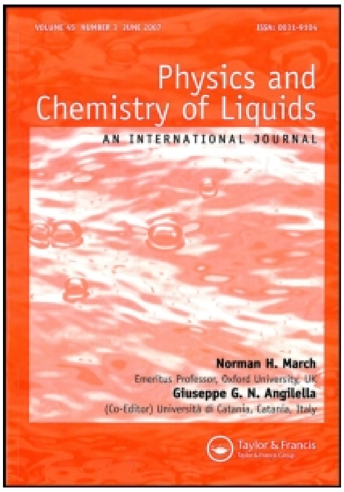

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Viscosity and Excess Viscosity of Dilute Aqueous Solutions of Ethylenediamine, Trimethylenediamine and N , N - Dimethyltrimethylenediamine

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VISCOSITY AND EXCESS VISCOSITY OF DILUTE AQUEOUS SOLUTIONS OF ETHYLENEDIAMINE, TRIMETHYLENEDIAMINE AND *N*,*N*-DIMETHYLTRIMETHYLENEDIAMINE

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Viscosities of the systems, water (W) + ethylenediamine (ED), W + trimethylenediamine (TMD) and W + *N*,*N*-dimethyltrimethylenediamine (DMTMD) were determined from 303.15 to 323.15 K and in the composition range, $0 \leq X_2 \leq 0.45$, where X_2 is the mole fraction of solutes. On addition of the solutes to water the viscosities increase sharply, pass through maxima and then decline; the heights of maxima vary as, W + DMTMD > W + TMD > W + ED. The maxima occur at X_2 0.225, 0.300 and 0.325 for the systems, W + DMTMD, W + TMD and W + ED, respectively. The position of maximum of a particular system remains unchanged with temperature. The rapidly ascending part of viscosity curves is accounted for by the combined effect of hydrophobic hydration and hydrophilic effect, while the declining part of the curves is thought to be due to predominance of hydrophobic interaction.

Keywords: Viscosity; Excess viscosity; Hydrophobic hydration; Ethylenediamine; Trimethylenediamine; *N*,*N*-dimethyltrimethylenediamine

1. INTRODUCTION

This is a part of our programme of studying molecular interactions through the measurement of volumetric and viscometric properties

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of binary liquid systems with special reference to aqueous solutions of hydrophobic solutes. Recently, we reported the volumetric and viscometric properties of aqueous solutions of isomers of butylamine [1,2]. We observed large volume contraction and large increase of viscosity in water-rich region for these systems. The results were found to be influenced strongly by the structural diversities of the hydrocarbon moieties of these amines. We thought then that it would be interesting to extend our work to aqueous diamine systems for a number of reasons. Firstly, as far as we are aware, hardly any work of this kind on aqueous diamines is available in literature. This prompted us to undertake the present studies with the hope of collecting new data *hitherto* not known. Secondly, we wished to see how the structural differences of the diamines influence the volumetric and viscometric properties of the systems. As these properties are thought to be strongly dependent upon the hydrophobic hydration and hydrophilic effect in water-rich region, we restricted the compositions of the systems within this region and collected large number of data at closely-spaced compositions, so that the variation of these properties as a function of solute concentration could be observed more precisely. In this paper, we report the viscosity data of the aqueous solutions of ethylenediamine, trimethylenediamine and *N*,*N*-dimethyltrimethylenediamine in the composition range of 0–0.45 mole fraction of diamines.

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%). 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.

The density was measured by a 25 mL specific gravity bottle previously calibrated with distilled water. An Ostwald U-tube viscometer of the British Standard Institution with sufficiently long efflux time was used so that no kinetic energy correction was necessary in viscosity measurement. The time of flow was recorded by a timer accurate up to ± 0.1 s. 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 maximum uncertainty in the measured viscosity was estimated to be ± 0.3%.

3. RESULTS AND DISCUSSION

The coefficients of viscosity, η, of three diamines, ethylenediamine (ED), trimethylenediamine (TMD) and *N*,*N*-dimethyltrimethylenediamine (DMTMD) are shown in Table I at different temperatures together with literature values for comparison. The viscosities and excess viscosities 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 organic compound), are listed in Table II. The viscosities of the systems are represented by a polynomial equation of the form,

$$\eta/\mathrm{kg\,m^{-1}\,s^{-1}} = \sum_{i=0}^{n} a_i X_2^i \tag{1}$$

TABLE I 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

Compounds	*Property*	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
ED	ρ	0.8997 0.8994^a	0.8952	0.8908	0.8861	0.8814	0.8767	0.8716
	η	16.03	14.35 15.4^a	12.99	11.91	10.80	9.86	9.04
TMD	ρ	–	0.8846	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

Ref. [3].

TABLE II Experimental viscosities, $\eta \times 10^4/\mathrm{kg\,m^{-1}\,s^{-1}}$ and excess viscosities, $\eta^E \times 10^4/\mathrm{kg\,m^{-1}\,s^{-1}}$ of aqueous diamines

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) + Ethylenediamine (X_2)										
0.0000	8.00	0.00	7.22	0.00	6.56	0.00	5.98	0.00	5.49	0.00
0.0500	13.68	5.48	12.08	4.68	10.75	4.03	9.64	3.50	8.70	3.07
0.0999	22.91	14.50	19.71	12.12	17.17	10.28	15.15	8.86	13.34	7.57
0.1500	36.35	27.74	30.59	22.81	26.02	18.96	22.43	15.98	19.50	13.58
0.1998	52.92	44.10	43.47	35.50	36.18	28.94	30.48	23.87	26.02	19.96
0.2488	67.97	58.94	54.84	46.68	44.89	37.47	37.33	30.56	31.44	25.22
0.2749	73.72	64.58	59.20	50.93	48.25	40.74	39.93	33.07	33.47	27.17
0.2997	76.78	67.53	61.33	52.96	49.97	42.36	41.14	34.20	34.39	28.01
0.3246	77.67	68.30	62.13	53.66	50.42	42.72	41.54	34.51	34.76	28.30
0.3488	76.70	67.22	61.33	52.77	49.87	42.08	41.17	34.05	34.40	27.87
0.3739	73.84	64.24	59.18	50.51	48.26	40.38	39.91	32.71	33.46	26.84
0.3944	70.20	60.51	56.43	47.67	46.21	38.25	38.40	31.12	32.34	25.65
0.4542	59.65	49.68	48.71	39.69	40.32	32.12	33.85	26.35	28.75	21.86
1.0000	12.99	0.00	11.91	0.00	10.80	0.00	9.86	0.00	9.04	0.00
Water (X_1) + Trimethylenediamine (X_2)										
0.0518	16.37	8.06	14.37	6.89	12.67	5.79	11.27	5.06	10.08	4.39
0.1000	29.91	21.33	25.34	17.60	21.74	14.62	18.87	12.45	16.50	10.61
0.1498	48.82	39.93	40.12	32.11	33.45	26.10	28.27	21.63	24.17	18.08
0.2004	67.62	58.41	54.46	46.16	44.67	37.05	37.14	30.27	31.32	25.02
0.2498	78.72	69.19	63.09	54.50	51.28	43.41	42.36	35.24	35.48	28.96
0.2734	80.88	71.20	64.73	56.00	52.68	44.68	43.51	36.28	36.46	29.84
0.2984	81.08	71.22	65.02	56.13	52.97	44.92	43.79	36.43	36.62	29.88
0.3248	79.18	69.14	63.64	54.59	51.99	43.78	43.07	35.59	36.19	29.33
0.3502	76.14	65.92	61.55	52.34	50.27	41.92	41.89	34.27	35.18	28.20
0.3766	71.21	60.79	57.74	48.36	47.54	39.04	39.72	31.96	33.54	26.43
0.4041	66.81	56.19	54.64	45.08	45.09	36.43	37.87	29.96	32.11	24.87
0.4467	59.11	48.18	48.71	38.86	40.68	31.75	34.45	26.31	29.35	21.89
1.0000	15.94	0.00	14.23	0.00	12.97	0.00	11.81	0.00	10.70	0.00
Water (X_1) + *N*,*N*-Dimethyltrimethylenediamine (X_2)										
0.0488	23.76	15.69	20.23	12.95	17.41	10.79	15.20	9.15	13.36	7.81
0.0999	50.10	41.96	40.70	33.34	33.59	26.91	28.16	22.05	23.93	18.32
0.1470	71.75	63.55	57.21	49.80	46.35	39.60	38.21	32.04	32.06	26.39
0.1743	79.60	71.36	63.15	55.70	50.89	44.10	41.76	35.56	34.85	29.15
0.1999	83.48	75.21	66.16	58.67	53.16	46.35	43.62	37.39	36.18	30.45
0.2247	83.78	75.48	66.43	58.91	53.56	46.71	43.87	37.60	36.35	30.59
0.2497	81.94	73.60	64.99	57.44	52.48	45.60	43.01	36.71	35.72	29.93
0.2744	77.87	69.50	62.16	54.58	50.23	43.32	41.32	35.00	34.44	28.62
0.2998	72.75	64.35	58.12	50.50	47.23	40.28	39.04	32.68	32.65	26.80
0.3238	67.28	58.84	54.16	46.51	44.23	37.26	36.72	30.33	30.81	24.93
0.3744	55.64	47.13	45.40	37.67	37.57	30.52	31.55	25.10	26.73	20.79
0.3988	50.44	41.90	41.43	33.68	34.48	27.41	29.05	22.56	24.75	18.77
0.4365	43.26	34.66	35.86	28.05	30.13	23.01	25.66	19.13	22.05	16.03
1.0000	9.41	0.00	8.62	0.00	7.93	0.00	7.31	0.00	6.78	0.00

The coefficients of this equation and r^2 are listed in Table III. The viscosities of the systems are plotted in Figs. 1–3 for the systems, W + ED, W + TMD and W + DMTMD, respectively, against X_2. Figure 4 shows the comparison of the viscosities of the three systems at 303.15 and 323.15 K. This clearly shows that the effect of temperature on viscosity is extremely large.

The excess viscosities, η^E, were calculated by using the following equation,

$$\eta^E = \eta - \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2), \tag{2}$$

where η is the measured viscosity of the mixtures, η_1 and η_2 are the viscosities of water and diamines, respectively, and X_1 and X_2 are the corresponding mole fractions. The excess viscosities are fitted to the polynomial equation of the type,

$$\eta^E/\mathrm{kg\,m^{-1}\,s^{-1}} = \sum_{i=1}^{n} a_i X_2^i \tag{3}$$

The coefficients of Eq. (3) and r^2 are listed in Table IV. The plots of η^E against X_2 are shown in Figs. 5–7. Figure 8 shows the comparison of excess viscosity curves at 303.15 and 323.15 K.

Examination of the viscosity and excess viscosity curves shows the following characteristics:

(a) Viscosities and excess viscosities for all systems increase rapidly on addition of diamines, pass through maxima and then decline.
(b) Both η and η^E show well-defined maxima at $X_2 = 0.3246$, 0.2984 and 0.2247, respectively, for W + ED, W + TMD and W + DMTMD.
(c) The heights of maxima of both η and η^E are found to be in the order, W + DMTMD > W + TMD > W + ED.
(d) The position of maxima of η and η^E for any particular system remains virtually unchanged with the change of temperature.

The ratio of maximum viscosities to ideal viscosities, η_{max}/η_{id}, ($\eta_{id} = \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2)$), at X_2 corresponding to η_{max}, have been found to be very high, ranging between 8 and 10, at 303.15 K for the systems. At other compositions the ratios are also found to be large, implying that the systems are highly non-ideal with respect

TABLE III Coefficients, a_i, of Eq. (1) expressing coefficient of viscosity, $\eta \times 10^4/\mathrm{kg\,m^{-1}\,s^{-1}}$ and the square of the regression coefficient, r^2 for the systems

Systems	*Temperature* K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	r^2
W + ED	303.15	7.968	137.67	− 1170.3	18,605	− 68,220	81,985	− 22,116	1.0000
	308.15	7.2019	109.55	− 750.58	13,390	− 51,206	64,529	− 20,060	1.0000
	313.15	6.5470	89.965	− 492.18	9879.6	− 39,520	52,681	− 19,098	1.0000
	318.15	5.9688	75.272	− 305.21	7260.7	− 30,640	43,365	− 17,987	1.0000
	323.15	5.4852	64.612	− 234.34	5983.8	− 26,625	40,898	− 20,028	1.0000
W + TMD	303.15	8.0029	154.39	− 1005.8	29,413	− 158,446	315,080	− 218,268	1.0000
	308.15	7.2206	128.59	− 607.26	20,517	− 113,144	226,990	− 158,059	0.9999
	313.15	6.5605	103.39	− 220.41	13,259	− 76,812	155,690	− 108,329	1.0000
	318.15	5.9800	85.355	16.531	8367.6	− 51,956	107,035	− 74,738	1.0000
	323.15	5.4887	73.314	83.154	5867.5	− 38,519	80,829	− 57,066	1.0000
W + DMTMD	303.15	8.0449	75.282	6639.7	− 37,351	59,961	3122.5	− 55,321	0.9999
	308.15	7.2517	87.858	4830.3	− 27,812	45,567	323.15	− 39,962	0.9999
	313.15	6.5803	91.925	3569.3	− 21,199	36,200	− 3754.3	− 272.19	0.9999
	318.15	5.9983	91.316	2697.4	− 16,695	30,482	− 8760.1	− 16407	0.9999
	323.15	5.5080	81.427	2245	− 14,969	32,470	− 23,775	− 554.05	0.9999

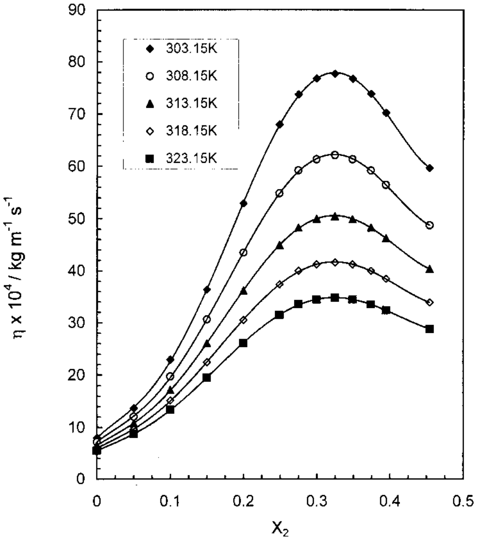


FIGURE 1 Viscosity as a function of mole fraction of ED (X_2) at different temperatures.

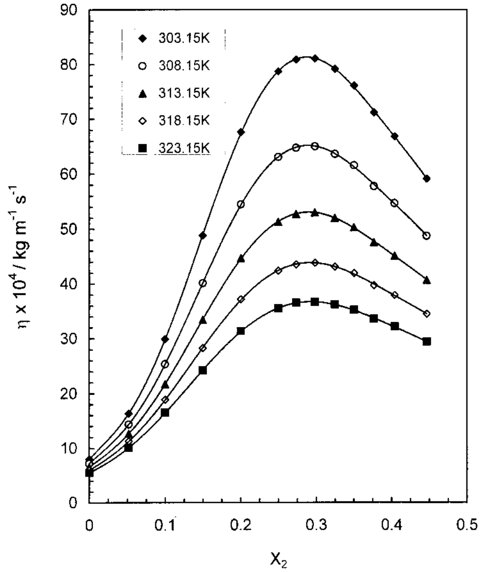


FIGURE 2 Viscosity as a function of mole fraction of TMD (X_2) at different temperatures.

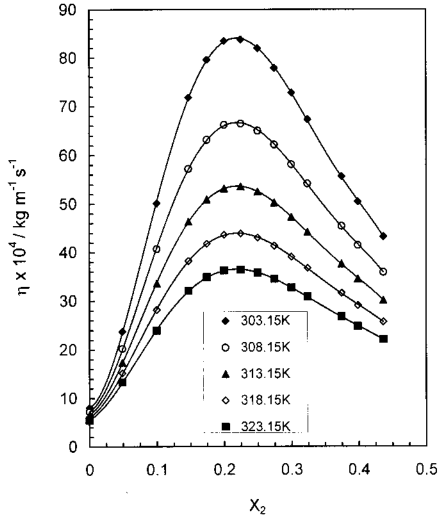


FIGURE 3 Viscosity as a function of mole fraction of DMTMD (X_2) at different temperatures.

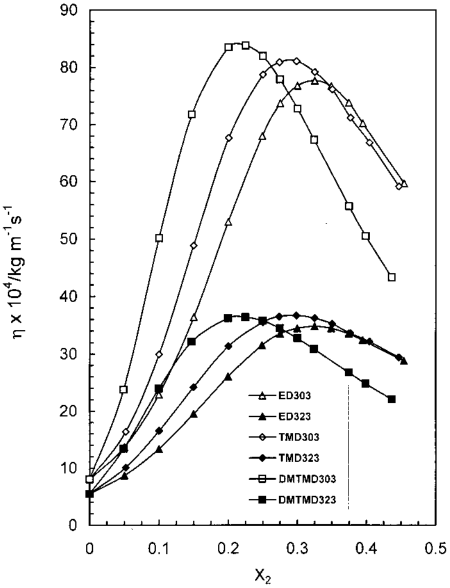


FIGURE 4 Comparison of viscosities of the systems W (X_1) + ED (X_2), + TMD (X_2), + DMTMD (X_2) at 303.15 K and 323.15 K.

TABLE IV Coefficients, a_i, of Eq. (3) expressing excess viscosity, $\eta^E \times 10^4/\mathrm{kg\,m^{-1}s^{-1}}$ and the square of the regression coefficient, r^2, for the systems

Systems	*Temperature* K	a_1	a_2	a_3	a_4	a_5	a_6	r^2
W + ED	303.15	131.75	− 1134.6	18,315	− 67,131	80,067	− 20,834	1.0000
	308.15	106.41	− 776.37	13,674	− 52,528	67,250	− 22,118	1.0000
	313.15	86.412	− 489.94	9870.8	− 39,541	52,816	− 19,255	1.0000
	318.15	71.48	− 293.92	7179.6	− 30,361	42,887	− 17,667	1.0000
	323.15	62.22	− 250.44	61,166	− 27,529	42,894	− 21,642	1.0000
W + TMD	303.15	148.02	− 989.33	29,247	− 157,743	313,673	− 217,199	1.0000
	308.15	123.87	− 615.64	20,573	− 113,380	227,458	− 158,411	0.9999
	313.15	94.546	− 142.65	12,595	− 74,104	150,514	− 104,608	1.0000
	318.15	80.421	30.576	8244.4	− 51,486	106,176	− 74,136	1.0000
	323.15	69.725	78.391	5956.7	− 38,912	81,609	− 57,645	1.0000
W + DMTMD	303.15	75.656	6613.4	− 37,160	59,260	4391.7	− 56,220	0.9999
	308.15	88.145	4803.3	− 27,610	44,821	1651.2	− 40,876	0.9999
	313.15	91.657	3555.3	− 21,114	35,948	− 3397.1	− 27,408	0.9999
	318.15	90.212	2699.3	− 16,729	30,663	− 9168.7	− 16,073	0.9999
	323.15	80.823	2238	− 14,935	32,402	− 23746	− 516.83	0.9999

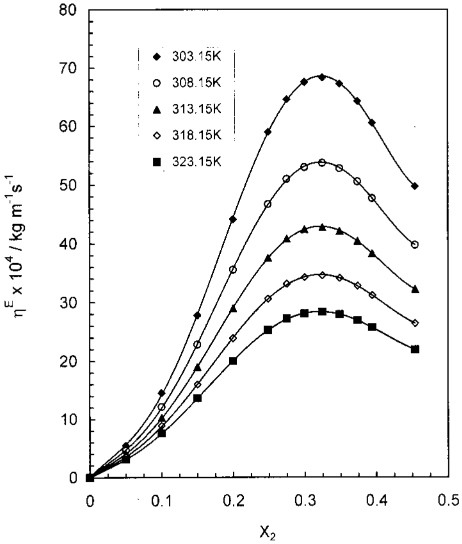


FIGURE 5 Excess viscosity as a function of mole fraction of ED (X_2) at different temperatures.

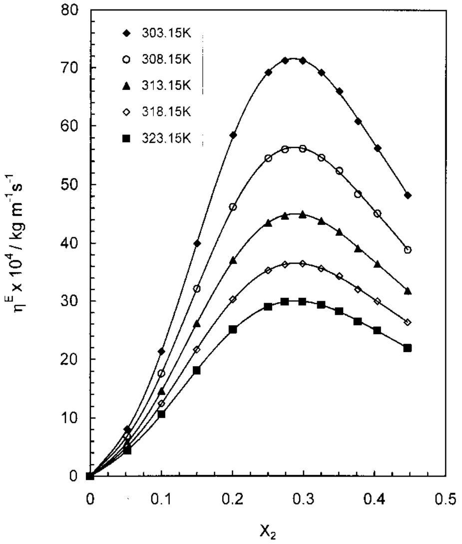


FIGURE 6 Excess viscosity as a function of mole fraction of TMD (X_2) at different temperatures.

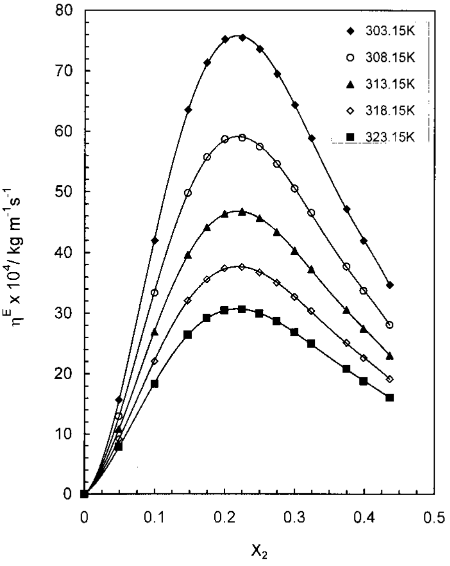


FIGURE 7 Excess viscosity as a function of mole fraction of DMTMD (X_2) at different temperatures.

to flow behaviour. The observed viscosities and excess viscosities over the range of composition studied are accounted for mainly by the following effects:

(a) Hydrophobic hydration of the diamines.
(b) Strong water–diamine interaction due to hydrophilic effect.
(c) Diamine–diamine interaction in the post-maximum viscosity region. This occurs as a result of the phenomenon known as hydrophobic interaction.

The rapidly ascending part of viscosity is thought to be due to combined effect of hydrophilicity and hydrophobicity. In the former, hydrogen bonding is thought to be formed by the polar group of the diamines with water, while in the latter, water molecules form a long range structural aggregates around the hydrocarbon moieties, known as hydrophobic hydration. This is considered to be the major factor which severely deters the motion of the fluids. With continued addition of solutes such aggregates increase in size or in number, and hence the rapid and unusually large increase of η and η^E. Still on further increase

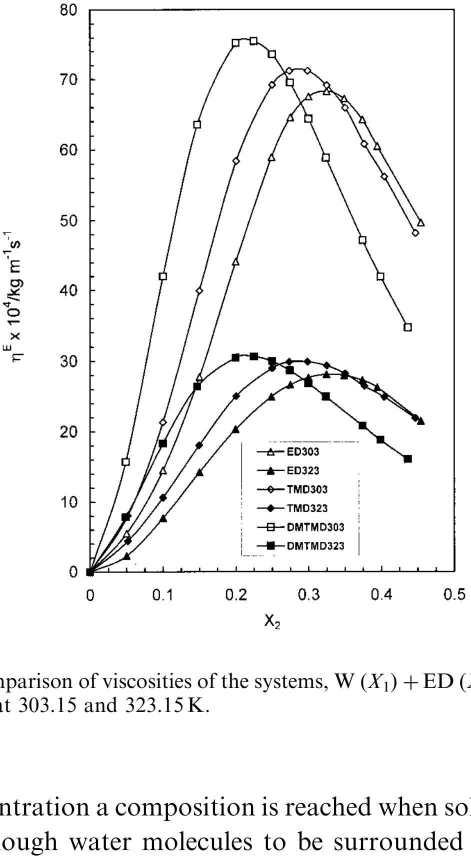
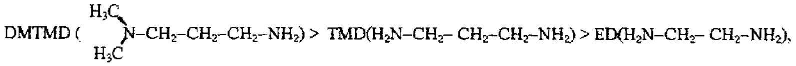


FIGURE 8 Comparison of viscosities of the systems, W (X_1) + ED (X_2), + TMD (X_2), + DMTMD (X_2) at 303.15 and 323.15 K.

of 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 of the aggregates begins, giving away to the formation of diamine–diamine associates – a kind of association known as hydrophobic interaction. This causes the viscosity to decline. The maxima may be regarded as a balance mainly between two opposing effects – formation and destruction of the aggregates of water molecules. This behaviour of viscosity is typical of hydrophobic solutes, such as acetone [4], amines [2], mono- and disubstituted amides [5,6], alcohols [7–10], glycol ethers [11], dimethylsulfoxide, tetrahydrofuran, 1,4-dioxane [12], *n*-alkoxy ethanols [13], only to mention a few.

The hydrophobic effect obviously 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.* [14] showed that hydrophobic effect varies according to hydrocarbon groups as, $CH_3 > CH_2 > CH$. Assuming that the major cause for the large increase of viscosity as due to hydrophobic hydration and considering in conjunction Andini's principle and structural aspects of the diamines, as shown below, it is possible to predict that the viscosities and their maxima should vary in the following order,



$$\text{DMTMD}\,(\overset{\text{H}_3\text{C}}{\underset{\text{H}_3\text{C}}{\text{N}}}\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{–NH}_2) > \text{TMD}(\text{H}_2\text{N–CH}_2\text{–CH}_2\text{–CH}_2\text{–NH}_2) > \text{ED}(\text{H}_2\text{N–CH}_2\text{–CH}_2\text{–NH}_2),$$

which is in complete agreement with experimental observation.

The water–water aggregates formed as a result of hydrophobic effect are considered to be much more labile and thermally less stable than the water–water association in normal water structure [15,16]. The thermal effect on viscosity is thus expected to be more apparent with systems which are more hydrophobic in nature, that is, having the capacity of forming larger aggregates of water structure. The depressions of viscosity at compositions corresponding to maximum viscosities, $|\Delta\eta_{\max}|$, are found to be, 47.43, 44.46 and 43.27 ($10^{-4}\,\text{kg}\,\text{m}^{-1}\text{s}^{-1}$) for the systems, W + DMTMD, W + TMD and W + ED, respectively, in the range of temperature, 303.15–323.15 K. The values are indeed very large and are in full concordance with the order as expected.

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