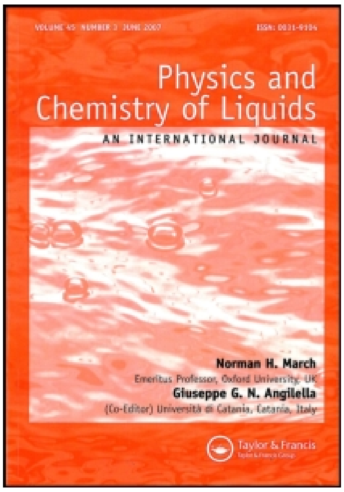

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Viscosity of Aqueous Solutions of Formamide, *N*-Methylformamide and *N,N*-Dimethylformamide

Shamim Akhtar[a]; A. N. M. Omar Faruk[b]; M. A. Saleh[a]
[a] Department of Chemistry, University of Chittagong, Chittagong, Bangladesh [b] Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), Dhaka

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VISCOSITY OF AQUEOUS SOLUTIONS OF FORMAMIDE, *N*-METHYLFORMAMIDE AND *N*,*N*-DIMETHYLFORMAMIDE

SHAMIM AKHTAR*, A. N. M. OMAR FARUK†
and M. A. SALEH

Department of Chemistry, University of Chittagong,
Chittagong-4331, Bangladesh

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Viscosities of aqueous solutions of formamide, *N*-methylformamide and *N*,*N*-dimethylformamide have been measured at temperatures 303.15, 308.15, 313.15, 318.15 and 323.15 K. For formamide + water system the viscosity increases exponentially with respect to the mole fraction of formamide. In contrast, *N*-methylformamide + water and *N*,*N*-dimethylformamide + water systems exhibit maxima in water-rich region, the maxima of the latter being higher and sharper than those of the former system. The excess viscosities of formamide + water system are positive at 323.15 K, which turn to negative values at 303.15 K, the magnitude of the values being very small irrespective of their sign. On the other hand, *N*-methylformamide + water and *N*,*N*-dimethylformamide + water systems show large positive excess viscosities for the whole range of composition. The viscosities and excess viscosities for the system formamide + water have been explained by assuming some complex formation between the components with the simultaneous disruption of water structures. For *N*-methylformamide + water and *N*,*N*-dimethylformamide + water systems, it has been assumed that cluster-like structure of water is formed around methyl group(s) attached to *N*-atom of the amides, which influences the viscosity behaviour of these systems strongly.

Keywords: Excess viscosity; Aqueous solutions of formamide; *N*-methylformamide and *N*,*N*-dimethylformamide

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*Corresponding author.

†Present address: Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), Dhaka - 1000.

1. INTRODUCTION

The present study is a part of our continuing research on volumetric and viscometric properties of aqueous organic systems [1–5]. The three amides chosen for the present investigation are formamide, *N*-methylformamide and *N,N*-dimethylformamide. Substitution of aminic hydrogen of formamide successively by methyl group produces *N*-methylformamide and *N,N*-dimethylformamide, which differ considerably not only in physical properties, but also in the mode of interaction towards water in a complex manner from their parent compound, formamide. All these amides are soluble in water in all proportions, which allows us to measure the viscosity of the aqueous solutions for the whole range of composition. We endeavour to understand the interaction between each of the amides and water from the analysis of the viscosity data.

2. EXPERIMENTAL

The amides under investigation were procured from Aldrich, with quoted purity – formamide (99+%), *N*-methylformamide (99%) and *N,N*-dimethylformamide (99.9+%). They were used without further purification except that each of the amides was kept over molecular sieve (4*A*) for at least two weeks before use. Thrice distilled water was used in the preparation of all the aqueous amide solutions. The measured density and viscosity of pure liquids corresponded well with literature values.

The density was measured by a 25 ml sp. gr. bottle previously calibrated. An Ostwald viscometer (*A*-type) of the British Standard Institution with sufficient 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. For every measurement, a thermostatic water bath controlled up to ± 0.05 K was used. In all cases the average uncertainty in the measured viscosity was not more than 1.6×10^{-3} mp.

3. RESULTS AND DISCUSSION

Viscosities and densities of formamide (F), *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide (DMF) at different temperatures are shown in Table I. The literature values, available only for DMF, are quoted for comparison, showing satisfactory agreement with our data. The variation of viscosity of the amides as a function of temperature is shown in Figure 1. Examination of Table I shows that the density (ρ) and viscosity (η) of the pure amides follow the order at 303.15 K, F ($\rho = 1.1237$ g cm^{-3}) > NMF ($\rho = 0.9946$ g cm^{-3}) > DMF ($\rho = 0.9386$ g cm^{-3}) and F ($\eta = 28.018$ mp) > NMF ($\eta = 15.859$ mp) > DMF ($\eta = 7.485$ mp). At all other temperatures the density and viscosity follow the same order. The boiling points are also found to be of the same order, F (b.p. 491 K) > NMF (b.p. 456 K) > DMF (b.p. 423 K) [6].

The physical data suggest that F is extensively associated through H-bonding. NMF is also associated through H-bonding, but much less extensively, as can be understood by the existence of only one aminic hydrogen capable of H-bond formation and by the steric effect. Unlike these two amides, DMF is associated through weak physical forces, such as, dipole–dipole and dipole-induced dipole interactions.

Viscosities (η) and excess viscosities (η^E) of the three systems at different temperatures are shown in Table II. The viscosities of aqueous solutions of the amides at different temperatures are plotted in Figures 2–4 as a function of mole fraction of amides. The viscosities of the three systems at 303.15 K are plotted in Figure 5 for comparison. The viscosity *vs.* composition curves show the following characteristics:

(a) For F + W system the viscosity increases exponentially with the mole fraction of F.

(b) Addition of NMF and DMF to water increases the viscosity at a much faster rate in the highly water-rich region. Both systems show maxima. However, the maxima for NMF + W occur around 0.4 mole fraction of NMF, but for the system DMF + W the maxima occur at about 0.3 mole fraction of DMF.

TABLE I Density, ρ, and viscosity, η, of formamide (F), *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide (DMF) at different temperatures

	ρ/gcm^{-3}					η/mp				
T/K	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
F	1.1237	1.1194	1.1154	1.1115	1.1073	28.018	24.980	22.435	20.324	18.464
NMF	0.9946	0.9903	0.9861	0.9820	0.9776	15.859	14.627	13.520	12.557	11.669
DMF	0.9386	0.9344	0.9296	0.9251	0.9204	7.485	7.063	6.683	6.330	6.004
	(0.93904)[c]	(0.9347)[b]	(0.92944)[a]	(0.9252)[b]	(0.9204)[b]	(7.648)[c]	(7.217)[c]	(7.143)[a]	(6.461)[d]	(6.128)[d]
		(0.93425)[c]						(6.831)[d]		

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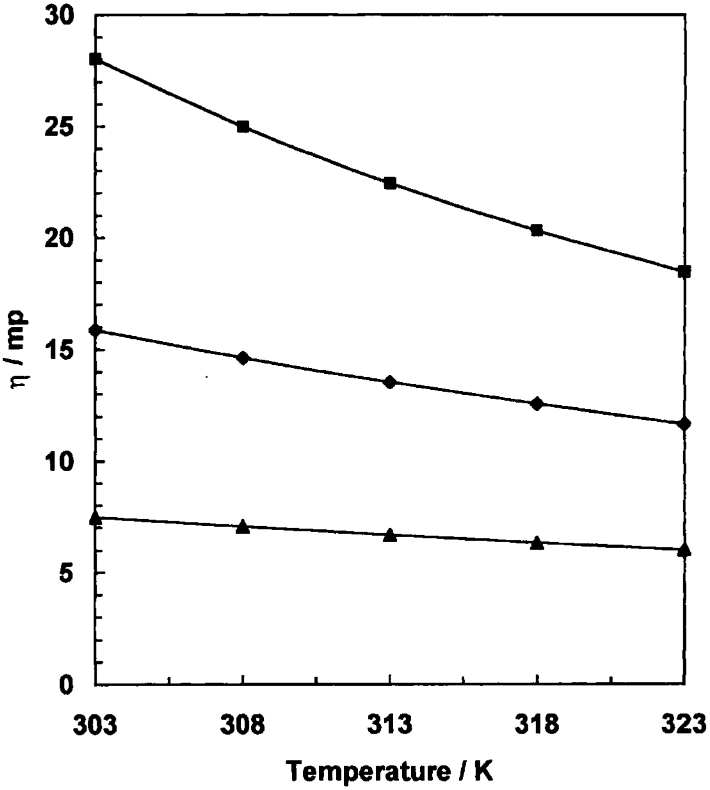

FIGURE 1 Viscosity of pure Formamide (F), *N*-methylformamide (NMF) and *N*,*N*-dimethyl-formamide (DMF) as a function of temperature ■ – F, ◆ – NMF and ▲ – DMF.

(c) With the rise of temperature, the broad maxima of NMF+W system gradually disappear, and the sharpness of the maxima of the system DMF+W is greatly reduced.

Excess viscosities, η^E, were calculated using the equation,

$$\eta^E = \eta - \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \tag{1}$$

where η is the measured viscosity of the mixtures, and η_1 and η_2 are the viscosities of water and amides, respectively, and X_1 and X_2 are the respective mole fractions. The excess viscosities were fitted to a

TABLE II Coefficient of viscosity, η, and excess viscosity. η^E, in mp of water (X_1)+amide (X_2) systems at different temperatures

Temp/K		303.15		308.15		313.15		318.15		323.15	
System	X_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
W+F	0.0	8.010	0.0	7.224	0.0	6.554	0.0	5.989	0.0	5.496	0.0
	0.0964	8.965	−0.073	8.135	−0.007	7.424	0.044	6.812	0.076	6.275	0.098
	0.1998	10.147	−0.140	9.213	−0.044	8.455	0.075	7.768	0.123	7.165	0.163
	0.2994	11.498	−0.155	10.472	−0.002	9.584	0.110	8.815	0.181	8.121	0.221
	0.3996	12.977	−0.234	11.817	−0.043	10.804	0.087	9.930	0.171	9.187	0.267
	0.4999	14.739	−0.240	13.399	−0.033	12.206	0.081	11.213	0.182	10.325	0.253
	0.5995	16.622	−0.347	15.059	−0.140	13.732	0.026	12.593	0.134	11.581	0.217
	0.6999	18.781	−0.461	16.967	−0.247	15.426	−0.082	14.086	0.001	12.925	0.091
	0.8001	21.391	−0.422	19.259	−0.235	17.462	−0.081	15.901	−0.018	14.565	0.073
	0.9000	24.317	−0.404	21.797	−0.269	19.672	−0.166	17.882	−0.104	16.291	0.066
	1.0000	28.018	0.0	24.980	0.0	22.435	0.0	20.324	0.0	18.464	0.0
W+NMF	0.0969	12.164	3.606	10.855	3.120	9.740	2.709	8.818	2.384	8.012	2.100
	0.2015	15.286	6.094	13.601	5.274	12.188	4.604	10.984	4.031	9.948	3.551
	0.2996	17.178	7.349	15.310	6.386	13.730	5.588	12.404	4.927	11.242	4.355
	0.4005	17.918	7.388	16.031	6.449	14.445	5.686	13.079	5.023	11.875	4.445
	0.4994	17.889	6.623	16.098	5.823	14.579	5.169	13.267	4.599	12.112	4.107
	0.5995	17.534	5.471	15.759	4.733	14.431	4.315	13.203	3.868	12.097	3.466
	0.6999	16.930	4.010	15.416	3.580	14.115	3.235	12.962	2.907	11.934	2.625
	0.7999	16.491	2.658	15.093	2.392	13.881	2.185	12.786	1.958	11.820	1.783
	0.9001	16.099	1.286	14.783	1.151	13.610	1.034	12.609	0.947	11.639	0.815
	1.0000	15.859	0.0	14.627	0.0	13.520	0.0	12.557	0.0	11.669	0.0
W+DMF	0.0990	15.208	7.252	13.353	6.145	11.831	5.264	10.569	4.547	9.490	3.946
	0.2009	20.230	12.329	17.532	10.340	15.365	8.785	13.598	7.542	12.074	6.480
	0.3008	21.296	13.448	18.466	11.291	16.203	9.610	14.359	8.270	12.738	7.094
	0.3995	19.415	11.619	17.081	9.922	15.102	8.497	13.489	7.366	12.072	6.379
	0.5005	16.290	8.548	14.545	7.402	13.062	6.444	11.788	5.631	10.690	4.945
	0.5999	13.597	5.906	12.289	5.162	11.197	4.567	10.236	4.045	9.379	3.583
	0.6997	11.268	3.630	10.354	3.243	9.540	2.896	8.831	2.606	8.189	2.342
	0.7998	9.634	2.047	8.956	1.860	8.344	1.687	7.797	1.537	7.282	1.383
	0.9000	8.450	0.914	7.894	0.815	7.417	0.747	6.979	0.684	6.585	0.633
	1.0000	7.485	0.0	7.063	0.0	6.683	0.0	6.330	0.0	6.004	0.0

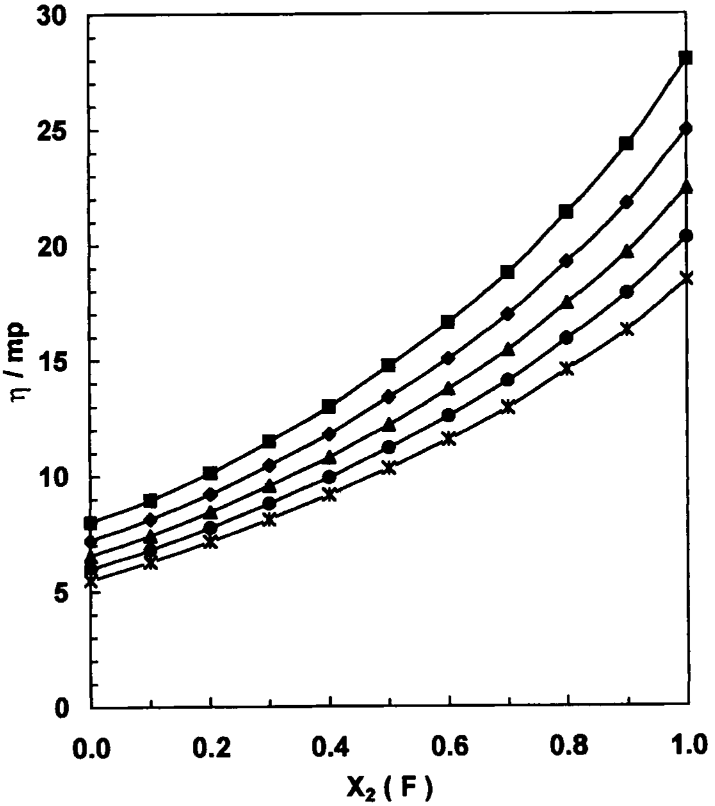

FIGURE 2 Viscosity of water (X_1)+formamide (X_2) system at different temperatures: ■ −303.15 K; ◆ −308.15 K; ▲−313.15 K; ● −318.15 K and ★−323.15 K.

polynomial of the form,

$$\eta^E = X_1 X_2 \sum_{i=0}^{n} A_i (2X_i - 1)^i \qquad (2)$$

where A_i is the fitting coefficient. Using $n = 3$, at each temperature four A_i values and the standard deviation, σ, were obtained through the least squares method. The coefficients and standard deviations are shown in Table III.

The plots of excess viscosities of the systems as a function of mole fraction of amides are shown in Figures 6–8. The following

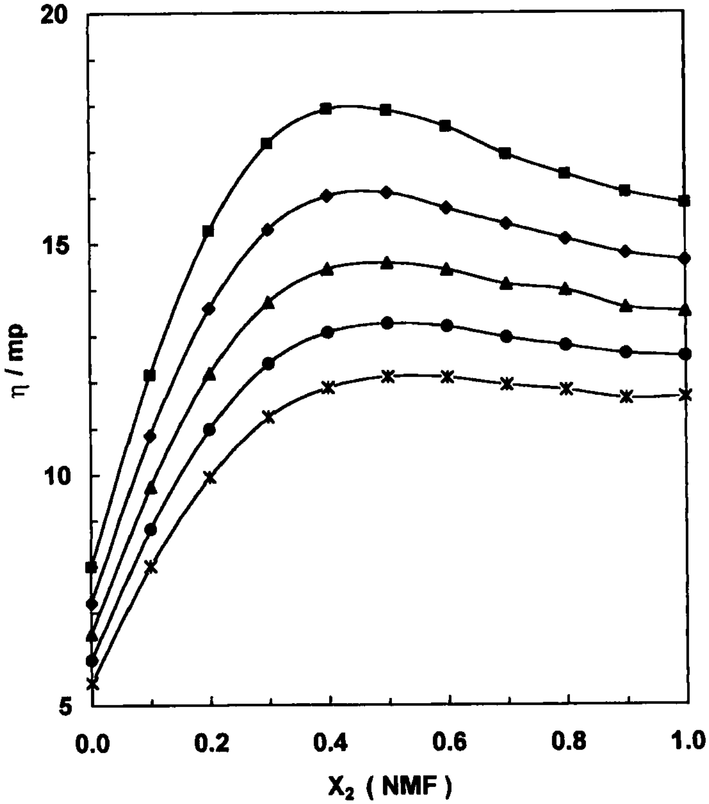

FIGURE 3 Viscosity of water (X_1)+*N*-methylformamide (X_2) system at different temperatures. Legends are the same as in Figure 2.

characteristics of excess viscosities have been observed:

(a) The excess viscosities for the system F+W are found to be positive at 323.15 K, and those at 303.15 K and 308.15 K are found to be negative, for the whole range of composition. At 313.15 K and 318.15 K the curves are sigmoid, showing both positive and negative values. The negative values are observed only at higher concentrations of F. The magnitude of the values is very small irrespective of their sign.

(b) For the systems, NMF+W and DMF+W, the excess viscosities are highly positive for the whole range of composition indicating that the systems are highly non-ideal. Both the systems show maxima, the magnitude of which is much greater for DMF+W

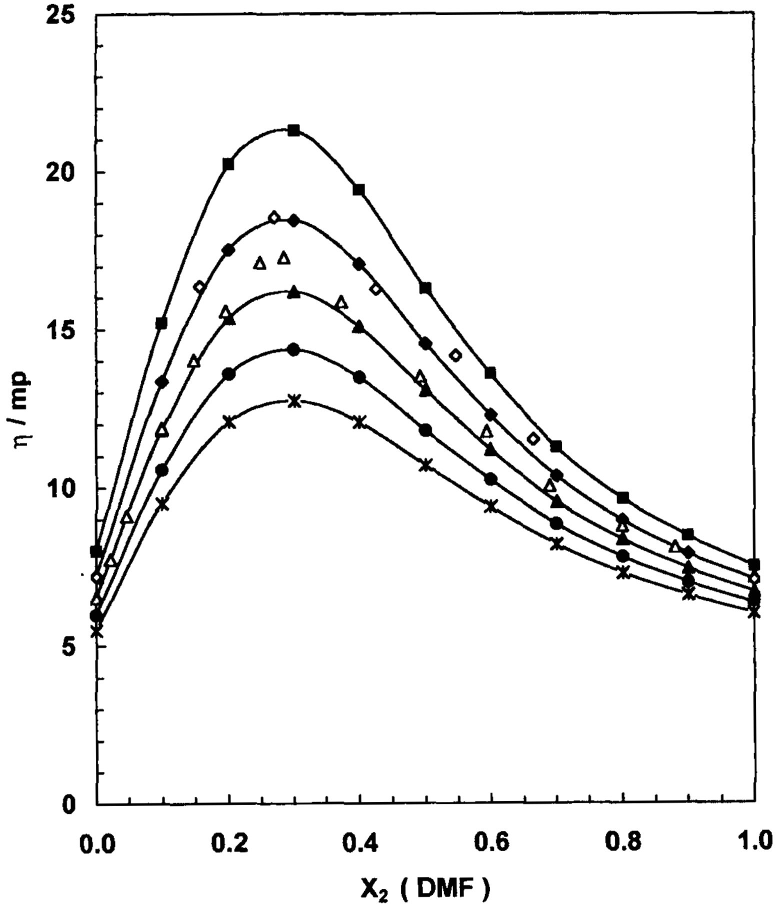

FIGURE 4 Viscosity of water (X_1)+*N,N*-dimethylformamide (X_2) system at different temperatures. Legends are the same as in Figure 2. ◇ – Ref. [10] and △ – Ref. [9].

than for NMF+W. The maxima for the system NMF+W lie between 0.3 and 0.4 mole fraction of NMF, and those for the system DMF+W occur at about 0.3 mole fraction of DMF. The temperature change seems to have little or no effect on the position of the maxima of η^E for these two systems.

(c) For F+W system $d\eta^E/dT$ is positive, and for NMF+W and DMF+W systems $d\eta^E/dT$ is negative.

For the purpose of comparison of the excess viscosities of the systems and to see the effect of temperature on them, the curves at 303.15 K and 323.15 K for each of these systems are shown in Figure 9.

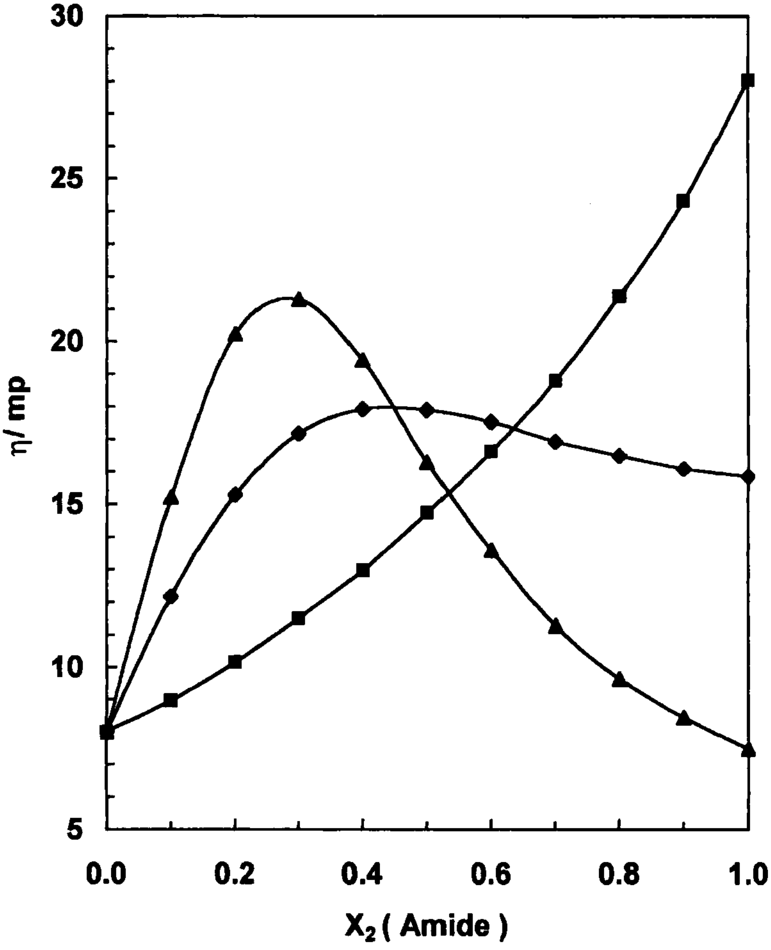

FIGURE 5 Comparison of viscosities of water (X_1)+amide (X_2) systems against mole fraction of the respective amide at 303.15 K. ■ –F+W; ◆–NMF+W; ▲–DMF+W.

Two approaches are considered for the interpretation of viscosities of the aqueous amide systems:

(a) Association of the amides with water through H-bonding.

(b) Enhancement of water structures by the methyl group(s) attached to nitrogen atom of NMF and DMF. Obviously, this concept applies only to NMF+W and DMF+W systems.

TABLE III Fitting coefficients (A_i) and the standard deviation (σ) in mp for water + amide systems at different temperatures

System	*Temp./K*	A_0	A_1	A_2	A_3	σ
	303.15	−1.0611	1.3318	−2.2833	1.1807	0.03372
	308.15	−0.2454	1.0412	−1.9355	0.8243	0.03364
W + F	313.15	0.3027	0.7547	−1.2503	0.8514	0.02821
	318.15	0.6868	0.6723	−1.2148	0.7378	0.02545
	323.15	0.9573	0.7975	−0.4557	0.8493	0.02888
	303.15	26.6537	20.4818	1.8053	−6.2921	0.04717
	308.15	23.3002	17.5195	1.6536	−5.8355	0.05140
W + NMF	313.15	20.7778	14.3893	0.9355	−4.0449	0.03946
	318.15	18.4724	12.2659	0.6529	−3.3076	0.03395
	323.15	16.4834	10.3172	0.2953	−2.0854	0.03903
	303.15	35.8147	62.5516	21.6553	−27.1967	0.37167
	308.15	30.8332	51.2753	17.3737	−21.1226	0.27434
W + DMF	313.15	26.7163	42.4866	14.4295	−16.4004	0.21162
	318.15	23.3089	35.6668	12.3811	−12.7804	0.16510
	323.15	20.3671	29.9277	10.3264	−10.1531	0.12560

The addition of F to water results in two effects : (i) dissociation of water structure which reduces the viscosity and (ii) the combination of the dissociated water molecules with formamide molecules which increases viscosity. Since these two opposing effects occur simultaneously, the overall values of the viscosity do not change significantly from the calculated values, as indicated by the very small excess viscosities. The disruption of water structure by the addition of F has been suggested by Rupley [7]. The effect of temperature on viscosity can also be explained qualitatively by the above views. At higher temperatures the breaking up of the associated F and water is greater, which leads to increased concentration of monomeric species of both of the components. It is assumed that the monomers so formed readily form 1:1 F − W complex. At lower temperatures, the dissociation of F and W into monomers is reduced, and therefore the F − W complex formation is also reduced. This seems to be a plausible interpretation for the positive excess viscosities at 323.15 K which gradually turn to negative values at 303.15 K.

A comparison of the viscosity curves of the three systems in Figure 5 shows that the viscosity increases exponentially with F concentration in F + W system, while the other two systems, NMF + W and DMF + W, strongly contrast with F + W system by showing maxima in their viscosity curves in water-rich regions. Assarson and Eirich [8] carried out viscometric studies on aqueous solutions of a large number

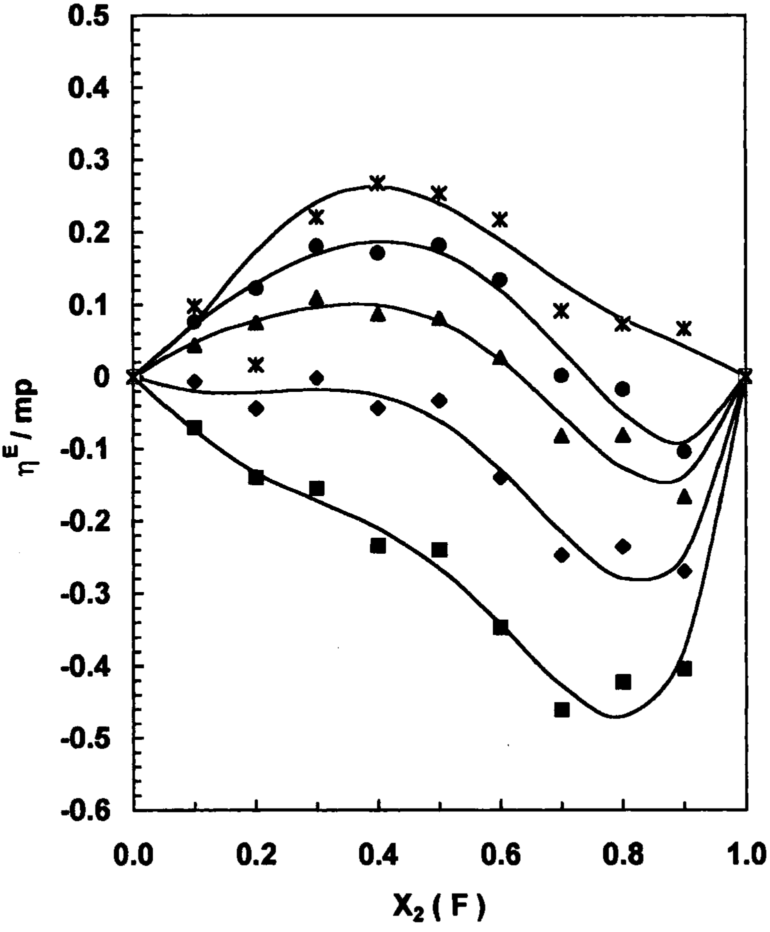

FIGURE 6 Excess viscosity of water (X_1)+formamide (X_2) system against X_2 at different temperatures. Legends are the same as in Figure 2.

of mono- and di-alkylated amides. The existence of maxima at or nearly at stoichiometric ratios prompted them to suggest some complex formation at definite ratios of amides and water. Meanwhile, Volpe *et al.* [9] suggested two different models to account for the viscosity of DMF+W system:

(a) Some strong, well-defined complexes of the type DMF · $(H_2O)_n$ are formed with $n = 3$.

(b) The DMF-H_2O interaction is due to the growth of extended, cluster-like structures where H-bonds play a relevant role.

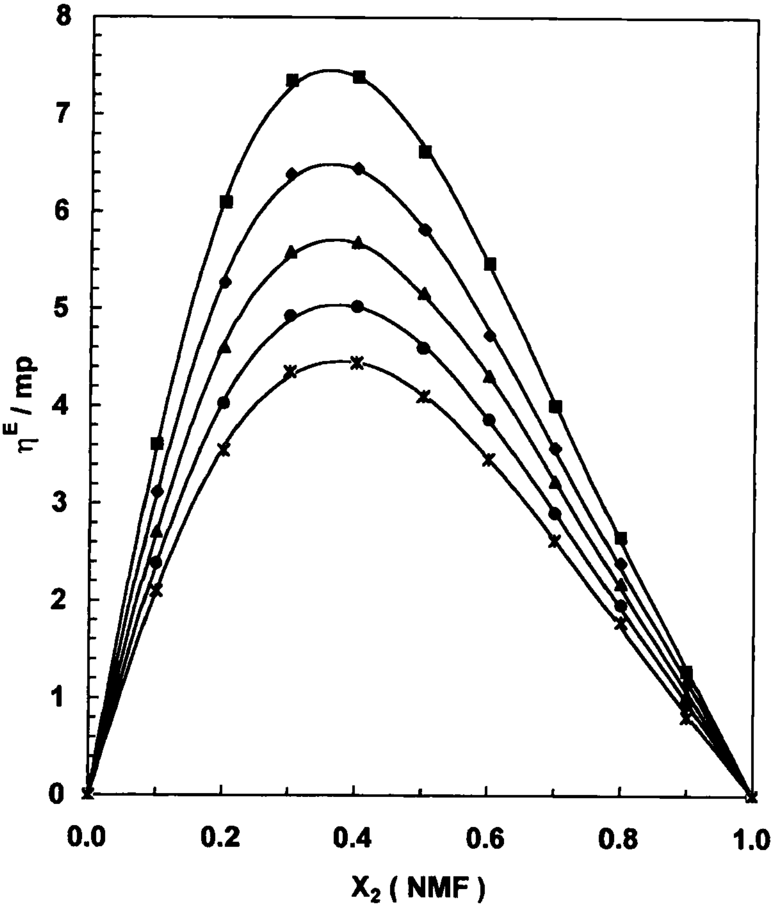

FIGURE 7 Excess viscosity of water (X_1)+*N*-methylformamide (X_2) system against X_2 at different temperatures. Legends are the same as in Figure 2.

Of the two models they favoured model (b) for the interpretation not only of viscosity, but also of other properties, such as, diffusion and refractive index of the DMF+water system. In explaining the maxima of viscosity of DMF+W system, Singh *et al.* [10] suggested the maximum amount of structure at about 25 mole% of DMF. In an attempt to rationalise the dielectric results of the aqueous solutions of varieties of amides and viscosity results of Assarson and Eirich as mentioned above, Rohdewald and Moldner [11] proposed that, mixing of unalkylated amides with water leads to a loose liquid structure while

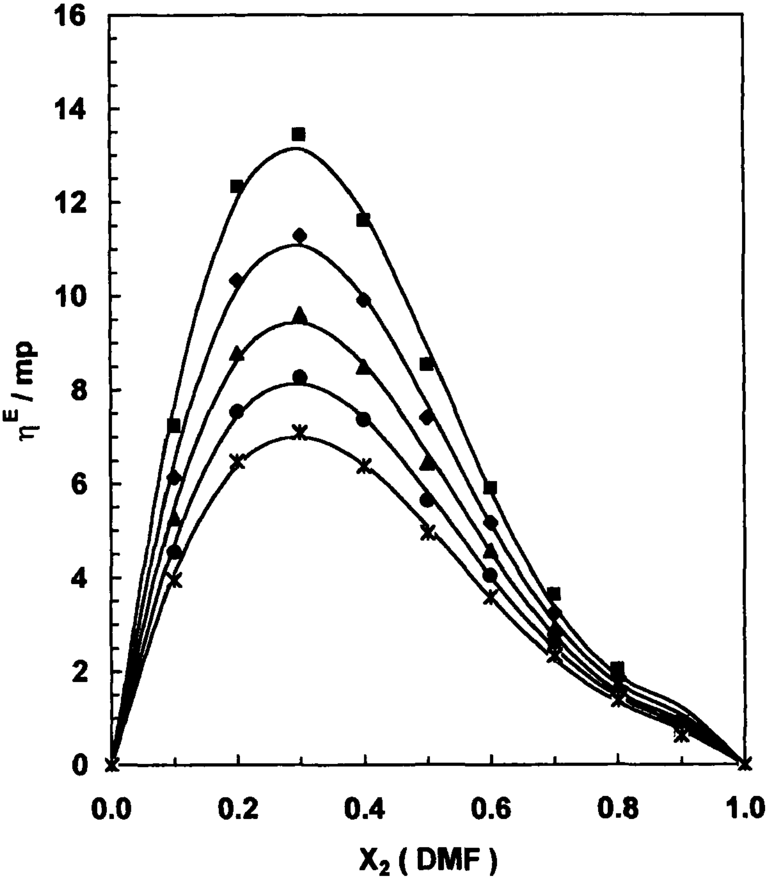

FIGURE 8 Excess viscosity of water (X_1)+*N*,*N*-dimethylformamide (X_2) system against X_2 at different temperatures. Legends are the same as in Figure 2.

forming amide–water complexes. On the other hand, with aqueous mono- and di-alkylated amide solutions a more structured liquid is formed. It was assumed that at high water content of the mixtures, alkyl groups of the amides are more exposed to water, which induce greater structural order of water molecules around the hydrocarbon moieties.

As far as F+W system is concerned the viscosity results can be satisfactorily explained by the formation of F–W complex with

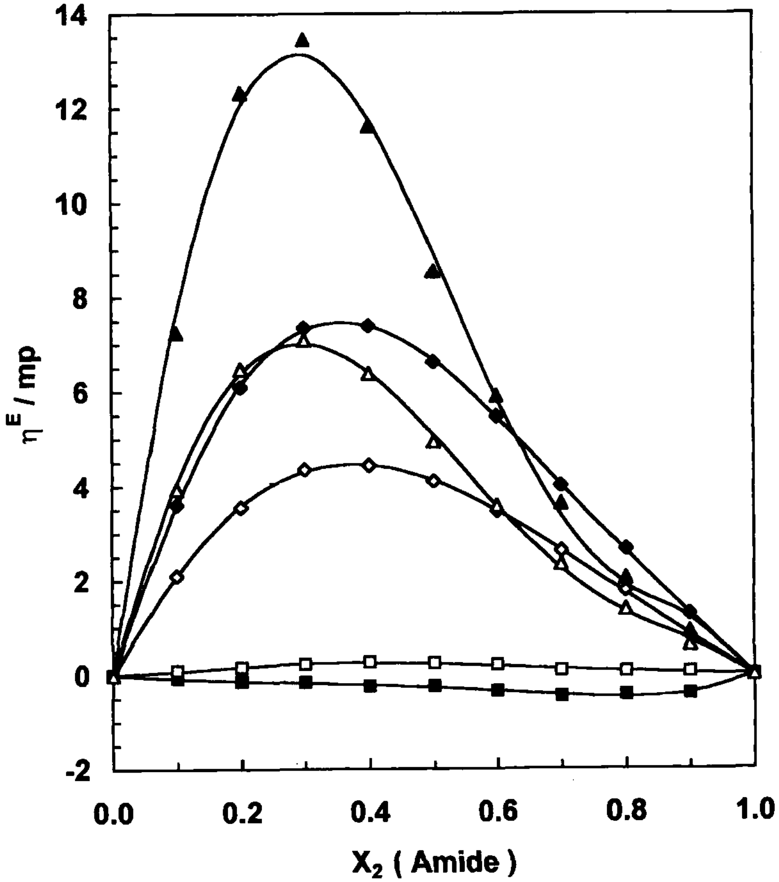

FIGURE 9 Comparison of excess viscosities of water (X_1)+amide (X_2) systems against the mole fraction of the respective amide at 303.15 K and 323.15 K. F+W: ■ – 303.15 K, □ – 323.15 K; NMF+W: ◆ – 303.15 K, ◇ – 323.15 K; DMF+W: ▲ – 303.15 K, △ – 323.15 K.

concomitant disruption of the water structure. But the viscosity behaviour of the alkylated amide–water systems, in which viscosity maxima are the major characteristics, cannot be explained satisfactorily with the help of the amide–water complex formation as suggested by Assarson and Eirich. Analysis of the viscosity results of amide–water systems so far published leads to the following general conclusions:

(a) All mono- and di-alkylated amides exhibit maxima at low concentration of amides.
(b) For the same alkyl group attached to N-atom of the amides, the height and sharpness of the viscosity maxima are always greater for di-alkylated amides than for mono-alkylated amides.
(c) The maxima increase with the increasing size of alkyl group attached either to aminic nitrogen or to carbonyl carbon.
(d) The branching of the alkyl group attached to N-atom increases the height of the viscosity maxima.

In the viscometric and volumetric-studies of the binary mixtures of aniline ($C_6H_5NH_2$), *N*-methylaniline ($C_6H_5NHCH_3$) and *N*,*N*-dimethylaniline ($C_6H_5N(CH_3)_2$) with a number of 1-alkanols it has been amply demonstrated by Begum [12] that, substitution of aminic hydrogen of $C_6H_5NH_2$ by CH_3 group(s) results in the drastic reduction of excess viscosity and increase of excess volume as a result of steric effect. Such an effect can not be ignored in NMF + W and DMF + W systems. The ability to form complexes between amides (*N*-alkylated and *N*,*N*-di-alkylated) and water is greatly reduced by steric effect. Now, if the amide – water complex formation could be the main cause of viscosity-maxima, one would have then expected the suppression of maxima due to any of the above factors (b), (c) and (d) as a result of steric hindrance, instead of enhancement of the maxima as has been practically observed.

It is interesting to notice that the viscosity-composition curve of F + W system closely resembles the ethylene glycol (CH_2OH-CH_2OH) (EG) + water viscosity curve [13]. The parallel behaviour of viscosities is also observed for the pair of systems, NMF + W and 2-methoxyethanol ($CH_3-OCH_2-CH_2OH$)(ME) + W and, DMF + W and 1,2-dimethoxyethane ($CH_3-OCH_2-CH_2OCH_3$)(DME) + W [14]. It is thus seen that, replacement of an aminic hydrogen of formamide by CH_3 group produces the similar viscosity effects as those due to replacement of alcoholic hydrogen of EG by CH_3 group(s). It was suggested earlier that the phenomenon of hydrophobic hydration plays the most significant role for the viscosities of the aqueous solutions of ME and DME in the water-rich region [14]. In view of strong similarities of viscosity results of the aqueous NMF and DMF solutions with those of aqueous ME and DME solutions, respectively, we envisage that a concept same as or similar to the above phenomenon may well be applied to explain the viscosity behaviour of the aqueous NMF and DMF solutions, and indeed, of all other *N*-alkylated and *N*,*N*-di-alkylated aqueous solutions studied so far.

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