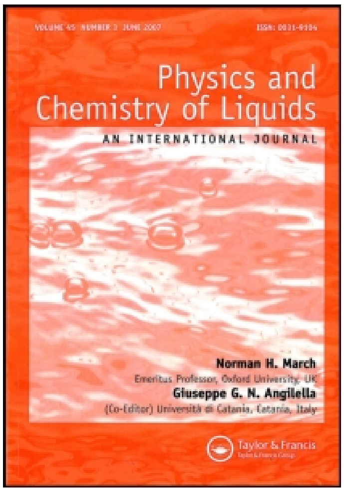

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VISCOSITY AND THERMODYNAMICS OF VISCOUS FLOW OF 1-PROPANOL WITH ANILINE, *N*-METHYLANILINE AND *N*,*N*-DIMETHYLANILINE

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Viscosities of the systems, 1-propanol + aniline, 1-propanol + *N*-methylaniline and 1-propanol + *N*,*N*-dimethylaniline have been measured in the temperature range 294.15 to 323.15 K for the whole range of composition. The viscosities have been plotted against mole fraction of anilines. The viscosity – composition curves show minima, though not well-defined, in highly rich, moderately rich and moderately poor regions of 1-propanol respectively for 1-propanol + aniline, 1-propanol + *N*-methylaniline and 1-propanol + *N*,*N*-dimethylaniline systems. The excess viscosities have been found to be negative for all the systems throughout the whole composition and plotted against mole fraction of anilines. The thermodynamic activation parameters, such as, enthalpies, entropies and free energies and their excess values have been evaluated. The excess free energies have been found to be negative for all the systems and over the whole range of composition. The excess free energies have been plotted against the mole fraction of anilines. The viscosities, excess viscosities and excess free energies have been explained by assuming that the associated compounds, aniline, *N*-methylaniline and 1-propanol, are dissociated into smaller units in the solution systems by the rupture of H-bonds.

Keywords: Viscosity; Thermodynamic activation parameters for viscous flow; Aniline; *N*-methylaniline and *N*,*N*-dimethylaniline

1. INTRODUCTION

The present paper involves a study on viscometric properties of the three binary systems formed by 1-propanol with aniline, *N*-methylani-

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line and *N,N*-dimethylaniline. This is a part of a series of systems constituted by alkanols and anilines for which volumetric and viscometric properties are currently being studied in our laboratory. The survey of literature covering the last few years shows, to the best of our knowledge, no such publications with which to compare our results. However, there are a few studies which have some relevance with our work and therefore are worthy of consideration [1–5]. The paper reports the viscosity data and the thermodynamic parameters for viscous flow which are ***hitherto*** not known, and gives some insight into the nature of interaction between 1-propanol and anilines.

2. EXPERIMENTAL

1-propanol used for experiment was procured from Aldrich, the quoted purity was 99%. It was allowed to stand over molecular sieves (4A) for 2–3 weeks prior to its use. Aniline, *N*-methylaniline and *N,N*-dimethylaniline were procured from B.D.H. The quoted purities were 98–99%. Anilines were purified by distillation using a simple distillation set and only colourless middle fractions were collected and used to prepare the mixtures. The mixtures of different compositions were made by carefully weighing the pure liquids. The densities of the pure liquids and mixtures were determined by using a bicapillary pyknometer. The pyknometer was calibrated with distilled water. An analytical balance with an accuracy of ± 0.1 mg was used for weighing. 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. 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 η is the measured viscosity, η_1 is the viscosity of 1-propanol and x_1 is its mole fraction. η_2 is the viscosity of aniline or *N*-methylaniline or *N,N*-dimethylaniline and x_2 is the respective mole fraction.

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,

$$\ln(\eta Vm/hN) = \Delta H^{\neq}/RT - \Delta S^{\neq}/R \tag{2}$$

All the terms of this equation have their usual meaning. In all cases we obtained excellent fitting of ln $(\eta Vm/hN)$ *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 $\Delta S^{\neq E}$ have been calculated by the following equation,

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

where Y is the thermodynamic property of the solution. Y_1 and Y_2 are the properties of the pure components forming the binary mixtures, and x_1 and x_2 are the respective mole fractions. The excess properties, η^E and $\Delta G^{\neq E}$, have been 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, have been obtained.

3. RESULTS AND DISCUSSION

Viscosities of the pure liquids, aniline (A), *N*-methylaniline (NMA), *N*,*N*-dimethylaniline (DMA) and 1-propanol (P) at different temperatures are shown in Table I. The viscosity data are found to agree extremely well with literature values. The compounds used in this

TABLE I Viscosities, η, of pure liquids at different temperatures

T/K				308.15			
Liquids	294.15	298.15	303.15	η/mP	313.15	318.15	323.15
Aniline	41.538	36.952 36.95^{a}	30.970 30.97^{a}	26.631 26.63^{a} 26.153^{c}	23.292 23.29^{a}		
N-methyl-aniline			17.883 17.34^{a}	16.053 15.47^{a} 15.146^{c}	14.468 14.02^{a}	13.209 12.69^{a}	12.059
N,*N*-dimethyl-aniline			11.908 11.80^{a}	11.066 10.96^{a}	10.394 10.20^{a}	9.716 9.68^{a}	9.055
1-propanol	20.978	19.413	17.289 17.28^{b}	15.488	13.663	12.452	11.209

^{a}Ref. [4]; ^{b}Ref. [7]; ^{c}Ref. [8].

study are all highly polar and associated through hydrogen bond and/or through such physical forces as dipole–dipole and dipole–induced dipole interactions in their pure state. The viscosities and densities of these liquids at 303.15 K are: A ($\eta = 30.97$ mP, $\rho = 1.0128$ g cm^{-3}), NMA ($\eta = 17.88$ mP, $\rho = 0.9781$ g cm^{-3}), DMA ($\eta = 11.91$ mP, $\rho = 0.9480$ g cm^{-3}) and P ($\eta = 17.29$ mP, $\rho = 0.7962$ g cm^{-3}). The density values have been taken from Ref. [6]. The physical data suggest that aniline is extensively associated as can be understood by the increased H-bonding by two aminic hydrogen. NMA has one hydrogen capable of H-bond formation and therefore is less extensively associated than aniline. The association is further complicated by CH_3 group because of steric hindrance. *N*,*N*-dimethylaniline having no aminic hydrogen and therefore is not associated through H-bonding; however, the molecule is associated through dipolar forces which are rather weak. 1-propanol is known to be strongly associated through H-bonding like other aliphatic alkanols.

The viscosities and excess viscosities of the systems, P+A, P+NMA and P+DMA, are shown in Table II. The excess viscosities are expressed by a polynomial equation (Eq. (5)). The coefficients of the equation, A_i, and the standard deviations, σ, are shown in Table III. Figure 1 shows the variation of viscosity of the system P+A as a function of mole fraction of A. As aniline is added to 1-propanol, the viscosity generally decreases initially slightly, and on continued addition, the viscosity increases at an increasing rate until the pure state of aniline is reached. The viscosity of the system, P+NMA, is

TABLE II Viscosity (η/mP) and excess viscosity (η^E/mP) of 1-propanol + anilines at different temperatures

T/K	294.15		298.15		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	η	η^E	η	η^E
1-propanol (x_1) + Aniline (x_2)														
0.1006	20.969	−1.501	19.017	−1.694	16.848	−1.485	15.012	−1.343	13.413	−1.003				
0.1991	21.226	−2.808	19.300	−2.767	17.032	−2.384	15.159	−2.093	13.567	−1.627				
0.2994	22.187	−3.552	19.931	−3.608	17.533	−3.052	15.596	−2.620	13.938	−2.091				
0.3992	23.357	−4.198	20.976	−4.124	18.460	−3.359	16.333	−2.896	14.458	−2.447				
0.5007	24.985	−4.548	22.335	−4.460	19.517	−3.632	17.270	−3.047	15.257	−2.589				
0.6011	26.892	−4.738	23.976	−4.608	20.923	−3.621	18.424	−3.029	16.382	−2.446				
0.7011	29.628	−4.215	26.405	−4.060	23.037	−2.966	20.003	−2.632	17.906	−1.942				
0.8002	32.888	−3.350	29.253	−3.239	25.745	−1.820	22.408	−1.489	19.807	−1.130				
0.8983	36.706	−2.044	32.451	−2.159	28.102	−1.085	24.552	−0.650	21.604	−0.458				
1-propanol (x_1) + N-methylaniline (x_2)														
0.1008					16.077	−1.275	14.326	−1.153	12.904	−0.973	11.608	−0.918	10.510	−0.782
0.1995					15.321	−2.088	13.704	−1.838	12.348	−1.592	11.162	−1.437	10.100	−1.274
0.2999					15.025	−2.443	13.451	−2.153	12.099	−1.907	10.963	−1.711	10.003	−1.455
0.4015					14.938	−2.589	13.368	−2.300	12.045	−2.027	10.922	−1.828	9.995	−1.548
0.5012					15.018	−2.569	13.472	−2.259	12.193	−1.944	10.075	−1.751	10.118	−1.510
0.6016					15.272	−2.373	13.678	−2.117	12.349	−1.854	11.234	−1.668	10.258	−1.455
0.7016					15.512	−2.194	13.921	−1.939	12.597	−1.672	11.448	−1.551	10.467	−1.333
0.8003					16.105	−1.658	14.464	−1.459	13.063	−1.271	11.879	−1.175	10.908	−0.977
0.9016					16.881	−0.942	15.119	−0.870	14.468	−0.735	12.468	−0.665	11.422	−0.551
1-propanol (x_1) + N,N-dimethylaniline (x_2)														
0.1011					15.869	−1.784	13.351	−1.556	12.049	−1.371	10.914	−1.229	9.913	−1.057
0.1989					13.448	−2.609	12.145	−2.286	10.997	−2.055	10.053	−1.799	9.196	−1.547
0.2994					12.487	−2.978	11.344	−2.615	10.327	−2.358	9.491	−2.070	8.709	−1.808
0.4015					−11.941	−2.947	10.905	−2.589	9.974	−2.349	9.328	−1.943	8.513	−1.776
0.4992					11.529	−2.826	10.567	−2.498	9.763	−2.221	9.019	−1.983	8.384	−1.693

TABLE II (Continued)

T/K	294.15		298.15		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	η	η^E	η	η^E
0.5980					11.259	−2.576	10.344	−2.299	9.608	−2.044	8.881	−1.854	8.254	−1.612
0.7024					11.173	−2.134	10.436	−1.777	9.650	−1.661	8.981	−1.479	8.357	−1.292
0.7980					11.261	−1.579	10.365	−1.467	9.602	−1.406	8.961	−1.254	8.364	−1.090
0.9026					11.539	−0.810	10.710	−0.721	9.947	−0.740	9.284	−0.671	8.751	−0.495

TABLE III Coefficients, A_i, of Redlich-Kister equation (Eq. (5)) and standard deviation, σ, for excess viscosities of different systems

System	*T/K*	A_0	A_1	A_2	A_3	$\sigma(mP)$
1-propanol (x_1)+ Aniline (x_2)	294.15	−18.3679	−4.2866	−2.0109	2.1289	0.08377
	298.15	−17.8428	−3.2572	−3.8350	1.0869	0.10434
	303.15	−14.5604	−0.7613	2.1135	7.3197	0.13711
	308.15	−12.4767	−1.4101	2.4872	10.7297	0.09400
	313.15	−10.3239	−0.0023	4.1711	6.3950	0.03860
1-propanol (x_1)+ *N*-methylaniline (x_2)	303.15	−10.2988	1.6747	3.7112	0.9407	0.04442
	308.15	−9.0932	1.4558	−3.4941	0.7966	0.03108
	313.15	−7.9607	1.5323	−2.7505	0.0999	0.03241
	318.15	−7.1580	1.1230	−2.8330	0.7284	0.03072
	323.15	−6.1678	0.7367	−2.3103	1.5015	0.03407
1-propanol (x_1)+ *N,N*-dimethyl-aniline (x_2)	303.15	−11.3241	4.1849	−4.9450	3.6693	0.02066
	308.15	−9.9504	3.8866	−4.4074	2.3790	0.05923
	313.15	−8.9157	3.5793	−4.7608	0.6325	0.04235
	318.15	−7.7938	2.3724	−4.5117	2.0921	0.06638
	323.15	−6.8851	2.1398	−3.2504	2.0941	0.05304

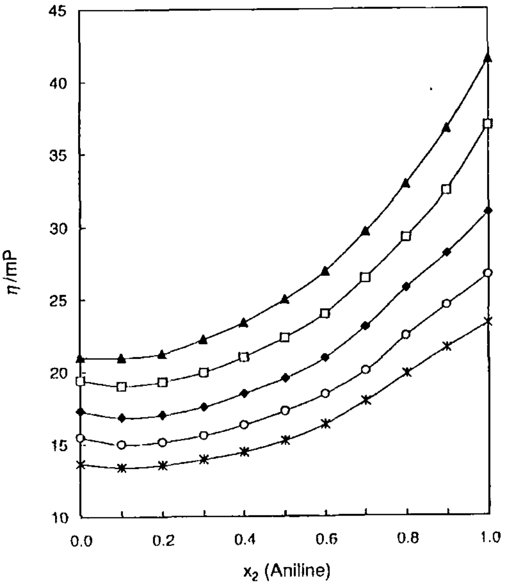

FIGURE 1 Viscosity of the system 1-propanol (x_1)+aniline (x_2) against mole fraction of aniline. Δ – 294.15 K, □ – 298.15 K, ◆ – 303.15 K, ○ – 308.15 K, ★ – 313.15 K.

represented by Figure 2 as a function of mole fraction of NMA. It is interesting to note that the viscosity decreases from both ends of the composition curve and forms a depression with broad minimum

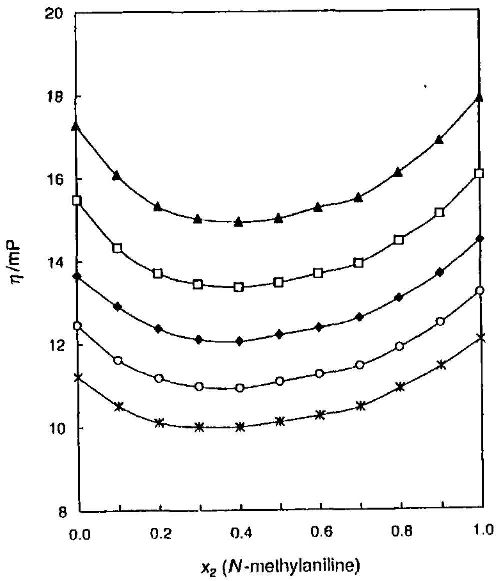

FIGURE 2 Viscosity of the system 1-propanol (x_1)+*N*-methylaniline (x_2) against mole fraction of *N*-methylaniline. Δ - 303.15 K, □ - 308.15 K, ◆ - 313.15 K, ○ - 318.15 K, ★ - 323.15 K.

occurring at ~0.4 mole fraction of NMA. Figure 3 shows the plots of viscosity against mole fraction of DMA. The viscosity decreases rather rapidly, and following a broad minimum, the viscosity continues to increase slowly up to the pure state of DMA. For comparison, the viscosities of the systems at 303.15 K are plotted in Figure 4. It is to be noted that the minima of the three systems, though not well-defined, shift from very rich, to moderately rich and then to moderately poor 1-propanol regions, respectively, for P+A, P+NMA and P+DMA systems. Assuming that the minima correspond to maximum dissociation of the associated components, one would naturally envisage that aniline is predominantly dissociated in alcohol – rich solution. *N*-methylaniline and 1-propanol are largely dissociated respectively in alcohol – rich and *N*-methylaniline – rich regions. But at about equimolar composition, the dissociation of both the components is thought to be mutually favoured and hence the broad minima at about the middle of the composition curve. In P+DMA system, 1-propanol is assumed to be predominantly dissociated in DMA - rich region.

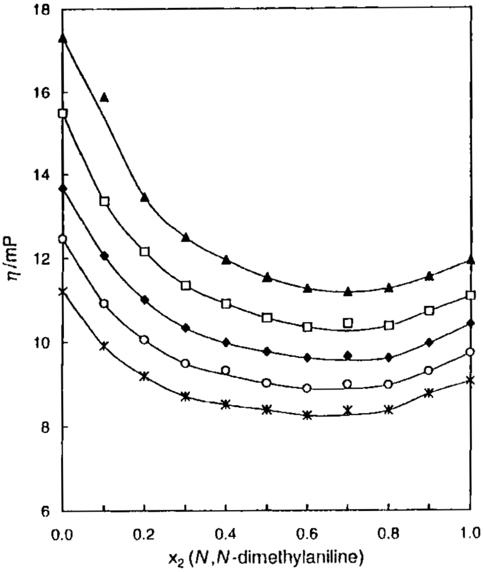

FIGURE 3 Viscosity of the system 1-propanol $(x_1)+N,N$-dimethylaniline (x_2) against mole fraction of *N*,*N*-dimethylaniline. Symbols are the same as in Figure 2.

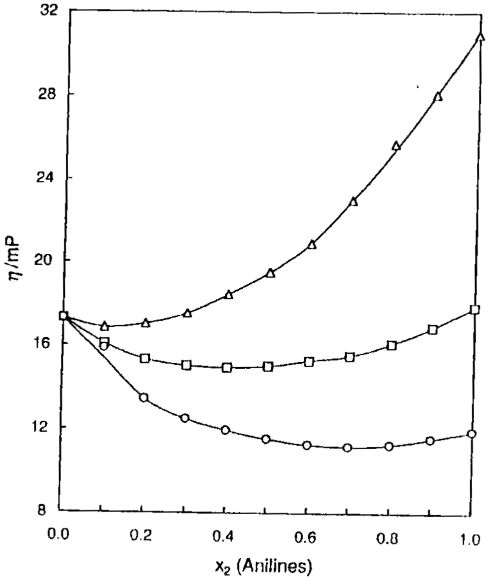

FIGURE 4 Comparison of the viscosities of the different systems at 303.15 K. The plots are drawn as viscosity against mole fraction of anilines. Δ – 1-propanol $(x_1)+$ aniline (x_2), □ – 1-propanol $(x_1)+N$-methylaniline (x_2), ○ – 1-propanol $(x_1)+N,N$-dimethylaniline (x_2).

The excess viscosities (η^E) were calculated by using Eq. (1). The values are represented in Figures 5 – 7 as a function of mole fraction of anilines at different temperatures. Examination of the figures shows that excess viscosities are negative for the whole range of composition of all the systems and that the values decrease with the increase of temperature.

In order to explain the negative excess viscosities, one is apt to consider the dissociation of one component in the other, especially when the latter is in large excess. Thus we can see in Figure 1 that, when aniline, whose viscosity is about twice as much the viscosity of 1-propanol, is added to the latter, the viscosity decreases, contrasting the usual expectation of the increase of viscosity. This is a consequence of large-scale dissociation of aniline in 1-propanol-rich solution. We observe a similar situation in P+DMA system (Fig. 3). When the concentration of 1-propanol is low compared to the concentration of *N*,*N*-dimethylaniline a similar decrease of viscosity of the mixture is observed. This again contrasts our expectation of increase of viscosity in view of the fact that the viscosity of 1-propanol is much more larger

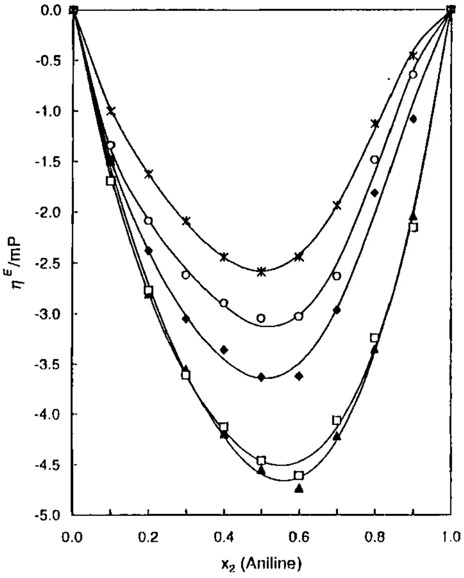

FIGURE 5 Excess viscosity of the system 1-propanol (x_1) + aniline (x_2) against mole fraction of aniline. Symbols are the same as in Figure 1.

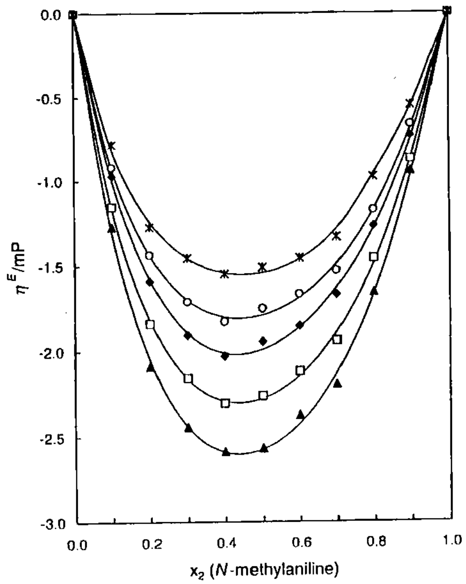

FIGURE 6 Excess viscosity of the system 1-propanol (x_1) + *N*-methylaniline (x_2) against mole fraction of *N*-methylaniline. Symbols are the same as in Figure 2.

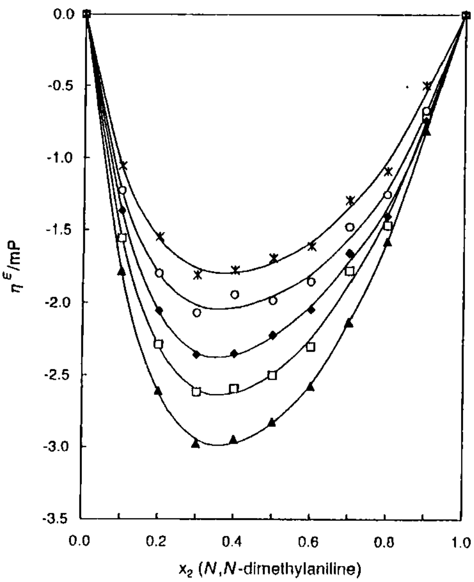

FIGURE 7 Excess viscosity of the system 1-propanol (x_1) + *N*,*N*-dimethylaniline (x_2) against mole fraction of *N*,*N*-dimethylaniline. Symbols are the same as in Figure 2.

than that of *N*,*N*-dimethylaniline. For the system P+NMA, in which the viscosities of both the components are comparable, the viscosity is found to decrease from both ends of the composition curve (Fig. 2), indicating that both the compounds are dissociated mutually in their co-solvents.

The viscosity behaviour and the negative excess viscosities of the three systems can best be explained by the following assumptions:

(i) Smaller units are formed by the dissociation of associated compounds by the rupture of H-bond in solution systems, which reduce the resistance to flow and hence the negative excess viscosities.

(ii) The dissociation of more viscous liquids (that is, the liquids which are more extensively associated through H-bond) takes place preferentially in solutions rich in less viscous liquids (that is, the liquids which are either less extensively associated through H-bonding or weakly associated through dipolar forces).

Table IV shows the thermodynamic activation parameters, enthalpy, $\Delta H^{\neq}$, entropy, $\Delta S^{\neq}$, and free energy, $\Delta G^{\neq}$, for viscous flow of the pure liquids. The high positive entropies of aniline and 1-propanol indicate that in the activated state of the flow process the species formed are structurally more disordered than those in the ground state, probably due to the rupture of hydrogen bonds of these compounds. *N*-methylaniline has $\Delta S^{\neq}$ value only marginally positive, which indicates that the overall order of the structure of the activated species is not virtually different from the structural order of the ground state species. The fairly high negative entropies of *N*,*N*-dimethylaniline indicate that the structure of the activated species is much more ordered than that in the ground state.

TABLE IV Enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$) and free energy ($\Delta G^{\neq}$) of activation for viscous flow of the pure liquids

	$\Delta H^{\neq}/kJ\,mol^{-1}$	$\Delta S^{\neq}/J\,mol^{-1}\,K^{-1}$	$\Delta G^{\neq}/kJ\,mol^{-1}$		
			303.15K	313.15K	323.15K
Aniline	23.020	21.239	15.759	15.616	15.472
N-methylaniline	15.341	−0.882	15.608	15.617	15.626
N,*N*-dimethylaniline	10.325	−15.364	14.983	15.136	15.290
1-propanol	16.510	6.369	14.579	14.516	14.452

TABLE V Enthalpy ($\Delta H^{\neq}$/kJ mol^{-1}), excess enthalpy ($\Delta H^{\neq E}$/kJ mol^{-1}), entropy ($\Delta S^{\neq}$/J mol^{-1} K^{-1}), excess entropy ($\Delta S^{\neq E}$/J mol^{-1} K^{-1}) free energy ($\Delta G^{\neq}$/kJ mol^{-1}) and excess free energy ($\Delta G^{\neq E}$/kJ mol^{-1}) of activation for viscous flow for different systems

					$\Delta G^{\neq}$			$\Delta G^{\neq E}$		
x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$	303.15 *K*	313.15 *K*	323.15 *K*	303.15 *K*	313.15 *K*	323.15 *K*
1-propanol (x_1) + Aniline (x_2)										
0.1006	17.200	0.035	8.669	0.804	14.572	14.485	14.399	−0.208	−0.217	−0.225
0.1991	17.328	−0.478	8.834	−0.496	14.650	14.562	14.473	−0.328	−0.323	−0.318
0.2994	17.932	−0.527	10.387	−0.434	14.783	14.679	14.575	−0.395	−0.392	−0.387
0.3992	18.508	−0.601	11.723	−0.582	14.954	14.837	14.720	−0.424	−0.419	−0.413
0.5007	19.088	−0.682	12.971	−0.843	15.156	15.026	14.896	−0.425	−0.418	−0.410
0.6011	19.610	−0.813	13.931	−1.376	15.387	15.248	15.108	−0.395	−0.382	−0.369
0.7001	19.774	−1.294	13.554	−3.225	15.665	15.530	15.394	−0.316	−0.283	−0.252
0.8002	19.708	−2.011	12.287	−5.981	15.983	15.860	15.737	−0.198	−0.139	−0.079
0.8983	20.657	−1.701	14.457	−5.270	16.274	16.130	15.985	−0.103	−0.051	−0.001
1-propanol (x_1) + *N*-methylaniline (x_2)										
0.1008	16.396	0.004	6.224	0.586	14.509	14.447	14.385	−0.174	−0.180	−0.185
0.1995	16.079	−0.198	5.234	0.312	14.492	14.440	14.388	−0.292	−0.296	−0.298
0.2999	15.768	−0.391	4.047	−0.147	14.541	14.501	14.460	−0.347	−0.345	−0.344
0.4015	15.617	−0.424	3.268	−0.190	14.626	14.594	14.561	−0.366	−0.364	−0.362
0.5015	15.286	−0.638	1.810	−0.923	14.737	14.719	14.701	−0.358	−0.349	−0.340
0.6016	15.405	−0.402	1.769	−0.238	14.869	14.851	14.833	−0.329	−0.327	−0.325
0.7016	15.277	−0.413	0.912	−0.370	15.001	14.991	14.982	−0.300	−0.297	−0.294
0.8003	15.165	−0.409	−0.045	−0.611	15.179	15.179	15.180	−0.224	−0.218	−0.212
0.9016	15.163	−0.293	−0.711	−0.542	15.379	15.386	15.393	−0.128	−0.123	−0.117
1-propanol (x_1) + *N*,*N*-dimethylaniline (x_2)										
0.1011	15.591	−0.294	4.011	−0.161	14.375	14.335	14.295	−0.245	−0.244	−0.242
0.1989	14.628	−0.652	1.162	−0.884	14.276	14.264	14.252	−0.383	−0.375	−0.367
0.2994	13.808	−0.850	−1.429	−1.291	14.241	14.255	14.270	−0.459	−0.447	−0.433
0.4015	12.750	−1.277	−5.018	−2.661	14.271	14.321	14.372	−0.470	−0.444	−0.416
0.4992	12.158	−1.264	−7.111	−2.631	14.314	14.385	14.456	−0.467	−0.441	−0.414

TABLE V (Continued)

					$\Delta G^{\neq}$			$\Delta G^{\neq E}$		
x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$	303.15 *K*	313.15 *K*	323.15 *K*	303.15 *K*	313.15 *K*	323.15 *K*
0.5980	11.806	−1.005	−8.496	−1.869	14.382	14.467	14.551	−0.439	−0.420	−0.402
0.7024	11.130	−1.036	−11.121	−2.225	14.501	14.613	14.724	−0.362	−0.338	−0.317
0.7980	11.267	−0.307	−11.036	−0.062	14.613	14.723	14.833	−0.288	−0.288	−0.288
0.9026	10.638	−0.289	−13.715	−0.468	14.796	14.933	15.070	−0.148	−0.143	−0.138

The enthalpies, entropies and free energies of activation for viscous flow and their excess values for the different systems are shown in Table V. The excess free energies, $\Delta G^{\neq E}$, are represented by a Redlich-Kister type equation (Eq. (5)). The coefficients of the equation and the standard deviation, σ, are listed in Table VI. The sign of $\Delta G^{\neq E}$ for a system is regarded to be a more reliable criterion as to tell about the strength of interaction. Thus, if $\Delta G^{\neq E}$ is positive the interaction between the components in a binary system is strong; the strength of interaction, however, depends upon the magnitude of $\Delta G^{\neq E}$. If, on the other hand, the sign of $\Delta G^{\neq E}$ is negative the interaction between component molecules is weak or very weak, depending upon the magnitude of negative $\Delta G^{\neq E}$. Figure 8 shows the variation of $\Delta G^{\neq E}$ as a function of mole fraction of anilines. It can be seen that for all the systems, the $\Delta G^{\neq E}$ values are negative over the whole range of composition, indicating that the interaction between 1-propanol and each of the anilines is weak. The negative $\Delta G^{\neq E}$ can be viewed as the reduction of the energy barrier that the species in the solution are to surmount in the flow process. The barrier height is reduced due to the formation of smaller units as a result of the breakage of H-bonds of the associated compounds. Earlier in this discussion, the negative excess viscosities of these systems have been explained by the same concept. Examination of Table V shows that excess entropies of all the systems are generally negative for all concentrations studied. The negative values indicate that the complexes formed in the activated state of the flow process are structurally more ordered than those in the ground state.

TABLE VI Coefficients, A_i, of Redlich-Kister equation and standard deviation, σ, for excess free energies of activation for viscous flow of different systems

System	T/K	A_0	A_1	A_2	A_3	σ (*kJmol*$^{-1}$)
1-propanol (x_1)+	303.15	−1.6963	0.2508	−0.2614	0.5202	0.04551
Aniline (x_2)	313.15	−1.6773	0.4591	0.4675	1.1963	0.01081
	323.15	−1.6486	0.5324	0.8603	1.7343	0.01538
1-propanol (x_1)+	303.15	−1.4435	0.3247	−0.4483	−0.0102	0.00642
N-methylaniline (x_2)	313.15	−1.4241	0.3161	−0.4902	0.1327	0.00726
	323.15	−1.4062	0.3088	−0.5148	0.2646	0.00875
1-propanol (x_1)+	303.15	−1.8712	0.4460	−0.5580	0.2777	0.00672
N,*N*-dimethyl-	313.15	−1.7698	0.4503	−0.7080	0.2771	0.01266
aniline (x_2)	323.15	−1.6670	0.4245	−0.8604	0.3269	0.01824

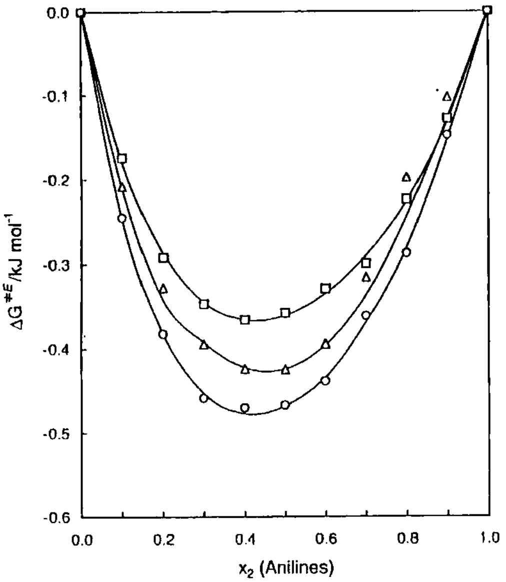

FIGURE 8 Excess free energy of activation for viscous flow against mole fraction of anilines. Symbols are the same as in Figure 4.

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