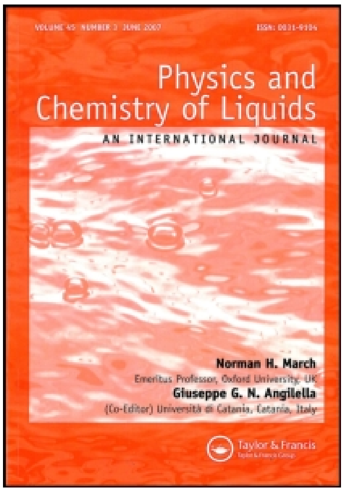

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Viscosity and Thermodynamics of Viscous Flow of the Systems, 1-Propanol Formamide, *N*-Methylformamide, *N,N*-Dimethylformamide

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To cite this Article Saleh, Mohammad A. and Uddin, Mohammad Hemayet(1999) 'Viscosity and Thermodynamics of Viscous Flow of the Systems, 1-Propanol Formamide, *N*-Methylformamide, *N,N*-Dimethylformamide', Physics and Chemistry of Liquids, 37: 6, 701 — 718

To link to this Article: DOI: 10.1080/00319109908035949

URL: http://dx.doi.org/10.1080/00319109908035949

Phys. Chem. Liq., 1999, Vol. 37, pp. 701–718
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VISCOSITY AND THERMODYNAMICS OF VISCOUS FLOW OF THE SYSTEMS, 1-PROPANOL + FORMAMIDE, + *N*-METHYLFORMAMIDE, + *N*,*N*-DIMETHYLFORMAMIDE

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(Received 17 June 1998)

Viscosities of the systems, 1-propanol(P) + formamide(F), + *N*-methylformamide (NMF), + *N*,*N*-dimethylformamide (DMF) have been measured in the temperature range 303.15–323.15 K with an interval of 5 K. For all the systems viscosities and excess viscosities have been plotted against mole fraction of 1-propanol. Excess viscosities for the system P + F have been found to be positive up to about 0.7 mole fraction of 1-propanol, followed by negative excess viscosities. The positive excess viscosities have been explained by the formation of P–F complex through H-bond, and the negative excess values have been interpreted by assuming that F is dissociated into smaller units in highly rich 1-propanol solution. For the systems, P + NMF and P + DMF, excess viscosities have been found to be negative for the whole range of composition. The negative values suggest that P and NMF are dissociated in their respective co-solvents. The interpretation put forward to account for the excess viscosities has been found to be consistent with the results of the excess thermodynamic activation parameters, $\Delta H^{\neq E}$, $\Delta G^{\neq E}$ and $\Delta S^{\neq E}$.

Keywords: Excess thermodynamic activation parameters for viscous flow; formamide; *N*-methylformamide; *N*,*N*-dimethylformamide

1. INTRODUCTION

The present work is a part of our continuing studies on molecular interaction of binary systems through the measurement of their

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volumetric and viscometric properties. As far as we are aware, no work on viscosity of binary mixtures of alkanols and amides is available with which to compare our results. However, a couple of studies can be mentioned here, which have some relevance to our present work. These are, excess volumes of *N*,*N*-dimethylformamide + an aliphatic alkanol studied by Rauf *et al.* [1] and the viscosity and activation energy of viscous flow of the system, *N*,*N*-dimethylformamide and 2-methoxyethanol studied by Corradini *et al.* [2]. In the present paper we report the results of viscosity and the thermodynamic activation parameters for viscous flow of the binary systems, 1-propanol + formamide, + *N*-methylformamide, + *N*,*N*-dimethylformamide. The systems allow us to examine the effect due to successive replacement of aminic hydrogen of formamide by methyl group on the properties studied.

2. EXPERIMENTAL

The amides used for experiment were procured from Aldrich, with quoted purities – formamide (99 + %), *N*-methylformamide (99%) and *N*,*N*-dimethylformamide (99.9%) and 1-propanol (99.5%). The chemicals were used without any further treatment except that each of them was kept over molecular sieve (4A) for at least two weeks prior to its use. The measured viscosities and densities corresponded well with literature values as far as available.

The density was measured by a 25 ml. specific gravity bottle previously calibrated. An Ostwald viscometer of the British Standard Institution with sufficiently long efflux time was used, so that no kinetic energy correction was necessary in the viscosity measurement. The time of flow was recorded by a timer accurate up to ±0.1 sec. An analytical balance weighing up to an accuracy of ±0.0001 g was used in the density measurement. Temperature was controlled by a thermostatic water bath with a fluctuation of ±0.05 K.

Excess viscosity, η^E, was calculated by the equation,

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (1)$$

where x_1 is the mole fraction of amide and η_1 is its viscosity in the pure state, x_2 is the mole fraction of 1-propanol and η_2 is its viscosity in the pure state. η is measured viscosity of solutions.

The enthalpy of activation, $\Delta H^{\neq}$, and entropy of activation, $\Delta S^{\neq}$, for viscous flow were calculated by using the Eyring equation of the form,

$$\ln \frac{\eta V_m}{hN} = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R} \tag{2}$$

All the terms of this equation have their usual meaning. In all cases we obtained excellent linear fitting of ln $(\eta V_m/hN)$ *versus* $(1/T)$ as indicated by very high correlation coefficients in the range of temperature studied. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been calculated from the slopes and intercepts, respectively, obtained by the least squares method. By using the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the free energy of activation for viscous flow, $\Delta G^{\neq}$, was calculated by the following equation,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{3}$$

The excess thermodynamic functions, $\Delta G^{\neq E}$, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ were calculated by the following equation,

$$Y^E = Y - (x_1 Y_1 + x_2 Y_2) \tag{4}$$

where Y is the measured thermodynamic property. Y_1 and Y_2 are the properties of the pure components, amides and 1-propanol, respectively, and x_1 and x_2 are the respective mole fractions. The excess properties, η^E and $\Delta G^{\neq E}$ were fitted to Redlich-Kister polynomial equation of the form,

$$\eta^E \text{ or } \Delta G^{\neq E} = x_1 x_2 \sum_{i=0}^{n} A_i (2x_1 - 1)^i \tag{5}$$

where A_i is the fitting coefficient. Using $n = 3$, at each temperature four A_i values and standard deviation, σ, were obtained.

3. RESULTS AND DISCUSSION

Densities and viscosities of the pure liquids, 1-propanol (P), formamide (F), *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide

(DMF) are shown in Table I. The literature values shown in the Table are in satisfactory agreement with the experimental results. The density and viscosity of the amides vary in the order, F > NMF > DMF. The boiling points of the amides also vary in the same order, F(b.p.210°C) > NMF (b.p.183°C) > DMF (b.p.153°C). These physical data suggest that F is extensively associated, as can be understood by the existence of two aminic hydrogen capable of H-bonding. NMF is less extensively associated, because it has only one aminic hydrogen available for H-bonding. Moreover the association through H-bonding is hampered by steric hindrance due to CH_3 group attached to *N* atom. No such association is possible with DMF, because of the absence of aminic hydrogen. However, this compound is associated by a rather weak physical force, such as, dipole–dipole and dipole–induced dipole interactions.

The viscosities, η, of the systems, P + F, P + NMF and P + DMF at different temperatures are listed in Table II. Figures 1–3 show the plots of viscosity against mole fraction of 1-propanol. Examination of the Figures reveals that:

(i) For P + F system, the viscosity decreases on increasing the concentration of P, initially slowly and then rapidly, up to about 0.8 mole fraction of P. At still higher concentration of P, the rate of decrease of viscosity is greatly reduced (Fig. 1).

(ii) On addition of P to NMF, the viscosity decreases up to ~0.6 mole fraction of P, which, following a broad minimum, increases until the pure state of 1-propanol is reached. With the rise of temperature the minimum becomes still broader (Fig. 2).

(iii) For P + DMF system, the viscosity increases slowly up to ~0.6 mole fraction of P. Beyond this concentration, the viscosity rises up at an increasing rate until the pure state of 1-propanol is reached (Fig. 3).

Excess viscosities, η^E, of the systems have been calculated by using Eq. (1) and are shown in Table II. The values are fitted to the polynomial equation (Eq. (5)). The coefficients of this equation, A_i, and the standard deviation, σ, are listed in Table V. The excess viscosities have been plotted in Figures 4–6 against mole fraction of 1-propanol for the three systems at different temperatures. We observe the following characteristics of excess viscosities:

TABLE I Density, ρ, and viscosity, η, of formamide, *N*-methylformamide, *N*,*N*-dimethylformamide and l-propanol at different temperatures

	$\rho/g\ cm^{-3}$					η/mP				
T/K	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
Formamide	1.1245	1.1203	1.1160	1.1118	1.1074	29.028	25.873	23.230	20.992	19.054
	1.1250^{a}	1.1211^{a}	1.1170^{a}	1.1131^{a}		29.663^{a}	26.531^{a}	24.039^{a}	21.993^{a}	
N-methylformamide	0.9949	0.9905	0.9862	0.9820	0.9779	15.973	14.728	13.612	12.632	11.746
N,*N*-dimethylformamide	0.9400	0.9353	0.9307	0.9262	0.9218	7.600	7.171	6.955	6.423	6.093
	0.940592^{b}	0.935717^{b}	0.930735^{b}	0.925986^{b}	0.921141^{b}	7.4648^{c}	7.217^{c}	6.831^{c}	6.461^{c}	6.128^{c}
l-propanol	0.7954	0.7913	0.7871	0.7831	0.7789	17.302	15.436	13.806	12.392	11.124
	0.79601^{d}	0.791411^{f}				17.28^{e}				

[a] Ref. [3] [b] Ref. [6]; [c] Ref. [2]; [d] Ref. [7]; [e] Ref. [4]; [f] Ref. [8].

TABLE II Coefficient of viscosity (η/mP) and excess viscosity (η^E/mP) of binary mixtures of formamides + 1-propanol

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
Formamide (X_1) + 1-propanol (X_2) system										
0.0000	29.028	0.000	25.873	0.000	23.230	0.000	20.992	0.000	19.054	0.000
0.0999	28.768	1.202	25.543	0.972	22.854	0.801	20.561	0.646	18.601	0.544
0.2004	28.131	1.962	24.921	1.593	22.231	1.301	19.953	1.065	18.007	0.901
0.3002	27.056	2.204	23.935	1.779	21.330	1.460	19.115	1.196	17.217	1.005
0.4000	25.537	1.936	22.605	1.562	20.147	1.282	18.042	1.040	16.236	0.873
0.5000	23.784	1.374	21.098	1.114	18.810	0.901	16.852	0.724	15.168	0.609
0.6000	21.912	0.632	19.488	0.510	17.398	0.398	15.607	0.307	14.055	0.259
0.6998	20.223	0.013	18.025	0.001	16.102	−0.038	14.471	−0.045	13.043	−0.031
0.8000	18.698	−0.491	16.688	−0.427	14.941	−0.379	13.440	−0.329	12.117	−0.271
0.9001	17.564	−0.656	15.689	−0.564	14.074	−0.468	12.661	−0.401	11.406	−0.332
1.0000	17.302	0.000	15.436	0.000	13.806	0.000	12.392	0.000	11.124	0.000
N-methylformamide (X_1) + 1-propanol (X_2) system										
0.0000	15.973	0.000	14.728	0.000	13.612	0.000	12.632	0.000	11.746	0.000
0.1009	15.452	−0.650	14.232	−0.566	13.162	−0.470	12.204	−0.403	11.338	−0.343
0.2001	15.097	−1.133	13.894	−0.972	12.841	−0.810	11.892	−0.692	11.046	−0.573
0.3003	14.751	−1.610	13.568	−1.369	12.520	−1.151	11.582	−0.978	10.749	−0.807
0.4003	14.537	−1.956	13.360	−1.647	12.314	−1.376	11.379	−1.157	10.538	−0.955
0.5005	14.409	−2.216	13.221	−1.857	12.161	−1.548	11.227	−1.285	10.356	−1.074
0.6000	14.435	−2.323	13.212	−1.937	12.131	−1.597	11.175	−1.312	10.302	−1.066
0.7001	14.638	−2.255	13.372	−1.848	12.247	−1.501	11.239	−1.224	10.337	−0.970
0.8009	15.199	−1.830	13.806	−1.486	12.578	−1.189	11.490	−0.949	10.507	−0.738
0.9007	16.048	−1.117	14.484	−0.880	13.101	−0.685	11.884	−0.531	10.792	−0.392
1.0000	17.302	0.000	15.436	0.000	13.806	0.000	12.392	0.000	11.124	0.000
N,*N*-dimethylformamide (X_1) + 1-propanol (X_2) system										
0.0000	7.599	0.000	7.171	0.000	6.783	0.000	6.423	0.000	6.093	0.000
0.1001	7.821	−0.431	7.366	−0.377	6.955	−0.328	6.569	−0.291	6.217	−0.254
0.2001	8.111	−0.849	7.618	−0.742	7.167	−0.653	6.752	−0.574	6.380	−0.493
0.3000	8.451	−1.275	7.912	−1.113	7.420	−0.974	6.980	−0.843	6.570	−0.729
0.3967	8.868	−1.664	8.273	−1.447	7.741	−1.251	7.256	−1.081	6.801	−0.935
0.5002	9.267	−2.201	8.623	−1.899	8.042	−1.636	7.517	−1.406	7.022	−1.212
0.6000	9.903	−2.546	9.169	−2.190	8.505	−1.884	7.912	−1.616	7.367	−1.376
0.7001	10.763	−2.756	9.904	−2.361	9.148	−2.008	8.466	−1.709	7.840	−1.447
0.8001	12.045	−2.633	11.005	−2.238	10.078	−1.900	9.264	−1.603	8.521	−1.342
0.9001	14.028	−1.909	12.715	−1.583	11.526	−1.333	10.744	−0.861	9.550	−0.925
1.0000	17.302	0.000	15.436	0.000	13.806	0.000	12.392	0.000	11.124	0.000

(i) For P + F system, the excess viscosity plots are sigmoid, showing both positive and negative values. In the region of positive excess viscosities a maximum is observed at ~0.3 mole fraction of 1-propanol, but in the negative excess viscosity region, which occurs only in the very high concentration of 1-propanol, a minimum is observed.

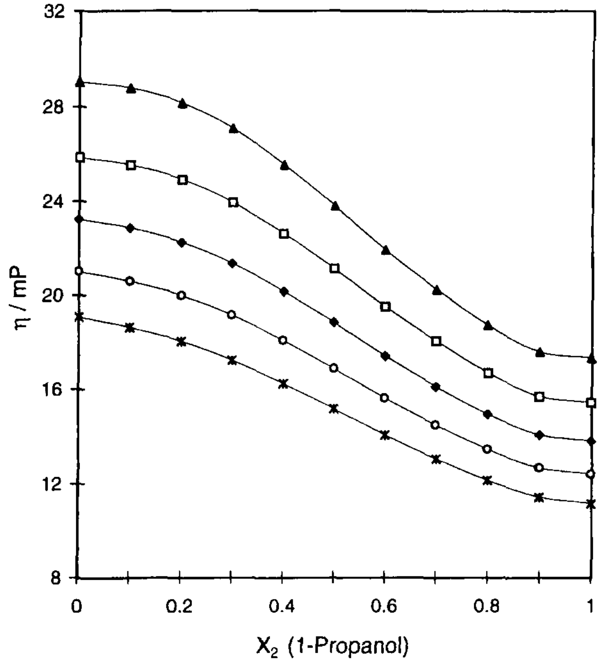

FIGURE 1 Viscosity of 1-propanol + formamide against mole fraction of 1-propanol. ▲-303.15 K, □-308.15 K, ◆-313.15 K, ○-318.15 K, ★-323.15 K.

(ii) The excess viscosities for the system P + NMF are found to be negative for the whole range of composition. The minima occur at ~0.6 mole fraction of 1-propanol, which virtually do not change their position with the change of temperature.

(iii) The plots of excess viscosities for the system, P + DMF, have been found to be negative for the whole range of composition.

The effect of temperature on excess viscosities of these systems, regardless of their sign, can be generalised by saying that the magnitude of the values, $|\eta^E|$, decreases on increase of temperature.

The positive excess viscosity for P + F system, extending over a large region of composition, is assumed to be due to strong specific interaction between the two components. The interaction leads to the formation of H-bond between P and F by one or more of the following

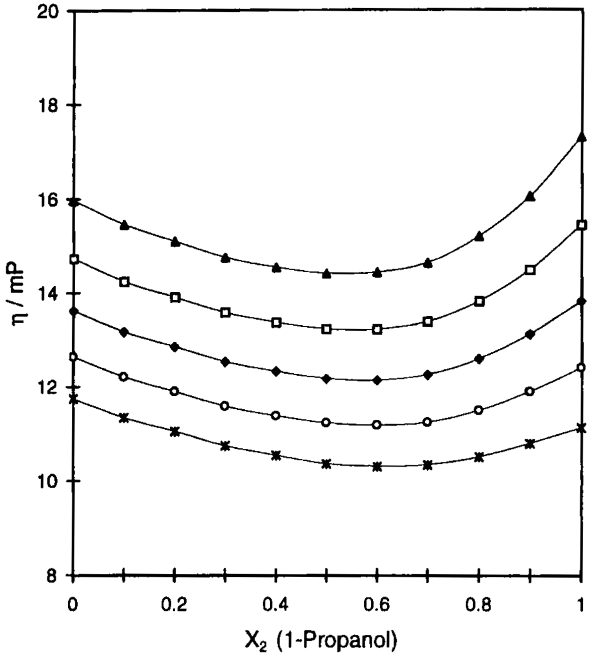

FIGURE 2 Viscosity of 1-propanol + *N*-methylformamide against mole fraction of 1-propanol. Symbols as in Figure 1.

ways: (i) $>C{=}O\cdots HO$—, (ii) —$H_2N\cdots HO$— and (iii) —$NH_2\cdots OH$—, though we believe that the first type of interaction is the most probable one. In the very rich region of 1-propanol the negative excess values are thought to be due primarily to the dissociation of one component into the other. The dissociation of formamide in highly rich 1-propanol composition seems to be more likely than the dissociation of 1-propanol in highly rich solution of formamide. This produces smaller species of formamide in 1-propanol rich solution. Consequently, the experimental viscosity becomes lower than the theoretical viscosity, and hence the negative excess viscosity in this region of concentration.

As a result of successive replacement of aminic hydrogen of formamide by CH_3 group, producing NMF and DMF, the electron density on *N* atom and carbonyl oxygen of the amides is increased, which theoretically should favour the H-bond formation of the type (i)

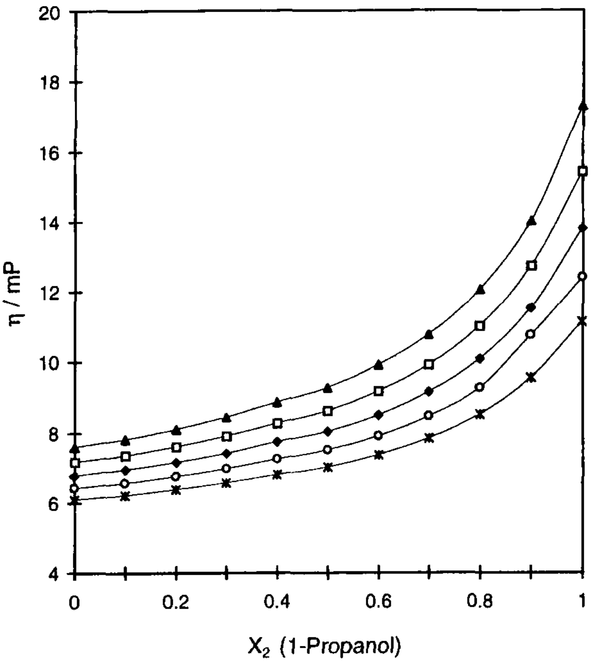

FIGURE 3 Viscosity of 1-propanol + *N*,*N*-dimethylformamide against mole fraction of 1-propanol. Symbols as in Figure 1.

and (ii) above, while at the same time this produces steric effect which opposes the amides to come sufficiently close to 1-propanol. In a situation like this, we envisage a weak interaction rather than a strong specific interaction between these substituted amides and 1-propanol. We notice that in the case of P + NMF system, the viscosity decreases from both ends of the composition axis and merges to a broad minimum as shown in Figure 2. The viscosity and negative excess viscosity for this system may be rationalised by assuming that, in excess NMF concentration 1-propanol is largely dissociated, and in excess 1-propanol concentration NMF is also similarly dissociated. The nearly symmetric behaviour of the negative excess viscosity of this system may be regarded to be a good support in favour of this assumption.

Addition of 1-propanol to DMF increases viscosity only slightly up to about 0.7 mole fraction of 1-propanol which is far smaller than the

TABLE III Free energy of activation ($\Delta G^{\neq}$/kJmol^{-1}) and excess free energy of activation ($\Delta G^{\neq E}$/kJmol^{-1}) for viscous flow of binary mixture of formamides + 1-propanol

T/K	303.15		308.15		313.15		318.15		323.15	
X_2	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$
Formamide (X_1) + 1-propanol (X_2)										
0.0000	14.294	0.000	14.258	0.000	14.222	0.000	14.186	0.000	14.149	0.000
0.0999	14.478	0.153	14.435	0.147	14.391	0.140	14.348	0.133	14.304	0.127
0.2004	14.618	0.262	14.570	0.252	14.523	0.242	14.475	0.231	14.427	0.221
0.3002	14.702	0.315	14.652	0.304	14.602	0.292	14.553	0.280	14.503	0.268
0.4000	14.728	0.311	14.678	0.300	14.629	0.289	14.580	0.278	14.530	0.267
0.5000	14.711	0.264	14.664	0.255	14.616	0.247	14.569	0.238	14.522	0.230
0.6000	14.658	0.180	14.614	0.176	14.570	0.171	14.526	0.167	14.482	0.162
0.6998	14.600	0.092	14.560	0.091	14.519	0.090	14.478	0.089	14.437	0.088
0.8000	14.540	0.001	14.502	0.003	14.464	0.006	14.426	0.008	14.388	0.011
0.9001	14.513	−0.056	14.477	−0.052	14.441	−0.047	14.404	−0.043	14.368	−0.038
1.0000	14.600	0.000	14.559	0.000	14.517	0.000	14.476	0.000	14.435	0.000
N-methylformamide (X_1) + 1-propanol (X_2)										
0.0000	13.788	0.000	13.820	0.000	13.853	0.000	13.885	0.000	13.918	0.000
0.1009	13.772	−0.098	13.804	−0.091	13.835	−0.085	13.867	−0.078	13.898	−0.072
0.2001	13.778	−0.172	13.808	−0.160	13.837	−0.149	13.867	−0.137	13.897	−0.125
0.3003	13.785	−0.246	13.813	−0.229	13.840	−0.213	13.867	−0.196	13.894	−0.179
0.4003	13.813	−0.300	13.837	−0.278	13.862	−0.257	13.887	−0.235	13.911	−0.213
0.5005	13.854	−0.340	13.874	−0.316	13.894	−0.291	13.914	−0.267	13.934	−0.243
0.6000	13.918	−0.357	13.934	−0.329	13.951	−0.301	13.968	−0.272	13.984	−0.244
0.7001	14.014	−0.343	14.025	−0.313	14.035	−0.283	14.046	−0.253	14.057	−0.223
0.8009	14.165	−0.273	14.165	−0.247	14.164	−0.221	14.164	−0.195	14.163	−0.168
0.9007	14.359	−0.161	14.343	−0.143	14.327	−0.125	14.311	−0.106	14.295	−0.088
1.0000	14.600	0.000	14.559	0.000	14.517	0.000	14.476	0.000	14.435	0.000
N,*N*-dimethylformamide (X_1) + 1-propanol (X_2)										
0.0000	12.597	0.000	12.669	0.000	12.742	0.000	12.815	0.000	12.887	0.000
0.1001	12.663	−0.135	12.731	−0.127	12.800	−0.120	12.869	−0.112	12.937	−0.105
0.2001	12.746	−0.251	12.809	−0.238	12.872	−0.225	12.935	−0.212	12.998	−0.199
0.3000	12.841	−0.357	12.898	−0.338	12.955	−0.320	13.012	−0.301	13.069	−0.283
0.3967	12.956	−0.436	13.006	−0.413	13.055	−0.391	13.105	−0.368	13.155	−0.346
0.5002	13.060	−0.539	13.103	−0.511	13.147	−0.483	13.190	−0.455	13.234	−0.427
0.6000	13.220	−0.579	13.254	0.549	13.287	−0.520	13.321	−0.490	13.355	−0.461
0.7001	13.422	−0.577	13.445	−0.547	13.468	−0.517	13.492	−0.486	13.515	−0.456
0.8001	13.698	−0.502	13.706	−0.475	13.714	−0.448	13.722	−0.422	13.730	−0.395
0.9001	14.079	−0.321	14.074	−0.296	14.068	−0.272	14.063	−0.247	14.058	−0.222
1.0000	14.600	0.000	14.559	0.000	14.517	0.000	14.476	0.000	14.435	0.000

expected increment (Fig. 3). It is assumed that as 1-propanol is added to DMF, the former is dissociated, and only in 1-propanol rich region, do the dissociated species of 1-propanol associate themselves at an increasing rate, and as a result the viscosity increases rapidly. The break down of the associated 1-propanol by DMF is supported by the

TABLE IV Enthalpy of activation, $\Delta H^{\neq}$, excess enthalpy of activation, $\Delta H^{\neq E}$, entropy of activation, $\Delta S^{\neq}$, and excess entropy of activation, $\Delta S^{\neq E}$, for viscous flow of formamides + 1-propanol

X_2	$\Delta H^{\neq}/kJ\ mol^{-1}$	$\Delta H^{\neq E}/kJ\ mol^{-1}$	$\Delta S^{\neq}/J\ mol^{-1}K^{-1}$	$\Delta S^{\neq E}/J\ mol^{-1}K^{-1}$
Formamide (X_1) + 1-propanol (X_2)				
0.0000	16.496	0.000	7.263	0.000
0.0999	17.111	0.554	8.685	1.321
0.2004	17.502	0.883	9.513	2.047
0.3002	17.706	1.026	9.912	2.345
0.4000	17.720	0.979	9.873	2.205
0.5000	17.579	0.777	9.462	1.693
0.6000	17.327	0.464	8.805	0.935
0.6998	17.074	0.149	8.160	0.189
0.8000	16.841	−0.145	7.591	−0.481
0.9001	16.717	−0.330	7.270	−0.904
1.0000	17.109	0.000	8.275	0.000
N-methylformamide (X_1) + 1-propanol (X_2)				
0.0000	11.810	0.000	−6.524	0.000
0.1009	11.858	−0.486	−6.312	−1.282
0.2001	11.974	−0.896	−5.949	−2.386
0.3003	12.136	−1.265	−5.442	−3.362
0.4003	12.318	−1.613	−4.932	−4.333
0.5005	12.640	−1.822	−4.005	−4.888
0.6000	12.916	−2.073	−3.306	−5.661
0.7001	13.355	−2.164	−2.172	−6.009
0.8009	14.194	−1.860	0.094	−5.235
0.9007	15.319	−1.264	3.167	−3.639
1.0000	17.109	0.000	8.275	0.000
N,*N*-dimethylformamide (X_1) + 1-propanol (X_2)				
0.0000	8.190	0.000	−14.536	0.000
0.1001	8.499	−0.584	−13.735	−1.482
0.2001	8.939	−1.036	−12.559	−2.587
0.3000	9.393	−1.472	−11.373	−3.680
0.3967	9.932	−1.796	−9.975	−4.488
0.5002	10.415	−2.236	−8.724	−5.598
0.6000	11.175	−2.367	−6.747	−5.897
0.7001	12.020	−2.414	−4.625	−6.059
0.8001	13.209	−2.117	−1.614	−5.329
0.9001	14.402	−1.816	1.066	−4.930
1.0000	17.109	0.000	8.275	0.000

negative excess viscosity over the whole region of composition. This view is supported by the work on the volumetric, viscometric and enthalpic properties of the systems formed by *N*,*N*-dimethylacetamide with aliphatic alcohols [4, 5]. From our unpublished results we observe that the viscosity behaviour of the systems 1-propanol + *N*-methylani-

TABLE V Coefficients, A_i, of Redlich-Kister equation (Eq. (5)) representing excess viscosity, η^E, and standard deviation, $\sigma(\eta^E)$, of the systems, formamides + 1-propanol

System	*Temperature/ K*	A_0	A_1	A_2	A_3	$\sigma(\eta^E)/mP$
Formamide + 1-propanol	303.15	5.5822	−13.2033	−3.1855	0.7272	0.05009
	308.15	4.5223	−10.6644	−2.8460	0.1495	0.04129
	313.15	3.6545	−9.0069	−2.3859	0.4488	0.02739
	381.15	2.9461	−7.4778	−2.0362	0.4225	0.02717
	323.15	2.4780	−6.2606	−1.6387	0.3428	0.02394
N-methylformamide + 1-propanol	303.15	−8.8813	−3.9809	−1.3779	0.9750	0.01804
	308.15	−7.4466	−3.0915	−0.8753	1.2444	0.01285
	313.15	−6.2006	−2.3387	−0.3073	1.1510	0.01213
	318.15	−5.1601	−1.6897	−0.0627	1.0994	0.01252
	323.15	−4.2547	−1.2284	0.3247	1.2288	0.01090
N,*N*-dimethylformamide + 1-propanol	303.15	−8.6072	−8.4968	−6.5098	−2.5605	0.03378
	308.15	−7.4565	−7.2505	−5.2137	−1.6596	0.02209
	313.15	−6.4332	−6.0592	−4.2866	−1.3414	0.02032
	318.15	−5.6496	−5.7659	−2.2282	2.2922	0.06422
	323.15	−4.7613	−4.2580	−2.7167	−0.5524	0.01469

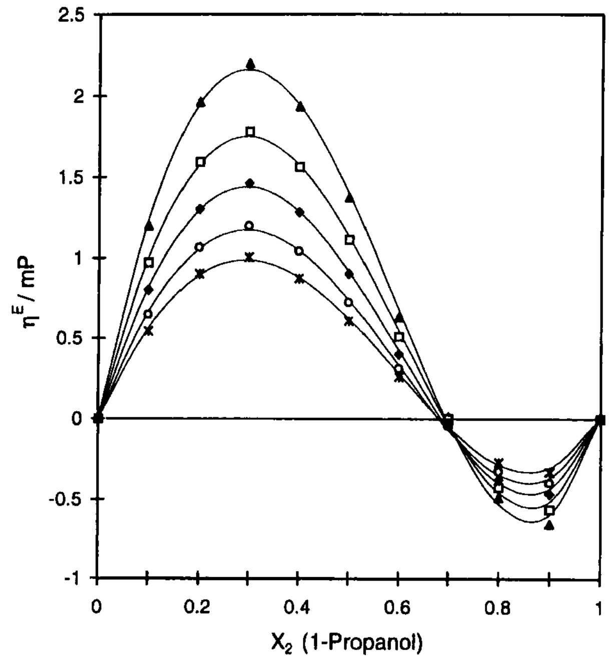

FIGURE 4 Excess viscosity of 1-propanol + formamide against mole fraction of 1-propanol. Symbols as in Figure 1.

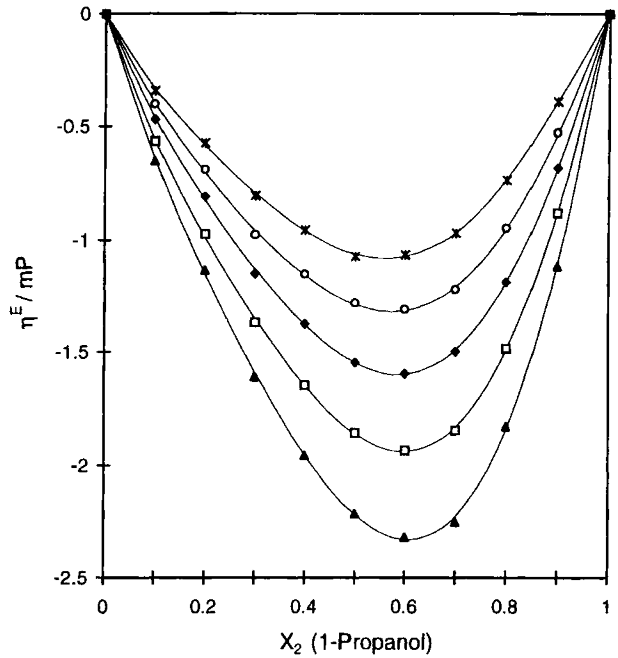

FIGURE 5 Excess viscosity of 1-propanol + *N*-methylformamide against mole fraction of 1-propanol. Symbols as in Figure 1.

line and 1-propanol + *N*,*N*-dimethylaniline closely resembles the viscosity behaviour of P + NMF and P + DMF systems, respectively.

Enthalpy of activation, $\Delta H^{\neq}$, entropy of activation, $\Delta S^{\neq}$, and free energy of activation, $\Delta G^{\neq}$, for viscous flow have been determined from the viscosity data following the procedure described in the experimental section. The free energies and excess free energies, $\Delta G^{\neq E}$, are shown in Table III for the three systems. The $\Delta G^{\neq E}$ values have been fitted to a polynomial equation (Eq. (5)), the coefficients of which and the standard deviation, σ, are listed in Table VI. The smoothed $\Delta G^{\neq E}$ *vs.* composition curves of these systems are shown in Figures 7–9.

The sign of excess free energy is probably the best criterion for ascertaining the nature of interaction between components in binary systems. If the excess free energies are positive the presence of strong or very strong interaction is predicted, depending upon their

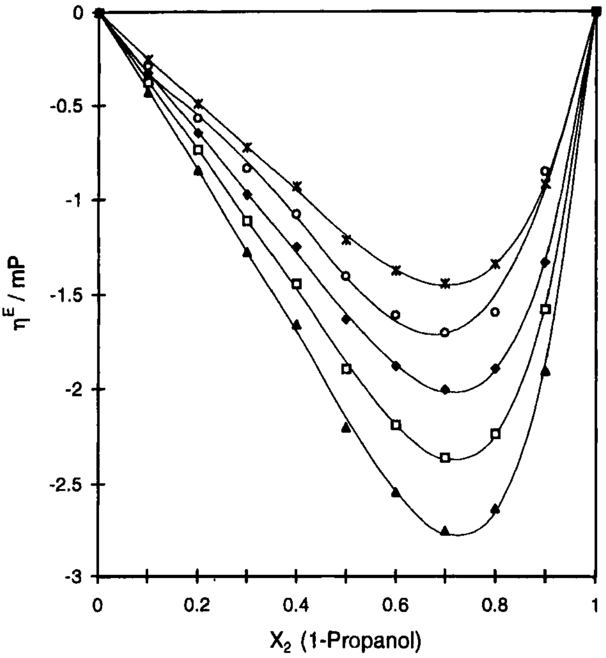

FIGURE 6 Excess viscosity of 1-propanol + *N*,*N*-dimethylformamide against mole fraction of 1-propanol. Symbols as in Figure 1.

TABLE VI Coefficients, A_i, of Redlich-Kister equation (Eq. (5)) representing excess free energy, $\Delta G^{\neq E}$, and standard deviation, $\sigma(\Delta G^{\neq E})$ of the different systems

System	*Temperature/ K*	A_0	A_1	A_2	A_3	$\sigma(\Delta G^{\neq E})$/ *kJ mol*$^{-1}$
Formamide	303.15	1.0641	−1.3011	−0.7284	−0.2114	0.00566
+	308.15	1.0299	−1.2418	−0.6981	−0.1865	0.00537
1-propanol	313.15	0.9955	−1.1802	−0.6666	−0.1652	0.00505
	318.15	0.9613	−1.1190	−0.6361	−0.1446	0.00473
	323.15	0.9267	−1.0591	−0.6054	−0.1203	0.00448
N-methyl-	303.15	−1.3678	−0.6156	−0.1073	0.2498	0.00272
formamide	308.15	−1.2672	−0.5421	−0.0500	0.2605	0.00242
+	313.15	−1.1664	−0.4697	0.0048	0.2753	0.00222
1-propanol	318.15	−1.0654	−0.3958	0.0605	0.2868	0.00216
	323.15	−0.9649	−0.3237	0.1172	0.2992	0.00228
N,*N*-	303.15	−2.1182	−1.3676	−0.6430	0.1407	0.00669
dimethyl-	308.15	−2.0128	−1.3143	−0.5630	0.2282	0.00624
formamide	313.15	−1.9074	−1.2606	−0.4826	0.3131	0.00650
+	318.15	−1.8020	−1.2078	−0.4023	0.4009	0.00738
1-propanol	323.15	−1.6964	−1.1538	−0.3238	0.4847	0.00866

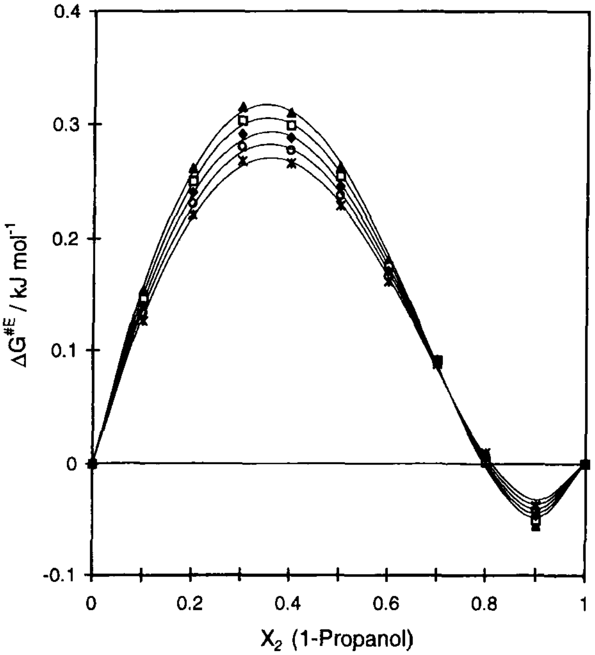

FIGURE 7 Excess free energy of activation for viscous flow of 1-propanol + formamide against mole fraction of 1-propanol. Symbols as in Figure 1.

magnitude. The negative excess free energies, on the other hand, indicate weak or very weak interaction, depending upon their magnitude.

Figure 7 shows the positive $\Delta G^{\neq E}$ values extending up to 0.8 mole fraction of 1-propanol. At a still higher concentration the values are found to be negative although their magnitude is small. The curves are strikingly similar to the excess viscosity curves as in Figure 4. The positive part of the curves is ascribed to strong specific interaction leading to the formation of H-bond between 1-propanol and formamide, and the negative part of the curve is ascribed to the break down of associated formamide into smaller units, as discussed more elaborately in connection with the interpretation of excess viscosity of this system earlier in this section.

The excess free energies for the systems, P + NMF and P + DMF are shown in Figures 8 and 9 respectively. The curves again closely resemble their respective excess viscosity curves in Figures 5 and 6. The

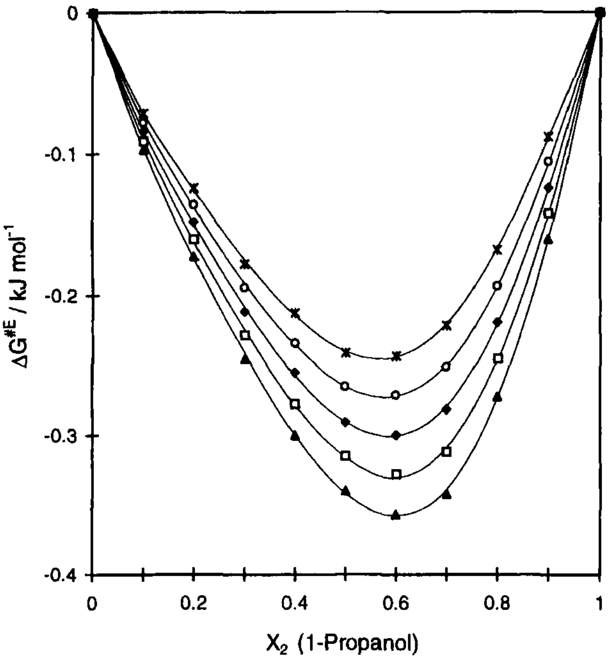

FIGURE 8 Excess free energy of activation for viscous flow of 1-propanol + *N*-methylformamide against mole fraction of 1-propanol. Symbols as in Figure 1.

explanation given for viscosities and excess viscosities for these systems earlier in this section seems to be entirely consistent with the behaviour of $\Delta G^{\neq E}$.

The enthalpies of activation, $\Delta H^{\neq}$, entropies of activation, $\Delta S^{\neq}$, and their excess values, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$, are listed in Table IV. For the system P + F, the $\Delta S^{\neq E}$ values are found to be positive up to about 0.7 mole fraction of 1-propanol, at still higher concentration, *i.e.*, in the very rich 1-propanol region, only small negative values are observed. In our recent studies, not yet published, we noticed that the positive $\Delta S^{\neq}$ values are always identified with those pure liquids which are strongly associated through H-bond, the only exception being methanol. We further noticed that in binary systems where the components are associated through H-bond, the $\Delta S^{\neq E}$ values become positive. A good example is a system, $CHCl_3 + CH_3COCH_3$, in which strong H-bond is formed between the components, and $\Delta S^{\neq E}$ is positive for the whole range of composition, although interestingly the

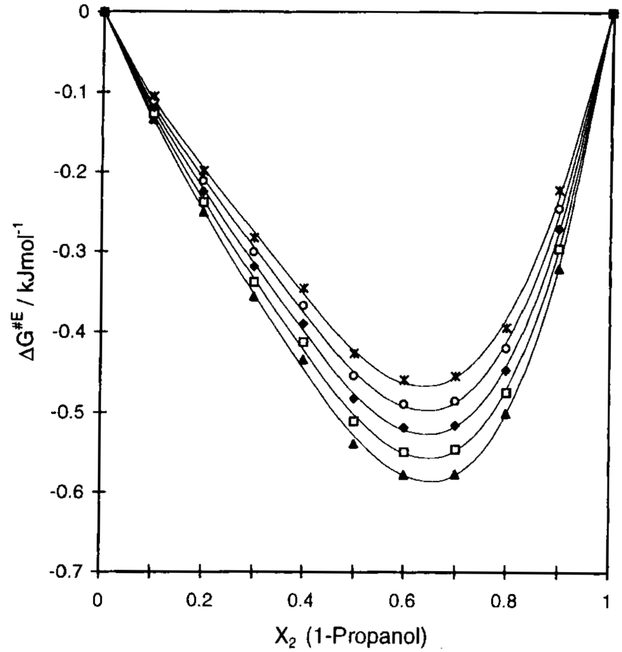

FIGURE 9 Excess free energy of activation for viscous flow of 1-propanol + *N,N*-dimethylformamide against mole fraction of 1-propanol. Symbols as in Figure 1.

$\Delta S^{\neq}$ values of the pure compounds are negative [8]. The positive values of η^E, $\Delta G^{\neq E}$ and $\Delta H^{\neq E}$ indicate strong specific interaction between P and F, which leads to the formation of H-bond. The positive $\Delta S^{\neq E}$ indicates the disruption of H-bond so formed, leading to the more disordered structure of the species in the activated state. The negative values of η^E, $\Delta G^{\neq E}$ and $\Delta H^{\neq E}$, on the other hand, can be rationalised by assuming that in 1-propanol rich region, the multimers of F are dissociated into smaller units. The species thus formed are assumed to be more ordered in the activated state in the flow process, in view of the negative $\Delta S^{\neq E}$ values in this region of composition.

The $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ values for the systems, P + NMF and P + DMF, as shown in Table IV, are negative for the whole range of composition. The negative $\Delta H^{\neq E}$ values are in full accord with the assumption of dissociation of both NMF and P into smaller species in P + NMF system and dissociation of P in P + DMF system. The negative $\Delta S^{\neq E}$ for both these systems indicate that the species formed in the activated state are structurally more ordered than those in the ground state.

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