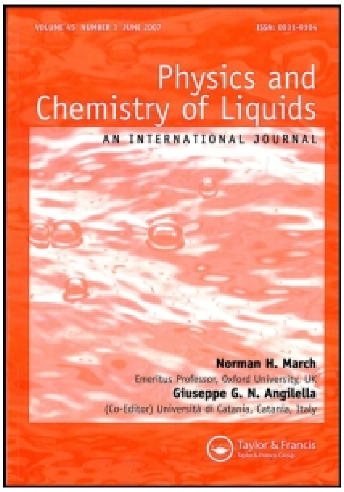

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VOLUMETRIC AND VISCOMETRIC PROPERTIES OF AQUEOUS SOLUTIONS OF *N*-METHYLFORMAMIDE, 1,2-DIAMINOPROPANE AND 2-METHYLPROPANE-2-OL

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Density and viscosity of aqueous solutions of *N*-methylformamide (NMF), 1,2-diaminopropane (DAP) and 2-methylpropane-2-ol (MPL) have been measured precisely over the entire composition range (i.e., $1 \geq x_2 \geq 0$) at five equidistant temperatures ranging from 298.15 to 318.15 K. Excess molar volume (V_m^E) and excess viscosity (η^E) have been calculated from measured density and viscosity data, respectively. Excess molar volume and excess viscosity have been fitted by the least squares method to the four parameters Redlich–Kister equation. The results have been interpreted on the basis of (i) interstitial incorporation, (ii) breakdown of the structure of pure liquids, (iii) hydrophobic hydration, (iv) hydrophobic interaction and (v) association between dissimilar liquids.

Keywords: Aqueous alcohol solutions; Viscosity; Interstitial incorporation; Hydrophobic interaction

1. INTRODUCTION

The physico-chemical properties of liquid mixtures are quite different from those of the pure components. Advancement on the theories of solutions was made to relate the physico-chemical properties of the mixture to measurable macroscopic properties of the pure liquid components. The theoretical attempts made by various workers [1–6] could explain several distinctive features of liquid mixtures. Despite numerous endeavours none of the proposed models has been unequivocally accepted and a theoretical model, which can explain quantitatively all the phenomena in liquid systems, is yet to be established.

The changes in the physical properties due to the mixing of two or more liquids are thought of arising from interactions between the constituent units (molecules), association, accommodation of one liquid into other, compound formation etc. Conversely, physico-chemical properties can provide us with the information about various interactions when two liquids are mixed together. A better understanding of the physico-chemical properties of liquid mixtures is, therefore, of vital importance in

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the field such as solution chemistry, because these properties are the eventual reflections of structural changes associated with liquid mixtures.

The thermodynamic and transport properties of liquid–liquid mixtures are different from those expected from additivity rule. Such studies may furnish important information regarding molecular interaction. Of the various thermodynamic and transport properties for the mixing process, the volume change and viscosity change on mixing at constant pressure are most interesting. Therefore, the volumetric and viscometric studies have entered in a phase of renewed interest and development.

The experimental data on various macroscopic properties give useful information for proper understanding of specific interaction between the components and structure of the solution and is also useful in providing a guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the proposed model on which theoretical treatments may be based.

The volumetric and viscometric study attracted considerable interest and will continue to be of interest simply because the experiments are relatively easy to perform with great precision and the volume and viscosity change on mixing are sensitive indicators to the accuracy of theories of solution. Moreover, precise experimental data are essential for the advancement of the theoretical models of solutions. With this in view, the volumetric and viscometric investigation of water + *N*-methylformamide (NMF), water + 1,2-diaminopropane (DAP) and water + 2-methylpropane-2-ol (MPL) mixtures, have been undertaken and are presented in the present communication. The density and viscosity of the above systems have been measured. The density and viscosity data have been used to calculate various thermodynamic functions of liquid mixtures, like molar volume (V_m), excess molar volume (V_m^E) and excess viscosity (η^E). The results have been discussed in the light of the latest development in this field.

2. EXPERIMENTAL

N-Methylformamide (MERCK-Schuchardt, purity (GC) > 99%), DAP (Fluka Chemika, assay (GC) > 98%) and MPL (BDH Chemicals Ltd Poole England, purity > 99%) were used without further purification. Water used for the preparation of the studied binary systems were de-ionized and redistilled (conductance $5 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$). Density of the pure liquid and liquid–liquid mixtures were measured using high precision vibrating tube digital densitimeter (DMA-5000, Anton Paar, Austria). At constant temperature, the natural vibration period of the U-tube is related to the density [7] of liquid filling the tube. In the latest version of Anton Paar digital densitimeter (DMA-5000), the natural vibration period is automatically converted into the density value and displayed directly on the LC display monitor of the densitimeter. The temperature of the sample tube is controlled to ± 0.001 K. Viscosity of various solutions was measured using a modified Cannon-Ubbelohde suspended level viscometer. The time of flow between the marks was determined with the help of an electronic stopwatch capable of reading up to 0.01 s. Equilibration time of about 15–20 min was given in order to allow the viscometer and the liquid inside to attain the temperature of the thermostat that was maintained constant with a precision of ± 0.05°C. An electronic balance with an accuracy of ± 0.1 mg was used for weighing.

3. RESULTS AND DISCUSSION

Densities and Volume

Densities of the aqueous solution of NMF, DAP and MPL (tert-butyl alcohol) were measured at 298.15, 303.15, 308.15, 313.15 and 318.15 K over the entire composition range ($0 \leq x_2 \leq 1$), where x_2 represents the mole fraction of organic component, which was considered as solute. The variation of density with mole fraction of organic solute (x_2) is shown in Fig. 1. The density (ρ) *vs* x_2 plots demonstrate that the density of water + NMF system increases with the increase in mole fraction of NMF and reaches a maximum value, after which it decreases almost linearly. The density of water + DAP system decreases with an increase in x_2, the mole fraction of DAP. The rate of decrease of density with x_2 in low ($x_2 < 0.3$) and high ($x_2 > 0.6$) mole fraction region is comparatively slower than that in the region $0.3 < x_2 < 0.6$. The density of water + MPL system shows an exponential decrease when x_2 is increased.

An idea about the nature of organic liquids is required in order to understand the behaviour of density *vs* x_2 plots. The density values of NMF, DAP and MPL

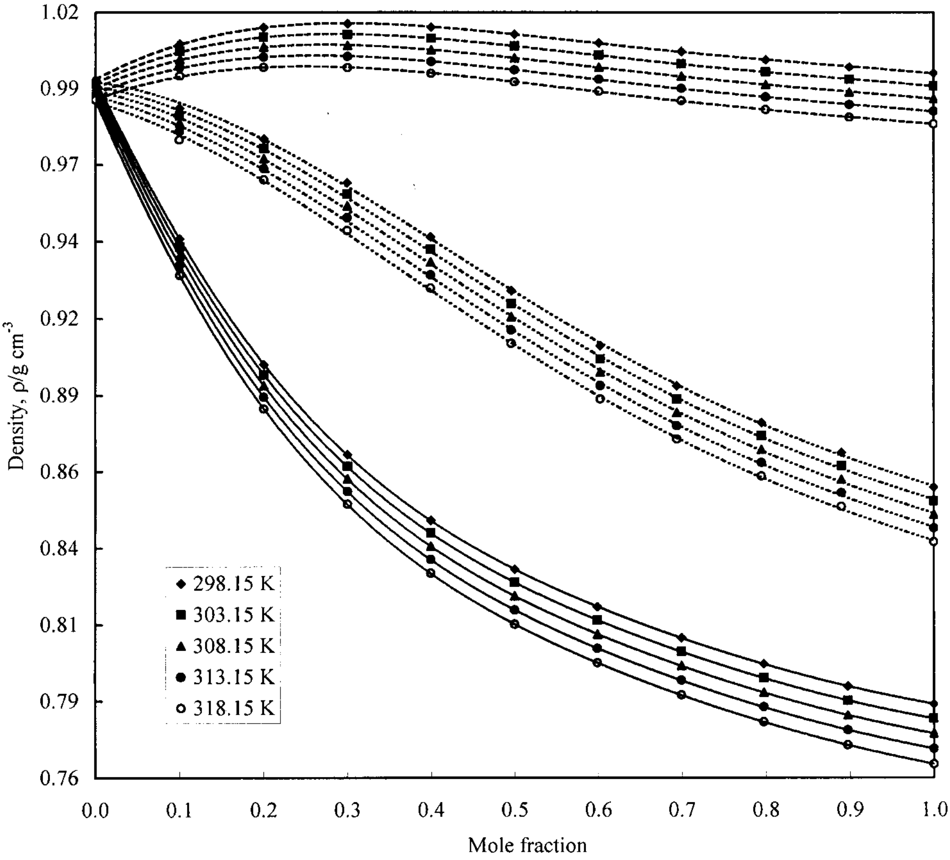

FIGURE 1 Variation of density with mole fraction of 2-methylpropane-2-ol (solid line), *N*-methylformamide (long dashed line) and 1,2-diaminopropane (dashed line).

(0.999178, 0.858471 and 0.784962 g cm^{-3} respectively at 298.15 K) reveal that NMF is more associated than the other two compounds. Of these two DAP is more associated than MPL. The high density of NMF may be attributed to the hydrogen bonding through $>$C=O and $>$NH groups. DAP may form very weak hydrogen bond, through –NH$_2$ groups. In MPL, three electron donating methyl groups attached to the carbon atom containing the –OH group, strongly suppress the hydrogen bond forming tendency of alcoholic oxygen atom by decreasing its polarity and steric hindrance. These effects make MPL less associated than DAP.

When NMF is added to water, hydrogen bond formation takes place between these two components and the tetrahedral structure of water breaks down forming dense monomer which make positive contribution to the density of the mixture. The increase in density due to these two effects outweighs the decrease in density due to the hydrophobic –CH$_3$ group. After the maximum, as the mole fraction of NMF increases the number of moles of water molecules decreases and hence association through hydrogen bonding, resulting a linear decrease in ρ with the increase in x_2 of NMF. The temperature co-efficient is negative for all the studied liquids. The higher magnitude of $d\rho/dT$ for NMF than that for DAP and MPL reveals the associated nature of NMF.

Excess molar volume (V_m^E) calculated from the experimentally determined density data have been presented in Table I along with the density value. The variation of excess molar volume as a function of mole fraction of non-aqueous components has been shown in Fig. 2. The V_m^E data have been fitted by least squares method to the Redlich–Kister equation

$$V_m^E = x_2(1 - x_2)\sum_{i=o}^{3} A_i(2x_2 - 1)^i \tag{1}$$

where, x_2 represents the mole fraction of non-aqueous components. The fitting parameters (A_0, A_1, A_2, A_3), the standard deviation of fit and the fitting values of V_m^E have been tabulated in Table III.

The excess molar volumes (V_m^E) of the studied systems are negative at all the five temperatures. The variation of V_m^E with the mole fraction of NMF, DAP and MPL is found to exhibit parabolic curves with minima around $x_2 \approx 0.4$, 0.4 and 0.28 at 298.15 K for water + NMF, water + DAP and water + MPL systems, respectively. The magnitude of V_m^E is different for different systems. The V_m^E values at minima for water + NMF, water + DAP and water + MPL at 298.15 K follow the order:

$$\text{water} + \text{DAP} > \text{water} + \text{MPL} > \text{water} + \text{NMF}$$

The temperature co-efficient of V_m^E i.e. dV_m^E/dT is positive for all the selected systems.

The negative excess molar volumes for all the three systems indicate that mixing of two liquids, to form a binary mixture, results in volume contraction. Similar results have been reported [8–14] for a good number of systems involving polar–polar, polar–non-polar and other systems in which one of the components is water. The negative V_m^E value for the binary aqueous mixtures have been interpreted by the early workers as due to the following factors:

(i) interstitial incorporation;
(ii) compression of solute molecules by strong cohesive forces of water;

TABLE I Experimental densities, ρ and excess molar volume in $g\,cm^{-3}$ and $cm\,mol^{-1}$ respectively of aqueous systems for different molar ratios at different temperatures

x_2	*298.15* K		*303.15* K		*308.15* K		*313.15* K		*318.15* K	
	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
(x_1) *Water* + (x_2) *N-methylformamide system*										
1.0000	0.999178	0.0000	0.994824	0.0000	0.990469	0.0000	0.986113	0.0000	0.981759	0.0000
0.8997	1.001358	−0.1236	0.997044	−0.1215	0.992721	−0.1193	0.988395	−0.1174	0.984060	−0.1152
0.8000	1.003850	−0.2446	0.999581	−0.2403	0.995306	−0.2365	0.991016	−0.2327	0.986715	−0.2289
0.6995	1.006618	−0.3573	1.002420	−0.3515	0.998199	−0.3458	0.993986	−0.3416	0.989755	−0.3375
0.6006	1.009591	−0.4559	1.005460	−0.4478	1.001302	−0.4401	0.997166	−0.4348	0.992991	−0.4291
0.4998	1.012536	−0.5281	1.008513	−0.5183	1.004465	−0.5095	1.000392	−0.5016	0.996291	−0.4942
0.4001	1.015040	−0.5618	1.011135	−0.5495	1.007205	−0.5387	1.003241	−0.5289	0.999237	−0.5197
0.3002	1.016130	−0.5336	1.012457	−0.5207	1.008739	−0.5092	1.004973	−0.4988	1.001150	−0.4890
0.1999	1.014852	−0.4362	1.011558	−0.4241	1.008216	−0.4139	1.004800	−0.4047	1.001309	−0.3962
0.1000	1.009292	−0.2566	1.006724	−0.2494	1.004034	−0.2431	1.001220	−0.2374	0.998290	−0.2322
0.0000	0.997043	0.0000	0.995645	0.0000	0.994029	0.0000	0.992212	0.0000	0.990208	0.0000
(x_1) *Water* + (x_2) *1,2-diaminopropane system*										
1.0000	0.858471	0.0000	0.853844	0.0000	0.849203	0.0000	0.844545	0.0000	0.839869	0.0000
0.8901	0.870382	−0.7629	0.865822	−0.7709	0.861210	−0.7761	0.856600	−0.7836	0.851963	−0.7908
0.7949	0.880590	−1.2341	0.876073	−1.2446	0.871481	−1.2511	0.866907	−1.2615	0.862292	−1.2709
0.6940	0.893147	−1.6835	0.888631	−1.6919	0.884113	−1.7027	0.879542	−1.7121	0.874956	−1.7231
0.6024	0.906804	−2.0577	0.902292	−2.0639	0.897808	−2.0746	0.893269	−2.0845	0.888682	−2.0941
0.4957	0.925434	−2.3922	0.920981	−2.3975	0.916562	−2.4076	0.912102	−2.4185	0.907521	−2.4256
0.3995	0.943564	−2.4961	0.939323	−2.5048	0.935045	−2.5151	0.930707	−2.5258	0.926276	−2.5353
0.2998	0.961860	−2.3199	0.957897	−2.3281	0.953932	−2.3398	0.949938	−2.3538	0.945633	−2.3591
0.2002	0.976760	−1.7935	0.973449	−1.8056	0.970081	−1.8198	0.966605	−1.8343	0.962840	−1.8432
0.0997	0.987327	−0.9635	0.984774	−0.9710	0.982197	−0.9819	0.979403	−0.9912	0.976438	−0.9998
0.0000	0.997043	0.0000	0.995645	0.0000	0.994029	0.0000	0.992212	0.0000	0.990208	−0.0000
(x_1) *Water* + (x_2) *2-methylpropane-2-ol system*										
1.0000	0.784962	0.0000	0.780015	0.0000	0.774979	0.0000	0.769856	0.0000	0.764638	0.0000
0.8976	0.790986	−0.1635	0.786134	−0.1701	0.781196	−0.1776	0.776176	−0.1862	0.771073	−0.1967
0.7978	0.798585	−0.3772	0.793825	−0.3887	0.788953	−0.3989	0.783990	−0.4097	0.778966	−0.4249
0.6995	0.807438	−0.5636	0.802768	−0.5776	0.797947	−0.5874	0.793035	−0.5981	0.788035	−0.6106
0.5989	0.818020	−0.6993	0.813452	−0.7138	0.808694	−0.7221	0.803842	−0.7313	0.798917	−0.7437
0.5001	0.830741	−0.7941	0.826280	−0.8068	0.821666	−0.8172	0.816936	−0.8274	0.812100	−0.8385
0.3997	0.847398	−0.8654	0.843097	−0.8765	0.838648	−0.8865	0.834086	−0.8971	0.829435	−0.9099
0.3000	0.869754	−0.9106	0.865764	−0.9234	0.861577	−0.9336	0.857266	−0.9444	0.852868	−0.9576
0.2001	0.900527	−0.8757	0.897001	−0.8882	0.893305	−0.9004	0.889387	−0.9101	0.885413	−0.9234
0.1000	0.942845	−0.6464	0.940109	−0.6562	0.937225	−0.6671	0.933994	−0.6734	0.930647	−0.6812
0.0000	0.997043	0.0000	0.995645	0.0000	0.994029	0.0000	0.992212	0.0000	0.990208	0.0000

(iii) hydrophobic hydration;
(iv) loss of freedom of internal rotation of solute molecules within the solvent water structure.

The structure of binary aqueous mixture is too complex to be described. Therefore, a large number of factors should be taken into consideration to account for the volume change on mixing of two liquids. The volume change on mixing two components can be thought of as arising from the following factors:

(i) structural changes of the components forming the mixture;
(ii) interaction between the component molecules;
(iii) dipole–dipole interaction, dipole-induced–dipole interaction and van der Waals force between component molecules;
(iv) hydrophobic interaction and hydrophobic hydration;

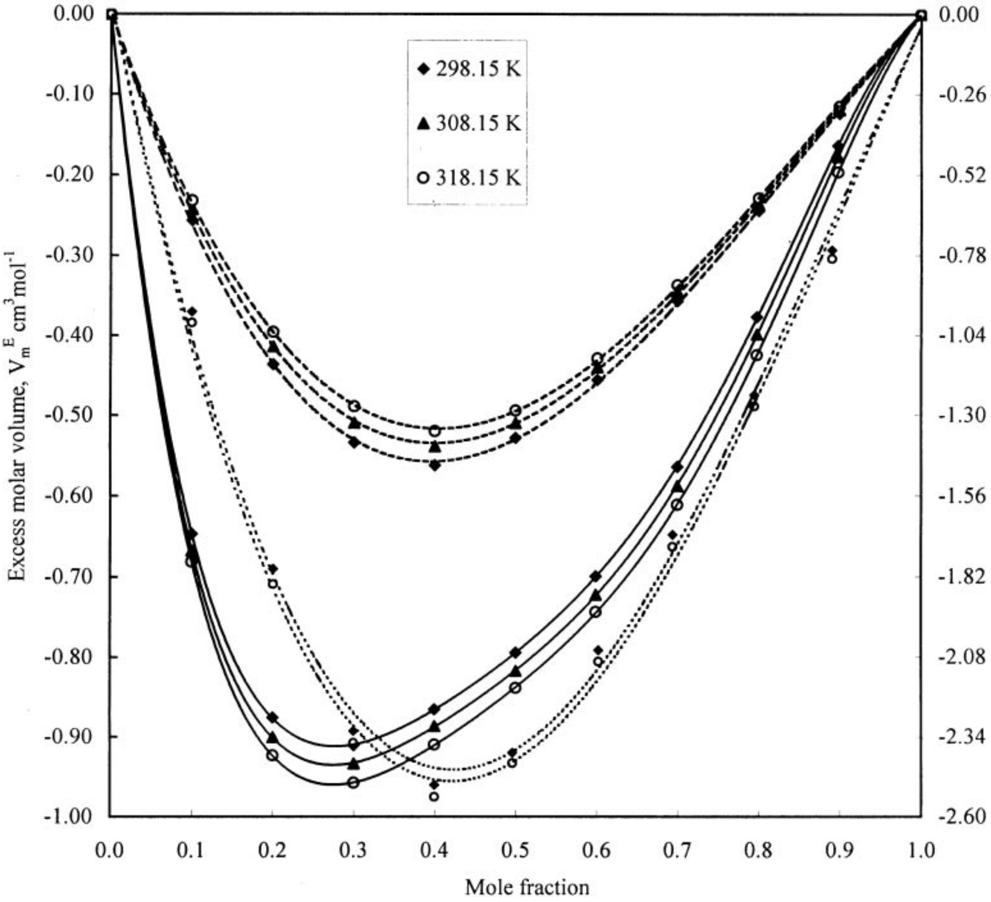

FIGURE 2 Variation of excess molar volume with mole fraction of 2-methylpropane-2-ol (solid line and left scale), *N*-methylformamide (long dashed line and left scale) and 1,2-diaminopropane (dashed line and right scale).

(v) interstitial incorporation of one species into the network structure of the other component;
(vi) favourable geometric fitting; etc.

In order to interpret the volumetric behaviour of aqueous binary liquid mixtures a detailed knowledge of solute–solute, water–water and water–solute interactions seems to be essential. Structure of water plays an important role in explaining the volumetric properties of aqueous mixture. According to the flickering cluster model [15,16] the tetrahedral hydrogen bonded clusters, called bulky water, are in dynamic equilibrium with the monomers, called the dense water. In liquid water short-lived clusters are surrounded by non-hydrogen bonded monomers. Introduction of solute molecules into water increases the average life of the clusters or the number of non-bonded dense monomers. Solute of the first kind, called structure maker, results in volume expansion. While, the solute of the second kind, called structure breaker, results volume contraction The negative V_m^E value i.e. volume contraction of all the three studied systems indicates that all the three substances may behave as water structure breaker. In forming binary aqueous mixture, destruction of structure of the pure liquid takes place before the interaction between the two different molecules comes into existence. The volume contraction due to the interaction between associated liquids and water should be less than that between less associated liquids and water. This explains the less volume contraction of water + NMF mixture. Three methyl-groups (hydrophobic) attached to the carbon atom containing the –OH group, in addition to their water structure making nature decreases the hydrogen bond forming tendency of –OH group with water rendering less volume contraction, which explains the less volume contraction of water + MPL compared to water + DAP.

The solute molecules may occupy the void spaces within the tetrahedral hydrogen bonded clusters of liquid water as proposed by the flickering cluster model [15] and a negative change in volume results from such occupation. Volume contraction due to interstitial incorporation becomes more effective for smaller solute molecules. Conversely, incorporation of relatively small water molecules in the structural void space of solute network may take place in solute rich region. An associated liquid has minimum void space to accommodate water molecules within its structural network. This also accounts for a small volume contraction for water + NMF system. Accommodation of water molecules in MPL is less favoured compared to that in DAP. The volume contraction due to the interstitial incorporation is, therefore, expected to be maximum in water + DAP, followed by water + MPL and water + NMF. Our observation is in full agreement with this order.

Hydrophobic hydration and hydrophobic interactions play an important role in determining the volumetric behaviour of binary aqueous mixture. Non-polar solutes and polar solutes containing non-polar (hydrocarbon) chain enhance and stabilize the tetrahedral structure of water. Such stability results from the fact that the neighbouring hydrophobic solute/hydrophobic part of polar solute protects the parts of the boundaries of the cluster from cluster disrupting forces. An ice-like patch forms readily in a volume element bound by non-polar solute or non-polar part of solute and once formed has a longer half-life leading to an extra structure. This situation is referred to as hydrophobic hydration where highly structured water molecules surround the solute molecules. In the water rich region, the hydrophobic part of the solutes form hydrophobic hydration sheath around it. As the solute concentration increases, the 'hydrophobic interaction' becomes inevitable. The tendency of non-polar groups to adhere one another in an aqueous environment is known as hydrophobic interaction or hydrophobic bond [17]. Hydrophobic interaction leads to disruption of hydrophobic hydration and brings volume contraction due to formation of dense water monomers.

According to the co-sphere overlap model, the hydrophobic interactions between the non-polar parts of solute molecules having hydration sphere resulting in a disruption of co-sphere around both the solute molecules and water molecules from structured co-sphere are transferred to the dense bulk yielding a volume shrinkage. Thus large hydrophobic group or large number of hydrophobic groups render volume contraction due to hydrophobic interaction. According to this concept, the volume contraction should be the maximum in water + MPL system. But three methyl groups to the same carbon minimizes the hydrophobic hydration around them and makes V_m^E less negative than that in water + DAP system.

The overall V_m^E values arise from the collective effect of all those factors upon which the volume of binary mixture depends. It is difficult to differentiate the separate contribution of each effect. The observed order of V_m^E

$$\text{water} + \text{DAP} > \text{water} + \text{MPL} > \text{water} + \text{NMF}$$

may, therefore, be attributed to the collective effect of all the factors.

The V_m^E of all the binary mixtures increase i.e. V_m^E values become less negative with the increase in temperature. The positive temperature co-efficient demonstrates that as the temperature increases the association of the components decreases due to thermal agitation of the molecules. The hydrogen bonded linkage between the solute and the solvent molecules breaks at higher temperature. This observation is in agreement with the findings of Neal and Goring [18].

Viscometric Properties

The co-efficient of viscosity (η) of the binary systems, water + NMF, water + DAP and water + MPL was determined at 298.15, 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. The excess viscosity η^E was calculated from the viscosity data. The η^E *vs* x_2 data were fitted by least squares method to the Redlich–Kister equation of the form

$$\eta^E = x_2(1 - x_2)\sum_{i=0}^{3} A_i(2x_2 - 1)^i \tag{2}$$

The viscosity (η) and excess viscosity (η^E) are listed in Table II. The fitting parameters (A_0, A_1, A_2, A_3), the standard deviation of fit and the fitting values of η^E have been tabulated in Table III.

The variation of η against x_2 is shown in Fig. 3. It is seen from the figure that η values of all the systems increases with the increase in x_2 and reaches up to a maximum value after which η decreases. The maxima were observed at $x_2 \approx 0.4$, 0.3 and 0.3 for water + NMF, water + DAP and water + MPL systems respectively. In all the cases, increase in temperature decreases η rapidly.

The excess viscosity of all the selected systems is positive over the whole composition range and at all the five temperatures. The η^E *vs* x_2 curve (Fig. 4) are upper convex having maxima at $x_2 \approx 0.35$ for water + NMF, $x_2 \approx 0.3$ for water + DAP and $x_2 \approx 0.3$ for water + MPL system.

Addition of NMF, DAP and MPL into water shows a sharp increase of viscosity in the water rich region. This indicates that enforcement of structure makes the mixtures more viscous and yields a high η value, which increases with an increase in solute concentration. Such structure enforcement may arise from

(i) break down of the original structure of pure liquids;
(ii) interstitial incorporation of solute molecules;
(iii) hydrophobic hydration and hydrophobic interaction;
(iv) association between dissimilar molecules.

TABLE II Experimental viscosities, η and excess viscosities, η^E in centipoises (cP) of aqueous systems for different molar ratios at different temperatures

x_2	*298.15* K		*303.15* K		*308.15* K		*313.15* K		*318.15* K	
	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
(x_1) *Water* + (x_2) *N-methylformamide system*										
1.0000	1.7465	0.0000	1.5803	0.0000	1.4342	0.0000	1.3057	0.0000	1.1914	0.0000
0.8997	1.7808	0.1485	1.6094	0.1338	1.4588	0.1205	1.3268	0.1087	1.2100	0.0985
0.8000	1.8364	0.3101	1.6581	0.2798	1.5016	0.2523	1.3640	0.2272	1.2426	0.2052
0.6995	1.9023	0.4759	1.7122	0.4255	1.5462	0.3805	1.4006	0.3403	1.2725	0.3048
0.6006	1.9748	0.6404	1.7724	0.5699	1.5899	0.5011	1.4365	0.4464	1.3040	0.4003
0.4998	2.0308	0.7840	1.8180	0.6955	1.6361	0.6204	1.4719	0.5485	1.3305	0.4878
0.4001	2.0438	0.8780	1.8047	0.7562	1.6076	0.6594	1.4397	0.5780	1.3000	0.5134
0.3002	1.9670	0.8771	1.7280	0.7488	1.5320	0.6470	1.3661	0.5620	1.2220	0.4880
0.1999	1.7538	0.7351	1.5392	0.6249	1.3627	0.5368	1.2152	0.4650	1.0840	0.3992
0.1000	1.3836	0.4313	1.2186	0.3647	1.0828	0.3119	0.9687	0.2687	0.8710	0.2320
0.0000	0.8903	0.0000	0.7975	0.0000	0.7195	0.0000	0.6532	0.0000	0.5963	0.0000
(x_1) *Water* + (x_2) *1,2-diaminopropane system*										
1.0000	1.4813	0.0000	1.3144	0.0000	1.1746	0.0000	1.0582	0.0000	0.9597	0.0000
0.8901	1.9747	0.5740	1.7523	0.5081	1.5081	0.3951	1.3374	0.3338	1.1994	0.2886
0.7949	2.8817	1.5473	2.4255	1.2391	2.0976	1.0353	1.8136	0.8551	1.5845	0.7141
0.6940	4.3495	3.0819	3.5663	2.4383	3.0667	2.0557	2.6030	1.6900	2.2298	1.4001
0.6024	6.0046	4.7948	4.9150	3.8374	4.1783	3.2117	3.5159	2.6424	2.9827	2.1885
0.4957	8.0367	6.8908	6.6486	5.6270	5.5907	4.6733	4.6900	3.8603	3.9614	3.2065
0.3995	9.5460	8.4549	7.9390	6.9653	6.6327	5.7575	5.5552	4.7632	4.6758	3.9546
0.2998	10.2359	9.1988	8.5418	7.6154	7.1206	6.2872	5.9563	5.2015	4.9931	4.3054
0.2002	9.4584	8.4726	7.9006	7.0192	6.6052	5.8115	5.5220	4.8026	4.6107	3.9548
0.0997	6.5271	5.5905	5.4786	4.6404	4.6254	3.8699	3.8784	3.1930	3.2373	2.6120
0.0000	0.8903	0.0000	0.7975	0.0000	0.7195	0.0000	0.6532	0.0000	0.5963	0.0000
(x_1) *Water* + (x_2) *2-methylpropane-2-ol system*										
1.0000	4.3128	0.0000	3.3193	0.0000	2.6137	0.0000	2.0988	0.0000	1.7112	0.0000
0.8976	4.3517	0.6824	3.3804	0.5121	2.6823	0.3920	2.1675	0.3051	1.7766	0.2405
0.7978	4.3994	1.2646	3.4511	0.9633	2.7632	0.7495	2.2473	0.5897	1.8480	0.4653
0.6995	4.5697	1.8853	3.5944	1.4320	2.8811	1.1073	2.3457	0.8679	1.9366	0.6900
0.5989	4.7516	2.4612	3.7493	1.8758	3.0135	1.4556	2.4595	1.1453	2.0300	0.9088
0.5001	4.9257	2.9659	3.8966	2.2694	3.1364	1.7649	2.5623	1.3912	2.1208	1.1105
0.3997	5.0222	3.3494	3.9829	2.5727	3.2206	2.0157	2.6327	1.5912	2.1847	1.2759
0.3000	4.9389	3.5097	3.9353	2.7121	3.1860	2.1265	2.5869	1.6598	2.1850	1.3668
0.2001	4.4562	3.2354	3.5477	2.4868	2.9030	1.9716	2.3919	1.5668	1.9998	1.2635
0.1000	3.1938	2.1513	2.5782	1.6585	2.1317	1.3132	1.7895	1.0554	1.5276	0.8650
0.0000	0.8903	0.0000	0.7975	0.0000	0.7195	0.0000	0.6532	0.0000	0.5963	0.0000

In the mixture the original structures of both the liquids are disrupted which may cause a decrease in viscosity. Again solute molecules and water form hydrogen bond and associated complex resulting in an increase in liquid structure and hence viscosity. In the very low concentration region, the solute molecules may occupy the void spaces of tetrahedral hydrogen bonded cluster of liquid water. The hydrophobic part of these molecules may stabilize the cluster around them. The hydrodynamic distortion of the fluid streamline by these molecules with hydration sphere results in an increase in viscosity. The positive contribution to η due to the factors (ii), (iii) and (iv) outweighs the negative contribution to η due to factor (i) resulting in an increase in η of the mixture. Very high η^E value for DAP may be attributed to the fact that proton released from H_2O may combine with $-NH_2$ groups to form quaternary ammonium ion which gives extra structure to the mixture and makes it more viscous. Beyond maxima factor (iii) produces a negative effect on η, factor (ii) becomes insignificant and

TABLE III Coefficients, A_i of Redlich–Kister equation and standard deviation, σ of excess molar volume in $cm^3\ mol^{-1}$ and of excess viscosity in centipoise of the systems

Temperature (K)	*Excess molar volume*					*Excess viscosity*				
	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ
(x_1) *Water* + (x_2) *N-methylformamide system*										
298.15	1.0984	−2.1186	−0.0072	−0.2728	0.0012	3.1616	−2.5225	0.2137	0.8614	0.0064
303.15	−2.0776	1.0536	0.0155	−0.2592	0.0009	2.7753	−2.0106	0.0696	0.6127	0.0047
308.15	−2.0404	1.0180	0.0335	−0.2499	0.0008	2.4461	−1.6716	−0.0156	0.5282	0.0059
313.15	−2.0092	0.9764	0.0551	−0.2212	0.0006	2.1599	−1.3899	−0.0576	0.4271	0.0054
318.15	−1.9791	0.9395	0.0751	−0.1934	0.0005	1.9214	−1.1569	−0.1317	0.3742	0.0042
(x_1) *Water* + (x_2) *1,2-diaminopropane system*										
298.15	−9.5251	4.6532	0.3688	−4.4770	0.0017	27.2755	−37.6141	10.5284	3.4251	0.0087
303.15	−9.5498	4.6633	0.2602	−4.4926	0.0009	22.2073	−32.1014	9.5707	4.7117	0.0080
308.15	−9.5908	4.6622	0.1905	−4.4093	0.0009	18.4445	−26.0334	7.8302	2.4653	0.0080
313.15	−9.6322	4.6858	0.1019	−4.4181	0.0010	15.2298	−21.6700	6.5094	2.4403	0.0081
318.15	−9.6641	4.6548	0.0287	−4.3492	0.0011	12.6456	−18.0395	5.1620	2.6704	0.0080
(x_1) *Water* + (x_2) *2-methylpropane-2-ol system*										
298.15	−3.1782	1.6314	−2.0203	2.7450	0.0010	11.8645	−9.5160	5.9718	−1.5686	0.0188
303.15	−3.2297	1.6071	−2.0846	2.8236	0.0013	9.0885	−7.4721	4.6086	−1.0716	0.0118
308.15	−3.2655	1.6088	−2.1796	2.8540	0.0011	7.0769	−5.9598	3.7901	−0.9290	0.0101
313.15	−3.3051	1.6182	−2.2470	2.8138	0.0013	5.5584	−4.6217	3.1046	−1.1101	0.0099
318.15	−3.3523	1.6263	−2.3456	2.7709	0.0009	4.4502	−3.8873	2.6208	−0.7877	0.0043

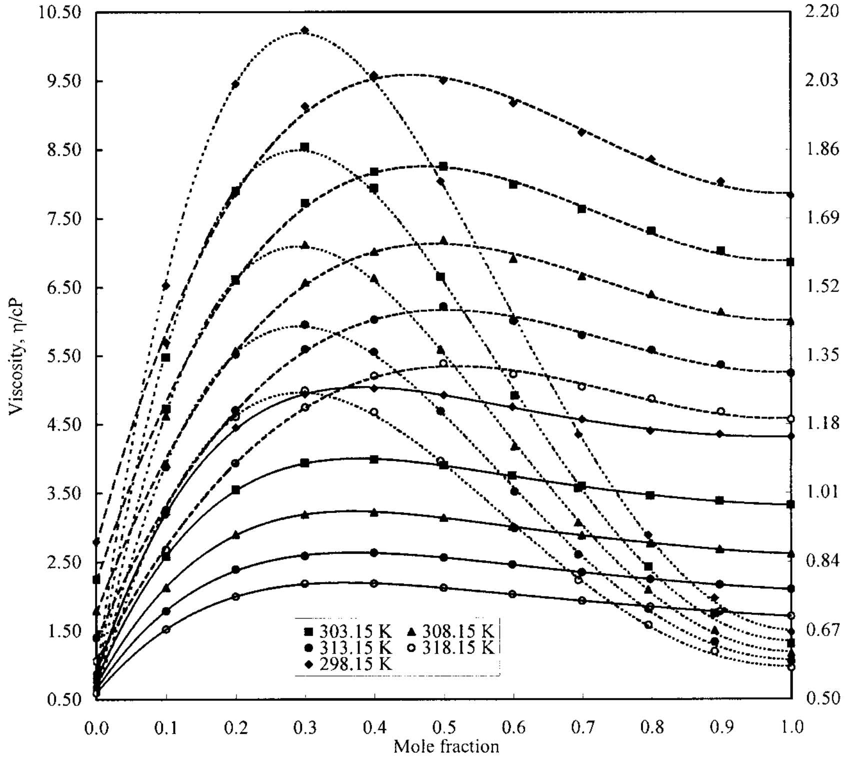

FIGURE 3 Variation of viscosity with mole fraction of 2-methylpropane-2-ol (solid line and left scale), *N*-methylformamide (long dashed line and right scale) and 1,2-diaminopropane (dashed line and left scale).

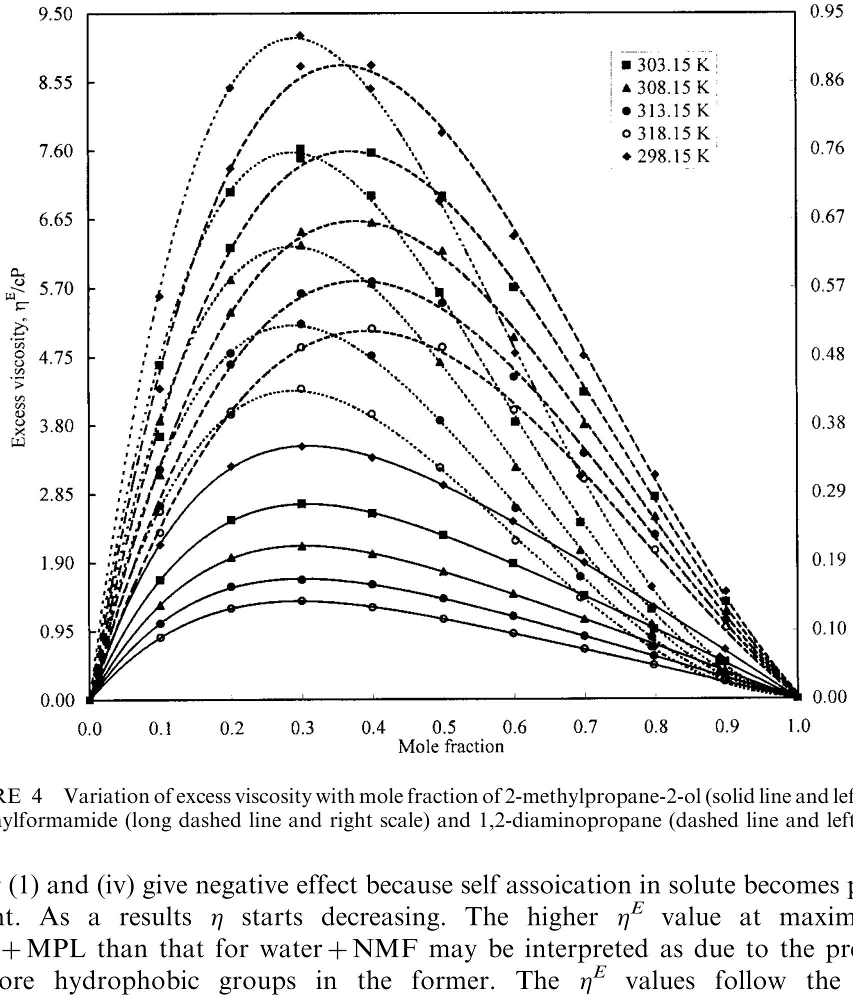

FIGURE 4 Variation of excess viscosity with mole fraction of 2-methylpropane-2-ol (solid line and left scale), *N*-methylformamide (long dashed line and right scale) and 1,2-diaminopropane (dashed line and left scale).

factor (1) and (iv) give negative effect because self assoication in solute becomes predominant. As a results η starts decreasing. The higher η^E value at maxima for water + MPL than that for water + NMF may be interpreted as due to the presence of more hydrophobic groups in the former. The η^E values follow the order water + DAP > water + MPL > water + NMF which is in agreement with the observed volumetric order.

The η and η^E values for all the studied systems decrease with the increase in temperature. An increase in temperature makes the mixtures less structured, due to thermal agitation, resulting in a decrease in η and η^E.

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