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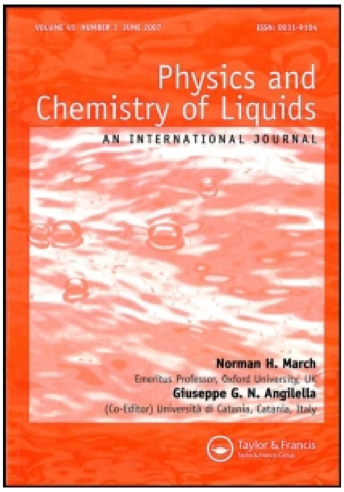

Physics and Chemistry of Liquids

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Online publication date: 27 October 2010

To cite this Article Akhtar, Shamim , Hossain, Kayes M. S. and Saleh, Muhammad A.(2002) 'Viscosity and Thermodynamics of Viscous Flow for the Systems of Isomeric Pentanols with Toluene', Physics and Chemistry of Liquids, 40: 4, 435 — 448

To link to this Article: DOI: 10.1080/0031910021000017753

URL: http://dx.doi.org/10.1080/0031910021000017753

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Phys. Chem. Liq., 2002, Vol. 40(4), pp. 435–448

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VISCOSITY AND THERMODYNAMICS OF VISCOUS FLOW FOR THE SYSTEMS OF ISOMERIC PENTANOLS WITH TOLUENE

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(Received 9 September 2001)

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Viscosities of the isomers of pentanol (1-pentanol, 2-pentanol and 3-pentanol) and their binary solutions with toluene in the whole range of composition have been measured at different temperatures between 303.15 and 323.15 K. Viscosities of pure components have been plotted against temperature and for binary mixtures, against the mole fraction of pentanols at different temperatures. At lower concentrations of pentanols, viscosities increase slowly, but at an increasing rate on the continued addition of pentanols in toluene. The excess viscosities and excess free energies of activation for viscous flow are in the order, 3-pentanol + > 2-pentanol + > 1-pentanol + toluene. Excess entropies are found to be negative for the systems 2-pentanol + toluene and 3-pentanol + toluene in the whole range of composition, but for 1-pentanol + toluene the values are small and they are either positive or negative at different compositions. The disruption of H-bonds in pentanols either by thermal effect or by the force of dispersion is in the order: 3-pentanol > 2-pentanol > 1-pentanol. This effect is considered to be quite significant in explaining the temperature dependence of viscosity of pure pentanols, negative excess values of viscosity, free energy and entropy for viscous flow as well as their orders for all the systems.

Keywords: Excess viscosity; Thermodynamics of viscous flow; Isomeric pentanols

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ISSN: 0031-9104. Online ISSN: 1029-0451 © 2002 Taylor & Francis Ltd
DOI: 10.1080/0031910021000017753

1. INTRODUCTION

The present investigation is a part of our continuing studies on the volumetric and viscometric properties of different alkanols and their mixtures with solvents of diverse physico-chemical properties. The primary objective of this study is to examine the effect of position of –OH group in pentanols (1-pentanol, 2-pentanol, 3-pentanol) on viscosities and thermodynamic properties for viscous flow of these isomers as well as their solutions in toluene. Recent studies about volumetric properties of these pentanols with toluene [1], viscometric and thermodynamic properties of pentanols + *n*-heptane [2,3] carried out in our laboratory are considered as highly relevant to the present work. Other works of sufficient interest in relation to the present one are those of D'Aprano [4–8]. We report here the viscosity and relevant thermodynamic activation parameters for the binary mixtures of 1-pentanol, 2-pentanol and 3-pentanol with toluene, which as far as we know, are not available in literature.

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2. EXPERIMENTAL

Chemicals used for the present experiments are: toluene (Merck, Gehalt > 99%). 1-pentanol (Merck-Schuchardt, Gehalt > 98%), 2-pentanol (Merck-Schuchardt, Gehalt > 98%), 3-pentanol (Merck, Gehalt > 98%). All these were used without further treatment except that the alkanols were kept over molecular sieve (4A) for at least three weeks prior to use. As measures of purity check, viscosities and densities of pure liquids are compared with the available literature values, which show satisfactory agreements as in Table I.

The density was measured by a 25 ml specific gravity bottle previously calibrated by thrice distilled water. An Ostwald Viscometer (British Standard Institution) with sufficient 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 s. An analytical balance weighing up to the accuracy of ± 0.0001 g was used in the density measurement. Temperature was controlled by a thermostatic water bath with the fluctuation of ± 0.05 K. The average uncertainty in the measured viscosity was estimated to be less than 6×10^{-3} mp.

TABLE I Density d (g cm^{-3}) and coefficient of viscosity η (mp) of pure liquids

T/K	*1-pentanol*		*2-pentanol*		*3-pentanol*		*toluene*	
	d	η	d	η	d	η	d	η
303.15	0.8073 (0.8073)[a] (0.8074)[b]	30.083 (30.0)[a]	0.8011 (0.8010)[a]	27.385 (27.7)[a]	0.8114	35.063 (35.01)[c]	0.8573	5.257 (5.25)
308.15	0.8036	25.436	0.7971	23.120	0.8070 (0.8071)[d]	27.726	0.8527 (0.8527)[e]	4.988 (4.92)[e]
313.15	0.7998	23.069	0.7928	19.429	0.8023	22.301	0.8479	4.754
318.15	0.7962	20.419	0.7883	16.606	0.7977	18.348	0.8424	4.508
323.15	0.7925	18.087	0.7851	14.795	0.7930	15.277	0.8381	4.321

[a]Reference [10]. [b]Reference [11]. [c]Reference [3]. [d]Reference [7]. [e]Reference [12].

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

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

Here, η is the measured viscosity of a particular solution, η_1 and η_2 are the viscosities and X_1 and X_2 are the mole fractions of the pure components 1(toluene) and 2(pentanol), respectively.

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

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

Here, all the terms have their usual meanings. For each of the systems, excellent linear fitting of ln ($\eta V_m/Nh$) versus $1/T$ was obtained as indicated by very high correlation coefficients in the studied range of temperature. $\Delta H^{\#}$ and $\Delta S^{\#}$ have been calculated from the slopes and intercepts, respectively, obtained by the least squares method. By using the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ thus obtained, free energy of activation for viscous flow, $\Delta G^{\#}$, was calculated by the following equation,

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

The excess thermodynamic functions, $\Delta G^{\#E}$, $\Delta H^{\#E}$ and $\Delta S^{\#E}$ were calculated by following a general equation of the type,

$$Y^E = Y - (X_1 Y_1 + X_2 Y_2) \tag{4}$$

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Here Y_1 and Y_2 are the properties of toluene and pentanol, respectively, and X_1 and X_2 are the corresponding mole fractions, and Y is the measured thermodynamic property for a particular solution. Each of the excess properties, η^E, $\Delta G^{\#E}$, $\Delta H^{\#E}$ and $\Delta S^{\#E}$, was fitted to the Redlich–Kister polynomial of the form,

$$Y^E = X_1 X_2 \sum_{i=0}^{n} A_i (X_2 - X_1)^i \tag{5}$$

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

3. RESULTS AND DISCUSSION

Viscosities of the isomers of pentanols (1-pentanol, 2-pentanol and 3-pentanol) and toluene are shown in Table I and the values as the function of temperature are represented in Fig. 1. There is a marked

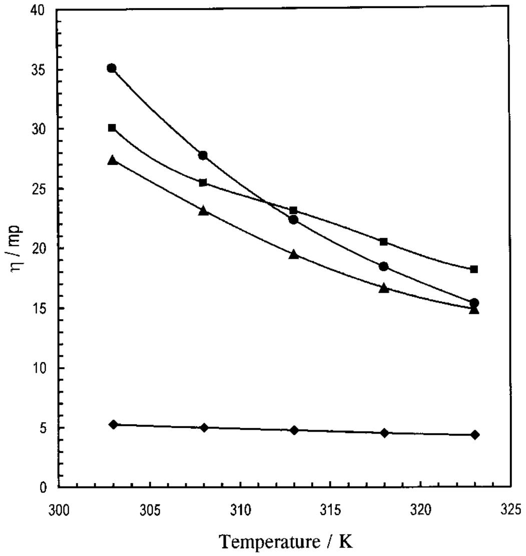

FIGURE 1 Coefficient of viscosity *vs.* temperature diagram for the pure liquids. ■, 1-pentanol; ▲, 2-pentanol; ●, 3-pentanol; ◆, toluene.

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decrease in the viscosity with increase of temperature for all the pentanols and by comparison the effect is almost insignificant for toluene. At 303.15 K, viscosity is found to be in the order: 3-pentanol > 1-pentanol > 2-pentanol, which however changes to 1-pentanol > 3-pentanol > 2-pentanol at 323.15 K. By using an empirical equation of the form,

$$\ln \eta = A + B/T,$$

the linear dependence of $\ln \eta$ against $1/T$ shows that at 290.15 K and below, the order of viscosity becomes 3-pentanol > 2-pentanol > 1-pentanol, but is reversed at 328.15 K and above. This change of order arises from the difference of temperature dependence of viscosity of pentanols as can be seen in Fig. 1. The viscosity of different isomers of pentanol as reported by D'Aprano *et al.* [6,7] and Saleh *et al.* [2] are in good agreement with the present values.

The viscosity and excess viscosity of the binary mixtures of pentanols in toluene at different temperatures are shown in Table II. Coefficients of the polynomial equation (Eq. 5) for excess viscosity of the three systems and the respective standard deviations are listed in Table III. The viscosity versus composition curves for all the systems are shown in Figs. 2–4, which are found to follow a general pattern – viscosity increases initially slowly and later on sharply on continued addition of pentanols. For dilute solutions in toluene it is believed that, pentanols which are known to exist in associated forms through H-bonding, are dissociated. This explains the low viscosity of the solutions in the toluene-rich regions. However, as the concentration of a particular pentanol is increased, multimers are formed, the extent of which increases with the rising concentration of pentanols. This accounts for the sharp rise in viscosity in the alcohol-rich regions.

Excess viscosity versus mole fraction (X_2) curves for different systems have been represented by the curves in Fig. 5 at 303.15 K. At other temperatures, the nature of the curves are almost similar. Examination of the data of excess viscosity in Table II at different temperatures and curves in Fig. 5 shows the following features:

(a) Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.7 and 0.8 mole fraction of pentanols.

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(b) The magnitude of negative excess viscosity over the whole range of concentration for the systems are in the order: 3-pentanol + toluene > 2-pentanol + toluene > 1-pentanol + toluene.

(c) An increase of temperature decreases the magnitude of negative excess viscosity, i.e., $d\eta^E/dT$ is positive. The order of the temperature dependence of negative excess viscosity is the same as in (b) above.

TABLE II Coefficient of viscosity (η) and excess viscosity (η^E) in mp of pentanol + toluene systems for different molar ratios at different temperatures

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
1-pentanol + toluene										
0.0000	5.257	0.000	4.988	0.000	4.754	0.000	4.508	0.000	4.321	0.000
0.0999	5.640	−0.619	5.329	−0.541	4.988	−0.578	4.725	−0.517	4.511	−0.475
0.1999	6.272	−1.178	5.883	−1.026	5.518	−1.001	5.195	−0.903	4.907	−0.846
0.3000	7.213	−1.659	6.717	−1.415	6.271	−1.365	5.876	−1.217	5.523	−1.116
0.4000	8.366	−2.198	7.723	−1.847	7.149	−1.794	6.645	−1.605	6.202	−1.459
0.4999	9.954	−2.620	9.102	−2.161	8.351	−2.120	7.703	−1.890	7.139	−1.701
0.6001	12.209	−2.766	11.061	−2.198	10.042	−2.224	9.178	−1.983	8.422	−1.781
0.6999	14.746	−3.077	13.244	−2.356	11.915	−2.450	10.802	−2.174	9.820	−1.950
0.8001	18.222	−3.005	16.170	−2.197	14.424	−2.399	12.961	−2.136	11.690	−1.896
0.9001	22.891	−2.382	20.769	−0.847	18.379	−1.322	16.298	−1.261	14.594	−1.082
1.0000	30.083	0.000	25.436	0.000	23.069	0.000	20.419	0.000	18.087	0.000
2-pentanol + toluene										
0.1002	5.378	−0.825	5.072	−0.745	4.802	−0.672	4.548	−0.589	4.322	−0.566
0.1998	5.727	−1.572	5.384	−1.383	5.063	−1.227	4.776	−1.066	4.524	−0.995
0.2999	6.290	−2.334	5.879	−2.022	5.503	−1.748	5.170	−1.495	4.862	−1.388
0.3994	6.912	−3.251	6.416	−2.788	5.965	−2.376	5.583	−2.006	5.226	−1.839
0.5004	7.892	−4.115	7.284	−3.462	6.696	−2.920	6.236	−2.421	5.786	−2.214
0.6006	9.188	−4.977	8.360	−4.170	7.628	−3.455	7.009	−2.856	6.466	−2.583
0.6993	11.291	−5.381	10.121	−4.458	9.099	−3.625	8.268	−2.952	7.539	−2.680
0.8004	14.277	−5.423	12.591	−4.432	11.140	−3.530	9.944	−2.857	8.904	−2.668
0.8998	19.256	−3.955	16.564	−3.263	14.350	−2.523	12.597	−1.975	11.102	−1.977
1.0000	27.385	0.000	23.120	0.000	19.429	0.000	16.606	0.000	14.795	0.000
3-pentanol + toluene										
0.1000	5.369	−0.987	5.072	−0.850	4.793	−0.755	4.555	−0.633	4.330	−0.572
0.1999	5.700	−1.982	5.352	−1.677	5.027	−1.448	4.739	−1.230	4.499	−1.062
0.2999	6.172	−3.116	5.765	−2.579	5.395	−2.163	5.062	−1.806	4.765	−1.546
0.4000	6.865	−4.366	6.364	−3.543	5.918	−2.904	5.515	−2.389	5.154	−2.006
0.4999	7.794	−5.780	7.145	−4.613	6.580	−3.716	6.092	−3.002	5.649	−2.474
0.6000	9.264	−7.150	8.369	−5.592	7.604	−4.413	6.951	−3.514	6.384	−2.834
0.6999	11.419	−8.421	10.152	−6.418	9.062	−4.962	8.461	−3.580	7.404	−3.054
0.8000	15.196	−8.795	13.133	−6.542	11.471	−4.900	10.128	−3.729	9.004	−2.863
0.9001	21.200	−7.808	17.668	−5.542	14.932	−4.178	12.847	−3.100	11.123	−2.343
1.0000	35.063	0.000	27.726	0.000	22.301	0.000	18.947	0.000	15.277	0.000

TABLE III Coefficients A_i of Redlich–Kister Eq. (5) and standard deviation σ in mp for pentanol + toluene systems at different temperatures

System	T/K	A_0	A_1	A_2	A_3	σ
1-pentanol + toluene	303.15	−10.0392	6.4845	−9.1406	8.9431	0.11418
	308.15	−8.6482	6.3556	−1.2888	−4.5610	0.25124
	313.15	−8.3455	6.4711	−4.8010	−0.5364	0.16107
	318.15	−7.4048	5.4986	−4.7140	0.5908	0.11948
	323.15	−6.7027	4.8265	−4.0274	0.0435	0.11438
2-pentanol + toluene	303.15	−16.3452	17.2808	−15.2851	7.0814	0.09076
	308.15	−13.7969	13.7423	−12.4136	5.7886	0.08310
	313.15	−11.6251	10.7551	−9.0582	3.2674	0.06089
	318.15	−9.7116	8.5560	−6.9031	1.7559	0.05282
	323.15	−8.7611	7.2126	−7.668	4.0150	0.07069
3-pentanol + toluene	303.15	−22.3215	25.9946	−35.9686	31.1423	0.41160
	308.15	−17.8717	19.0748	−24.8977	21.0121	0.30027
	313.15	−14.4499	14.0930	−17.3737	13.7329	0.22254
	318.15	−11.5771	9.2371	−11.9799	11.5634	0.20880
	323.15	−9.6895	7.7413	−8.5739	6.2966	0.12554

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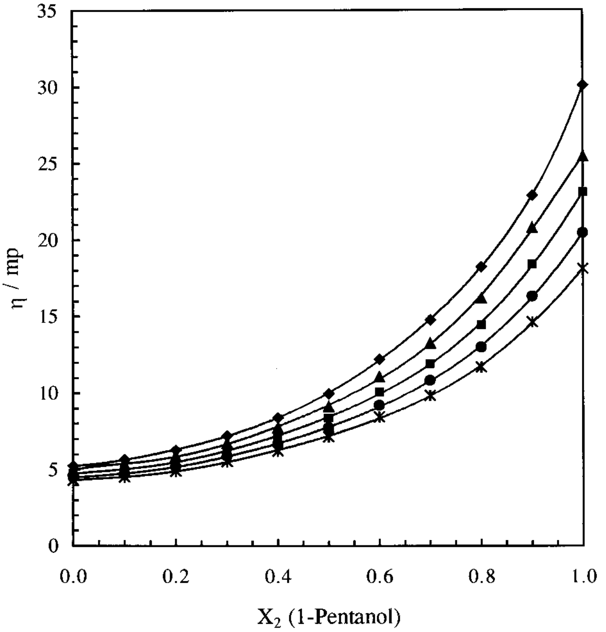

FIGURE 2 Viscosity of 1-pentanol+toluene system for different molar ratios at different temperatures. ◆, 303.15 K; ▲, 308.15 K; ■, 13.15 K; ●, 318.15 K; *, 323.15 K.

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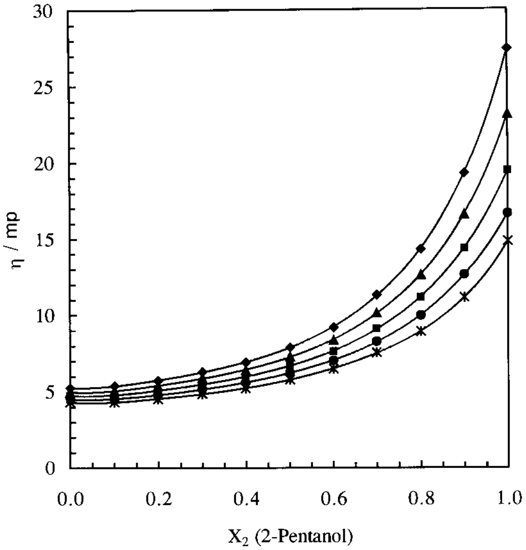

FIGURE 3 Viscosity of 2-pentanol + toluene system for different molar ratios at different temperatures. Symbols are the same as in Fig. 2.

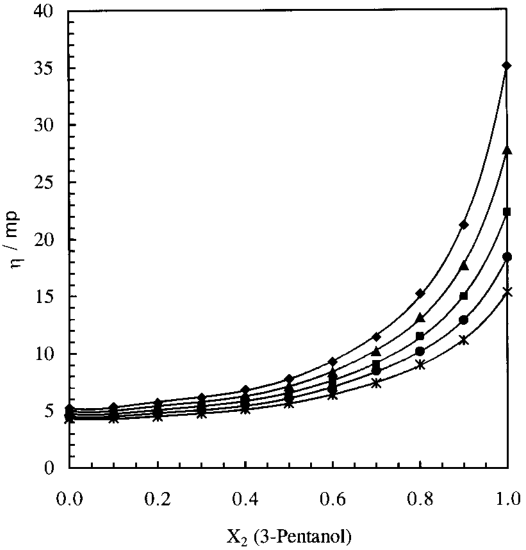

FIGURE 4 Viscosity of 3-pentanol + toluene system for different molar ratios at different temperatures. Symbols are the same as in Fig. 2.

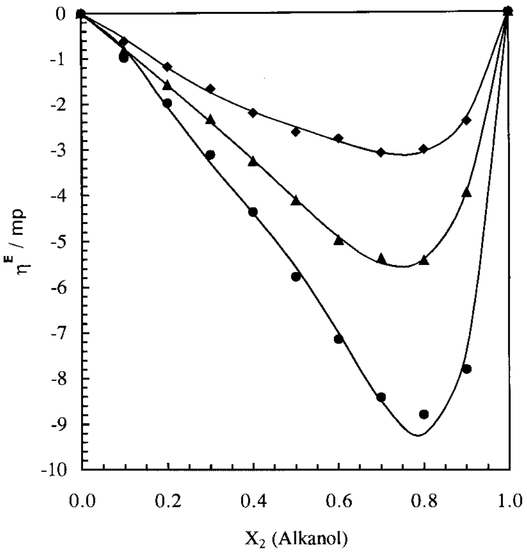

FIGURE 5 Comparison of excess viscosity of the pentanol + toluene systems at 303.15 K. ■, 1-pentanol + toluene; ▲, 2-pentanol + toluene; ●, 3-pentanol + toluene.

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The enthalpies ($\Delta H^{\#}$), entropies ($\Delta S^{\#}$) and free energies ($\Delta G^{\#}$) of activation for viscous flow and their excess values for different systems are shown in Table IV. Table V lists the coefficients and standard deviations of the Redlich–Kister polynomial equation (Eq. 5) for excess free energies and excess entropies. As it is found that $\Delta H^{\#}$ values are quite large in magnitude for all pentanols and vary as 3-pentanol > 2-pentanol > 1-pentanol, indicating that the order is related to the branching of isomers. This seems to be generally true for other alkanols as revealed by different studies notably by the works of D'Aprano *et al.* [8] and Senanayake *et al.* [9].

Plots of excess free energies, $\Delta G^{\#E}$, against the mole fraction of different pentanols at 303.15 K are shown in Fig. 6. The values are negative in the whole range of composition. The magnitude of negative values of $\Delta G^{\#E}$ is in the order: 3-pentanol + > 2-pentanol + > 1-pentanol + toluene.

The negative excess viscosities and negative excess free energies for all systems are accounted for due to the dissociation of the associated structures of pentanols in toluene. As pointed out earlier,

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TABLE IV Enthalpy ($\Delta H^{\#}$), entropy($\Delta S^{\#}$), and free energy ($\Delta G^{\#}$) of activation for viscous flow and excess values, $\Delta H^{\#E}$, $\Delta S^{\#E}$, $\Delta G^{\#E}$ at 303.15 K of pentanol + toluene systems for different molar ratios

X_2	*Enthalpy* (kJ mol^{-1})		*Entropy* (J mol^{-1}K^{-1})		*Free Energy* (kJ mol^{-1})	
	$\Delta H^{\#}$	$\Delta H^{\#E}$	$\Delta S^{\#}$	$\Delta S^{\#E}$	$\Delta G^{\#}$	$\Delta G^{\#E}$
1-pentanol + toluene						
0.0000	7.153	0.000	−17.596	0.000	12.487	0.000
0.0999	8.352	−0.026	−14.245	0.759	12.670	−0.256
0.1999	9.134	−0.471	−12.567	−0.159	12.943	−0.423
0.3000	9.998	−0.835	−10.886	−1.076	13.298	−0.509
0.4000	11.349	−0.711	−7.667	−0.453	13.674	−0.573
0.4999	12.703	−0.583	−4.656	−0.034	14.115	−0.572
0.6001	14.359	−0.176	−0.974	1.047	14.634	−0.494
0.6999	15.769	0.030	2.166	1.597	15.112	−0.455
0.8001	17.278	0.309	5.388	2.218	15.645	−0.363
0.9001	17.840	−0.356	5.219	−0.546	16.257	−0.190
1.0000	19.421 (20.352[a]) (20.5[b])	0.000	8.357 (11.26[a])	0.000	16.887 (16.939[a])	0.000
2-pentanol + toluene						
0.1002	7.920	−0.986	−15.286	−2.083	12.553	−0.354
0.1998	8.708	−1.922	−13.235	−4.356	12.721	−0.601
0.2999	9.550	−2.848	−11.262	−6.815	12.964	−0.782
0.3994	10.471	−3.668	−9.025	−8.941	13.206	−0.958
0.5004	11.721	−4.185	−6.025	−10.370	13.547	−1.041
0.6006	13.408	−4.251	−1.731	−10.470	13.932	−1.077
0.6993	15.557	−3.827	3.639	−9.427	14.454	−0.970
0.8004	18.322	−2.831	10.785	−6.714	15.052	−0.796
0.8998	21.543	−1.348	18.932	−2.925	15.804	−0.461
1.0000	24.664 (25.933[a])	0.000	26.251 (30.58[a])	0.000	16.686 (16.663[a])	0.000
3-pentanol + toluene						
0.1000	7.852	−1.875	−15.490	−4.808	12.547	−0.418
0.1999	8.746	−3.551	−13.048	−9.271	12.702	−0.741
0.2999	9.619	−5.253	−10.852	−13.989	12.909	−1.012
0.4000	10.722	−6.726	−8.106	−18.163	13.180	−1.220
0.4999	12.144	−7.876	−4.472	−21.435	13.500	−1.378
0.6000	14.217	−8.379	0.931	−22.953	13.935	−1.421
0.6999	16.149	−9.018	5.565	−25.224	14.462	−1.372
0.8000	20.373	−7.370	17.141	−20.569	15.177	−1.135
0.9001	25.297	−5.023	30.462	−13.988	16.008	−0.783
1.0000	32.891 (32.850[a])	0.000	51.536 (51.72[a])	0.000	17.268 (17.271[a])	0.000

[a] Reference [3]. [b] Reference [8].

excess viscosity and excess free energy follow the order: 3-pentanol > 2-pentanol > 1-pentanol, which in turn reflect the extent of dissociation mainly due to dispersion forces. D'Aprano *et al.* [7] calculated the Kirkwood correlation coefficient, I_K, from the dielectric

TABLE V Coefficients (A_i) and the standard deviation (σ) of the Redlich–Kister polynomial for excess entropy ($\Delta S^{\#E}$) and excess free energy ($\Delta G^{\#E}$) for viscous flow at 303.15 K of the pentanol + toluene systems

System	Y^E	A_0	A_1	A_2	A_3	σ
1-pentanol	$\Delta S^{\#E}$ (J mol^{-1}K^{-1})	0.6650	23.9828	7.7978	−45.0942	0.57382
+ toluene	$\Delta G^{\#E}$(kJ mol^{-1})	−2.2356	0.4401	−0.4707	−0.1314	0.01761
2-pentanol	$\Delta S^{\#E}$ (J mol^{-1}K^{-1})	−41.5133	−18.1832	19.9264	18.3158	0.11265
+ toluene	$\Delta G^{\#E}$(kJ mol^{-1})	−4.1726	−1.2597	−0.4871	0.7777	0.01382
3-pentanol	$\Delta S^{\#E}$ (J mol^{-1}K^{-1})	−85.8555	−59.8436	−27.6698	−4.7904	0.71489
+ toluene	$\Delta G^{\#E}$(kJ mol^{-1})	−5.4449	−1.9519	−1.5275	−0.7139	0.44788

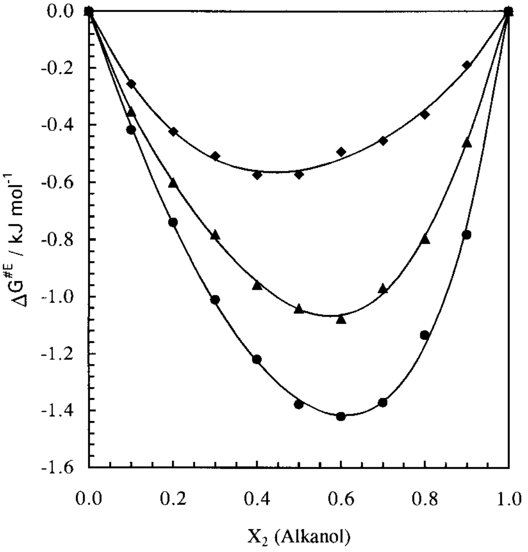

FIGURE 6 Excess free energy of activation for viscous flow *vs.* composition of pentanol + toluene systems at 303.15 K. Symbols are the same as in Fig. 5.

constant values of pentanol isomers in the temperature range of 303.15 and 323.15 K and found that the values of I_K vary in the order: 1-pentanol > 2-pentanol > 3-pentanol. Since I_K is a measure of the short range order in polar liquids, it follows that the pentanol whose I_K is larger, i.e., which is more strongly bounded by H-bond, is less likely to be dissociated than the pentanol with smaller I_K, i.e. which is less strongly bound by H-bonds. The relative ease of dissociation of the

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three pentanols either by thermal effect or by the force of dispersion in toluene should thus follow the order: 3-pentanol > 2-pentanol > 1-pentanol. This is of course as expected in terms of the branching of the hydrocarbon moieties in the isomeric pentanols. This provides a satisfactory explanation for the relative thermal effect on the viscosity of pentanols (Fig. 1) and relative magnitude of excess viscosities (Fig. 5) as well as excess energies (Fig. 6) of these systems.

Figure 7 shows the variation of entropy of activation for viscous flow, $\Delta S^{\#}$, against mole fraction of pentanols. The entropies of the systems increase almost linearly and at a similar rate up to about 0.6 mole fraction of the pentanols. Beyond this concentration, the system of 1-pentanol + toluene still follows the linear trend, while the other two show considerable divergences. The negative entropy values extend up to about 0.6 mole fraction of pentanols for all the systems; values however become significantly positive, particularly for 2-pentanol + toluene and 3-pentanol + toluene systems.

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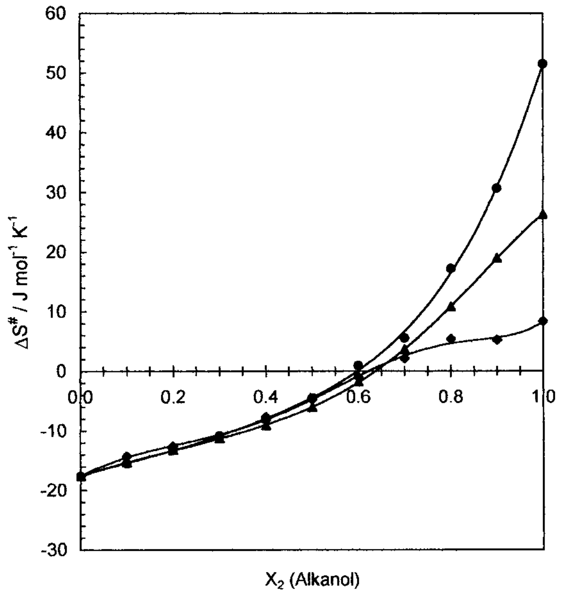

FIGURE 7 Entropy of activation for viscous flow *vs.* composition of pentanol + toluene systems. Symbols are the same as in Fig. 5.

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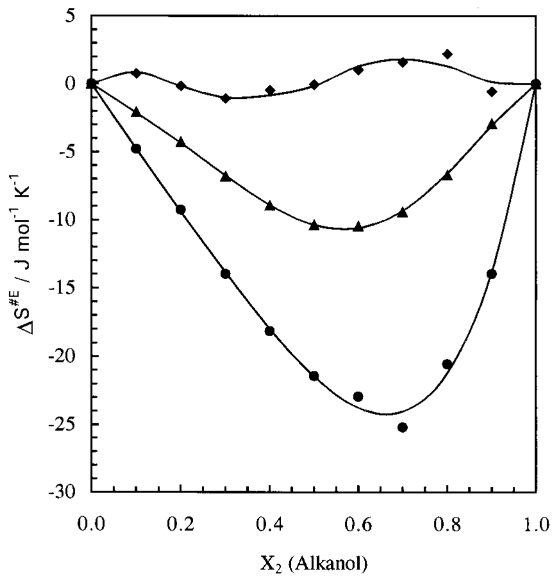

FIGURE 8 Comparison of excess entropy of activation for viscous flow *vs.* composition of the pentanol + toluene systems. Symbols are the same as in Fig. 5.

The excess entropies, $\Delta S^{\#E}$, of the systems are plotted as the function of mole fraction of pentanols in Fig. 8. The values for 1-pentanol + toluene are either slightly positive or negative, and show the maximum negative and positive values, respectively, at ~0.3 and 0.8 mole fractions of 1-pentanol. In a recent study, Saleh *et al.* [3] found that for 1-pentanol + *n*-heptane system, excess entropies were small negative in the whole range of concentration, except at 0.1 and 0.9 mole fractions of 1-pentanol for which the values are very slightly positive. Unlike 1-pentanol + toluene, both 2-pentanol + toluene and 3-pentanol + toluene systems show large negative $\Delta S^{\#E}$ with distinct minima at $X_2 = 0.6$ and 0.7, respectively. Also, the values are more negative for the latter than those of the former system in the whole range of composition.

On examination of curves for $\Delta S^{\#}$ and $\Delta S^{\#E}$ versus composition (Figs. 7 and 8), it is evident that systems with larger values of $\Delta S^{\#}$ show smaller values of $\Delta S^{\#E}$. The significance of this observation can be understood in the following manner. The larger $\Delta S^{\#}$ apparently indicates more random orientation of the complexes formed in the activated state. This is believed to be due to more severe rupturing of the H-bonds in pentanols producing greater population of smaller species in their activated states. The segregated species so formed in toluene are supposed to have lesser interactions among themselves. In this state the complexes themselves can reorient in the flow process, and thereby, reduce their motional degrees of freedom. This brings about relative decrease in the randomness of overall structures of activated complexes, and hence, smaller entropy values. The net result is, therefore, the negative excess entropy of the systems, which explains qualitatively the entropy–excess entropy correlation of the systems.

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