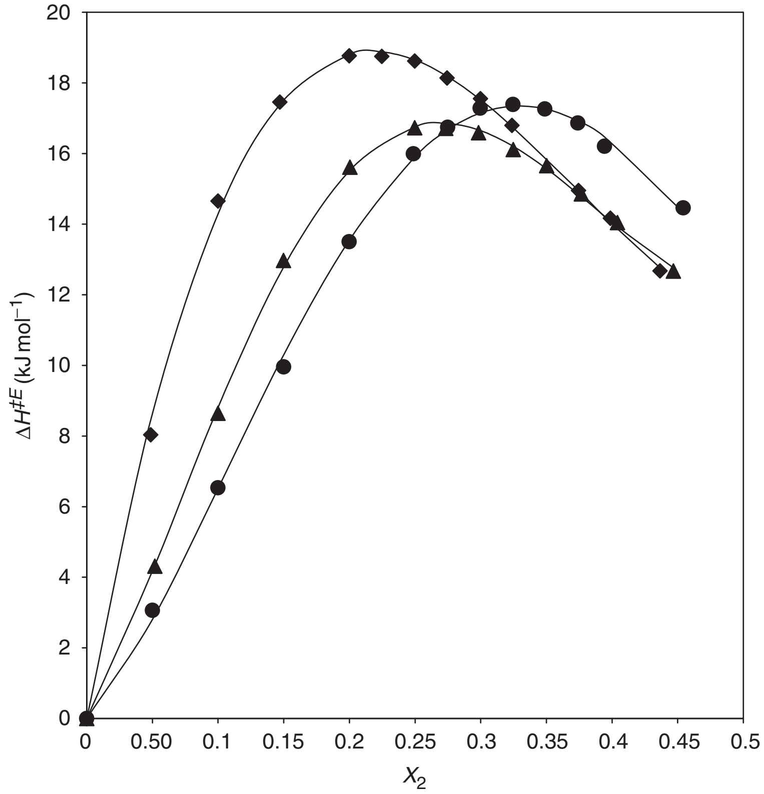

Figure 2. Comparison of excess enthalpy ($\Delta H^{\ddagger E}$) curves of the systems, W + ED (●), W + TMD (▲) and W + DMTMD (◆), against mole fraction of diamines (X_2).

follow similar trend as $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The excess thermodynamic parameters for the systems are always found to be positive; indicating that the species formed in the activated state are structurally more disordered than anticipated from ideal condition and use large amounts of energy for their passage to the activated state. The $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ *versus* X_2 curves for W + ED, W + TMD and W + DMTMD are characterised by maxima near $X_2 = 0.325$, 0.25 and 0.2 respectively. The order of increment of both $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ are as follows: W + DMTMD > W + ED > W + TMD.

Table 6 lists the $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ for all the systems at different temperatures. The $\Delta G^{\ddagger}$ values have been expressed by Equation (3). The coefficients of this equation are listed in Table 7 together with the r^2 values. In all cases studied, r^2 displays a value of one, indicating an excellent fitting of the data by the polynomial Equation (3). Figure 4 shows the plot of $\Delta G^{\ddagger}$ values of the water (W) + ethylenediamine (ED) against the mole fraction of ED in between 303.15 and 323.15 K. The excess values are fitted to the Redlich–Kister polynomial Equation (5) and the coefficients of the equation and the standard deviations are shown in Table 8. Figure 5 represents the variation of $\Delta G^{\ddagger E}$ of the system, W + ED, against the mole fraction of ED at temperatures 303.15–323.15 K. Since the curves of $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ *versus* X_2 for W + TMD and W + DMTMD are almost similar to that of W + ED, they are not shown graphically. Figures 6 and 7 represent the comparative

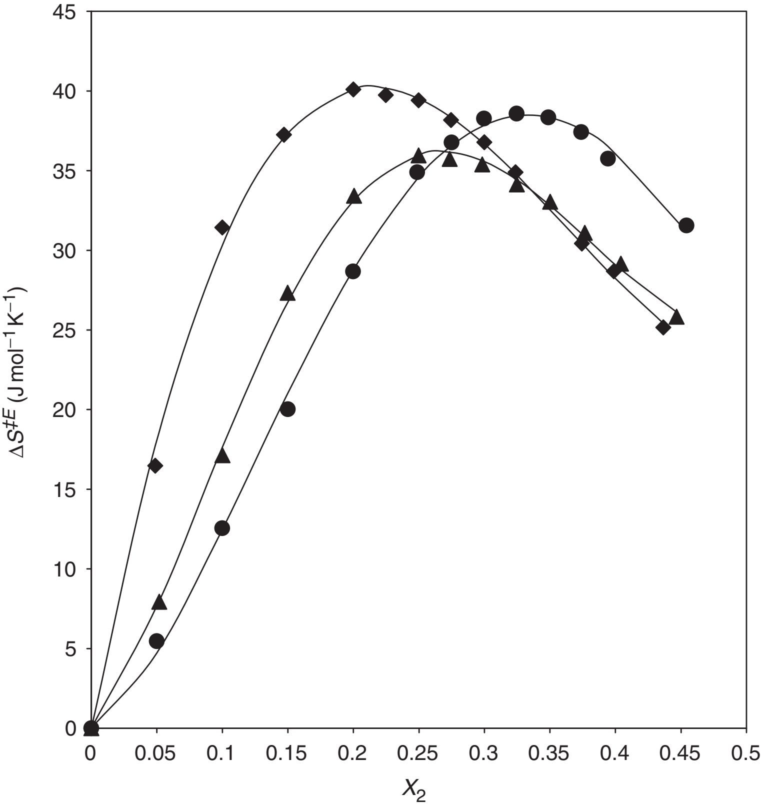

Figure 3. Comparison of excess entropy ($\Delta S^{\ddagger}$) curves of the systems, W + ED (●), W + TMD (▲) and W + DMTMD (◆), against mole fraction of diamines (X_2).

diagrams of $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ for W+ diamines at 303.15 K respectively. From the Figures (4–7), the following characteristic features of the free energy of activation for viscous flow of the three systems are obtained:

(a) For all systems, $\Delta G^{\ddagger}$ values increases rapidly in the lower concentration of diamines, followed by a maxima and then starts to decline as the concentration of diamine increases. However, in each system, values of $\Delta G^{\ddagger}$ are found to decrease with the increase in temperature (Figure 4).

(b) Variation of $\Delta G^{\ddagger E}$ with composition for all the systems under investigation are more or less similar in nature, all being associated with maxima and the curves are skewed towards the highly aqueous region (Figure 5).

(c) The variation of $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ with temperature is quite significant, particularly in the region at or around the maximum. However, the positions of maxima remain unchanged with the change in temperature (Figures 4 and 5).

(d) The compositions corresponding to maximum $\Delta G^{\ddagger E}$ for W + EDA, W + TMDA and W + DMTMDA systems are found to be near $X_2 = 0.325$, 0.275 and 0.225, respectively (Figure 7). The $\Delta G^{\ddagger E}$ values are found to be positive and large in magnitude, which indicate that the solutions are highly non-ideal, and the species formed in the solutions have to surmount a large additional energy barrier in order

Table 6. Free energy of activation, $\Delta G^{\ddagger}$ (kJ mol^{-1}), and excess free energy of activation, $\Delta G^{\ddagger E}$ (kJ mol^{-1}), for viscous flow of the systems, W + ED, W + TMD and W + DMTMD.

T/K	303.15		308.15		313.15		318.15		323.15	
X_2	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$
W (X_1) + ED (X_2)										
0.0000	9.04	0.00	8.94	0.00	8.85	0.00	8.751	0.00	8.653	0.00
0.0500	10.68	1.40	10.56	1.38	10.44	1.35	10.31	1.32	10.19	1.30
0.0999	12.22	2.72	12.07	2.66	11.92	2.60	11.77	2.54	11.62	2.47
0.1500	13.61	3.88	13.43	3.78	13.24	3.68	13.06	3.58	12.87	3.48
0.1998	14.76	4.81	14.54	4.67	14.32	4.52	14.09	4.38	13.87	4.24
0.2488	15.59	5.41	15.34	5.23	15.09	5.06	14.84	4.89	14.59	4.71
0.2749	15.89	5.60	15.63	5.41	15.38	5.23	15.12	5.04	14.86	4.86
0.2997	16.09	5.68	15.82	5.49	15.56	5.29	15.30	5.10	15.04	4.91
0.3246	16.21	5.69	15.95	5.49	15.69	5.30	15.42	5.11	15.16	4.92
0.3488	16.26	5.63	16.01	5.44	15.75	5.25	15.49	5.05	15.23	4.87
0.3739	16.26	5.51	16.01	5.33	15.76	5.14	15.50	4.95	15.25	4.76
0.3944	16.20	5.36	15.96	5.18	15.72	5.00	15.48	4.83	15.24	4.65
0.4542	16.00	4.89	15.78	4.73	15.57	4.57	15.36	4.42	15.14	4.26
1.0000	13.58	0.00	13.57	0.00	13.57	0.00	13.57	0.00	13.57	0.00
W (X_1) + TMD (X_2)										
0.0518	11.24	1.90	11.11	1.86	10.97	1.82	10.84	1.78	10.71	1.74
0.1000	13.06	3.45	12.88	3.36	12.71	3.28	12.53	3.19	12.36	3.10
0.1498	14.57	4.68	14.35	4.54	14.13	4.41	13.91	4.27	13.69	4.13
0.2004	15.65	5.48	15.41	5.31	15.16	5.14	14.91	4.98	14.67	4.81
0.2498	16.28	5.83	16.03	5.65	15.77	5.47	15.52	5.29	15.26	5.11
0.2734	16.46	5.87	16.21	5.69	15.96	5.52	15.71	5.34	15.45	5.16
0.2984	16.58	5.85	16.33	5.68	16.09	5.50	15.84	5.32	15.59	5.15
0.3248	16.64	5.76	16.40	5.59	16.16	5.42	15.92	5.25	15.68	5.08
0.3502	16.65	5.63	16.42	5.47	16.19	5.30	15.96	5.14	15.73	4.97
0.3766	16.59	5.42	16.37	5.27	16.15	5.11	15.93	4.96	15.71	4.80
0.4041	16.54	5.22	16.34	5.07	16.13	4.93	15.92	4.78	15.72	4.64
0.4467	16.40	4.84	16.21	4.71	16.03	4.58	15.84	4.45	15.66	4.32
1.0000	14.67	0.00	14.67	0.00	14.66	0.00	14.66	0.00	14.65	0.00
W (X_1) + DMTMD (X_2)										
0.0488	12.34	3.03	12.16	2.95	11.99	2.87	11.82	2.79	11.64	2.70
0.0999	14.70	5.12	14.45	4.96	14.21	4.80	13.97	4.65	13.72	4.49
0.1470	15.99	6.16	15.72	5.98	15.46	5.79	15.19	5.60	14.92	5.42
0.1743	16.46	6.49	16.18	6.29	15.91	6.09	15.64	5.90	15.37	5.70
0.1999	16.76	6.65	16.49	6.45	16.21	6.25	15.94	6.05	15.67	5.85
0.2247	16.94	6.70	16.67	6.50	16.40	6.30	16.13	6.10	15.86	5.90
0.2497	17.04	6.67	16.78	6.47	16.51	6.27	16.25	6.08	15.99	5.88
0.2744	17.06	6.56	16.81	6.37	16.55	6.18	16.30	5.99	16.05	5.80
0.2998	17.03	6.40	16.79	6.21	16.55	6.03	16.30	5.85	16.06	5.66
0.3238	16.97	6.21	16.74	6.04	16.51	5.86	16.28	5.69	16.05	5.51
0.3744	16.76	5.72	16.55	5.57	16.35	5.42	16.15	5.27	15.95	5.12
0.3988	16.63	5.47	16.44	5.32	16.25	5.18	16.06	5.04	15.87	4.89
0.4365	16.41	5.05	16.24	4.92	16.07	4.80	15.91	4.67	15.74	4.55
1.0000	14.34	0.00	14.37	0.00	14.40	0.00	14.43	0.00	14.47	0.00

Table 7. Coefficients, A_i, of Equation (3) expressing free energy of activation for viscous flow, $\Delta G^{\ddagger}$ (kJ mol^{-1}), and the square of the regression coefficient, r^2, for viscous flow of the systems, W + ED, W + TMD and W + DMTMD.

Systems	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
W + ED	303.15	9.0470	33.474	−16.161	61.172	−795.85	1609.9	−899.40	1.0000
	308.15	8.9484	32.999	−14.697	29.126	−647.45	1370.1	−771.83	1.0000
	313.15	8.8499	32.536	−13.508	−0.3937	−509.34	1149.4	−657.41	1.0000
	318.15	8.7513	32.075	−12.354	−29.664	−372.23	930.80	−544.75	1.0000
	323.15	8.6527	31.613	−11.211	−58.724	−236.15	714.17	−433.38	1.0000
W + TMD	303.15	9.0475	42.880	12.310	−489.41	1032.6	−628.22	−71.857	1.0000
	308.15	8.9487	42.527	5.0585	−459.11	1038.1	−783.54	99.258	1.0000
	313.15	8.8499	42.172	−2.230	−427.94	1038.6	−927.28	260.88	1.0000
	318.15	8.7510	41.821	−9.520	−397.13	1041.5	−1076.6	427.06	1.0000
	323.15	8.6522	41.468	−16.796	−366.32	1044.2	−1225.8	593.41	1.0000
W + DMTMD	303.15	9.0458	78.993	−229.99	−115.83	2014.7	−4293.7	3071.5	1.0000
	308.15	8.9476	77.490	−236.52	−1.4179	1528.7	−3384.6	2427.8	1.0000
	313.15	8.8493	75.971	−242.47	106.48	1074.1	−2542.3	1836.6	1.0000
	318.15	8.7509	74.481	−249.45	226.22	226.22	−1576.0	1147.8	1.0000
	323.15	8.6526	72.975	−255.86	339.57	80.467	−675.62	510.45	1.0000

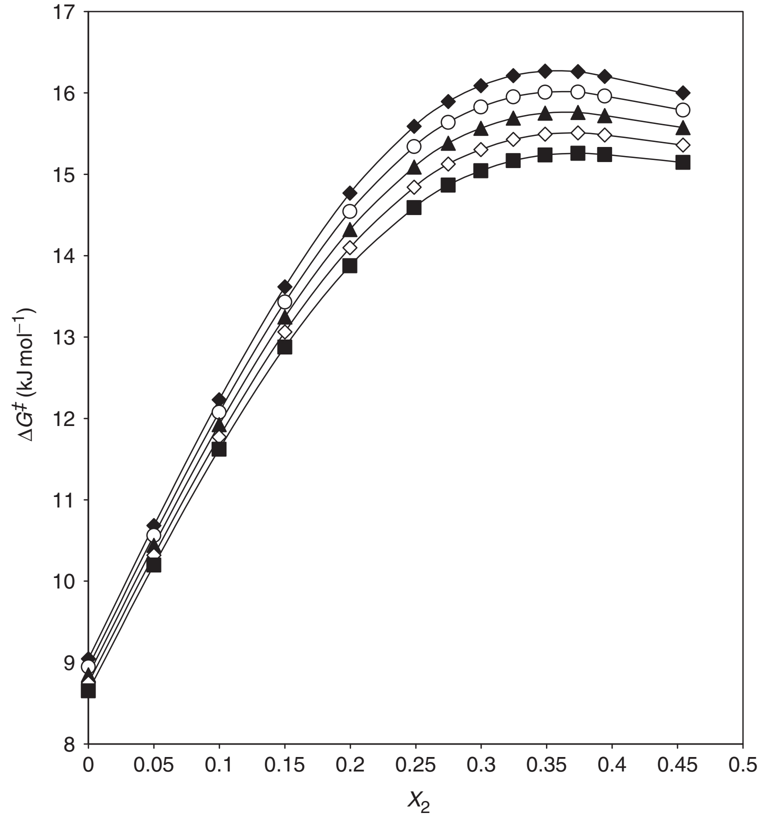

Figure 4. Variation of free energy ($\Delta G^{\ddagger}$) of the system, water + ED, against mole fraction of ED (X_2) at 303.15 K (◆), 308.15 K (○), 313.15 K (▲), 318.15 K (◇) and 323.15 K (■).

Table 8. Coefficients, A_i, of Redlich–Kister equation, Equation (5), expressing excess free energy of activation, $\triangle G^{\ddagger E}$ (kJ mol^{-1}), for viscous flow and SD, σ, of the systems, W + ED, W + TMD and W + DMTMD.

Systems	Temperature (K)	A_0	A_1	A_2	A_3	σ
W + ED	303.15	17.599	−21.347	17.474	30.203	0.0234
	308.15	17.090	−19.983	17.966	29.047	0.0205
	313.15	16.582	−18.605	18.513	27.938	0.0178
	318.15	16.093	−16.990	19.649	27.232	0.0154
	323.15	15.565	−15.855	19.576	25.692	0.0126
W + TMD	303.15	18.032	−9.6419	55.689	44.936	0.0146
	308.15	17.532	−9.7590	51.657	41.017	0.0131
	313.15	17.032	−9.8778	47.623	37.099	0.0117
	318.15	16.532	−10.001	43.575	33.169	0.0105
	323.15	16.032	−10.122	39.539	29.250	0.0097
W + DMTMD	303.15	17.658	−19.478	26.485	−12.707	0.0151
	308.15	17.216	−19.166	24.218	−13.604	0.0122
	313.15	16.769	−18.902	21.818	−14.598	0.0095
	318.15	16.333	−18.531	19.707	−15.383	0.0069
	323.15	15.892	−18.213	17.450	−16.274	0.0051

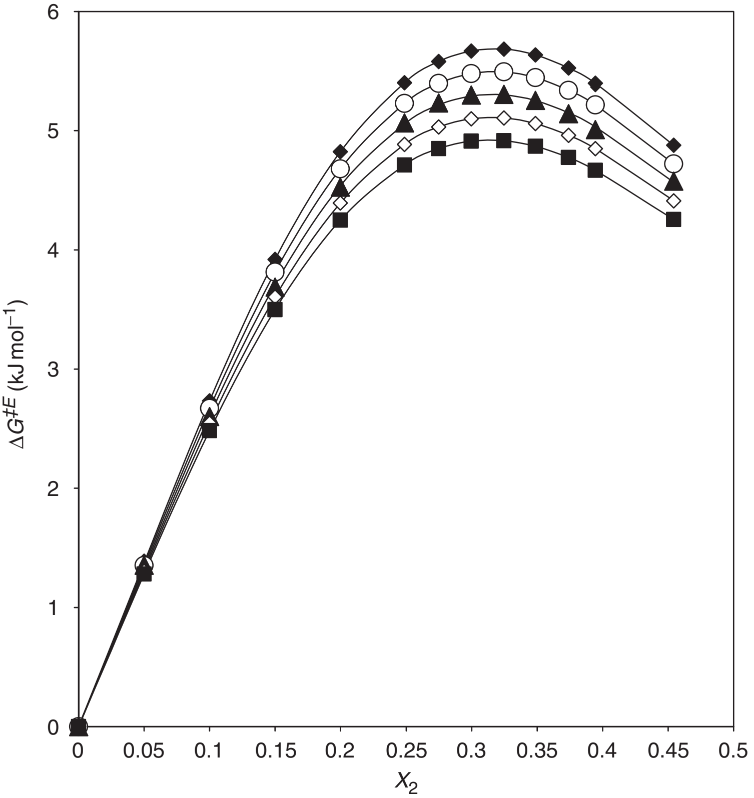

Figure 5. Variation of excess free energy ($\Delta G^{\ddagger E}$) of the system, W + ED, against mole fraction of ED (X_2) at 303.15 K (◆), 308.15 K (○), 313.15 K (▲), 318.15 K (◇) and 323.15 K (■).

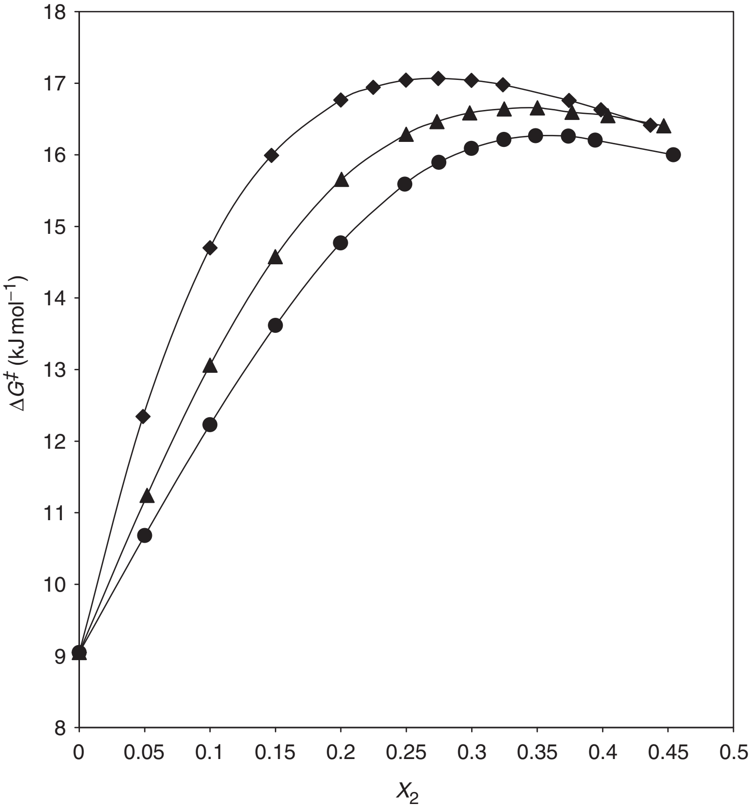

Figure 6. Comparison of free energy ($\Delta G^{\ddagger}$) curves of the systems, W + ED (●), W + TMD (▲) and W + DMTMD (◆), against mole fraction of diamines (X_2) at 303.15 K.

to flow. This implies that the species experience enhanced resistance to flow. The order of increment of $\Delta G^{\ddagger E}$ in the water-rich region is as follows: W + DMTMD > W + TMD > W + ED.

Among the solutes chosen in the current study, the simplest one is ethylenediamine, in which two –CH_2–NH_2 groups are joined together. In trimethylenediamine, two –CH_2–NH_2 groups are attached to a –CH_2– group on either sides and in *N*,*N*-dimethyltrimethylenediamine, two hydrogen atoms of an –NH_2 group are replaced by methyl groups. All three pure compounds are polar by virtue of the presence of an unshared electron pair on nitrogen atoms. Therefore, hydrogen bonding is thought to be formed by the polar group of the diamines and water due to the hydrophilic effect. However, since the electronegativity of nitrogen is low, the hydrophilic effect should also be low. Therefore, the large positive $\Delta G^{\ddagger E}$ cannot be explained by hydrophilic effect only and it is possible that hydrophobic hydration is playing a role here. According to hydrophobic hydration, in a very dilute solution, water molecules form a long-range structural aggregate around the hydrocarbon moieties; with continued addition of diamines; such aggregates increase causing a rapid rise of $\Delta G^{\ddagger E}$. With a further increase in solute concentration, a composition is reached when solute molecules cannot find enough water molecules to be surrounded by and from this point on, the destruction

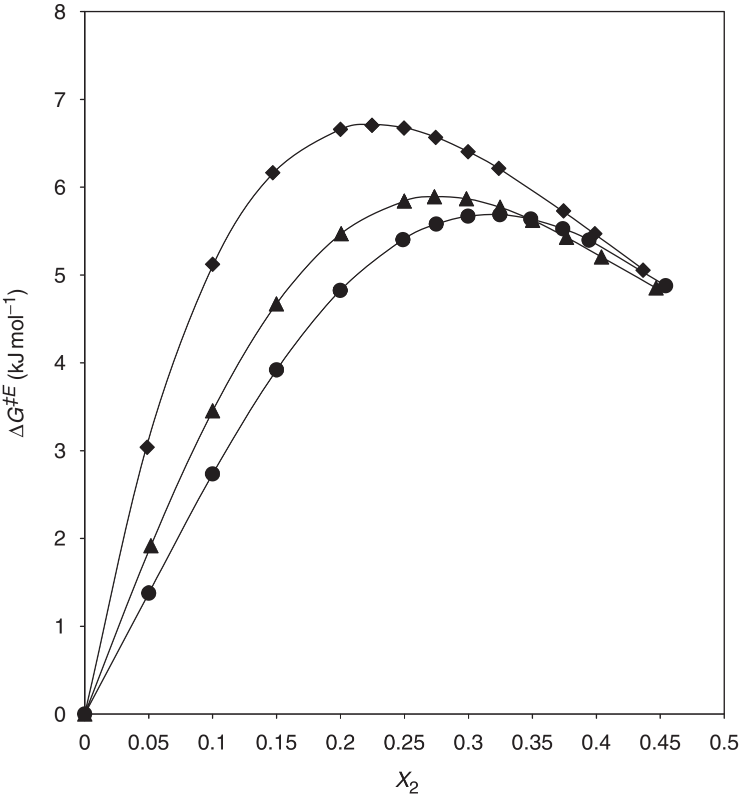

Figure 7. Comparison of excess free energy ($\Delta G^{\ddagger E}$) curves of the systems, W + ED (●), W + TMD (▲) and W + DMTMD (◆), against mole fraction of diamines (X_2) at 303.15 K.

of the aggregates begins. The maxima are therefore the result of a balance between the formation and decay of the aggregates formed by water molecules. Again, the hydrophobic effect increases with the increase of hydrocarbon moieties of diamines, while the hydrophilic effect, by which diamine–water association is formed through H-bonding, decreases. Andini *et al.* [19] showed that hydrophobic hydration varies according to hydrocarbon groups such as, $CH_3 > CH_2 > CH$. Hence by considering hydrophobic hydration, Andini's principle and the structural features of the diamines, it is possible to predict that the free energy and their maxima should vary in the following order: W + DMTMD > W + TMD > W + ED, which is in complete agreement with the present observations. The effect of temperature on $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$, particularly in the region at or around the maxima is significant (Figure 4 and 5). This may be due to the structures formed by hydrophobic hydration that are considered to be much more labile and thermally less stable than the normal water structure [27,28]. For the same reason, formation of species with increased disordered structures is possible in the process of activation and the species might require a large amount of energy for their passage in the activated state. This may be why large positive $\Delta H^{\ddagger E}$ and $\Delta S^{\ddagger E}$ are observed in our investigation. A portion of large $\Delta S^{\ddagger E}$ may also come from H-bonding between water and diamine due to the hydrophilic effect that is disrupted during the activation process.

As the concentration of solute increases, the free energy of the systems constantly declines. This may be due to the destruction of the aggregates formed by hydrophobic hydration. At increasingly higher concentration of diamines, it is thought that a new centrosymmetric species is formed that observe less resistance to flow and hence less energy of activation is required [29].

4. Conclusion

In the present article, thermodynamic activation parameters for viscous flow of very dilute aqueous ethylenediamine, trimethylenediamine and *N*,*N*-dimethyltrimethylenediamine have been studied between 303.15 and 323.15 K. These properties and their excess values have been found to increase rapidly in the very low concentration of diamines and then gradually decline as the concentration of diamine increases. It is thought that in very low composition of solutes, water molecules form a long-range structural aggregate around the hydrocarbon moieties of diamines, which cause rapid increase of the thermodynamic properties of the systems. In the higher concentration of diamines, the aggregates start to break down and the lowering of thermodynamic properties was observed. The maximum value for the $\Delta G^{\ddagger E}$ is found to follow the order $\mathrm{W+DMTMD > W+TMD > W+ED}$. This illustrates the increase of hydrophobic effect with the increase of hydrocarbon moieties of the systems.

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