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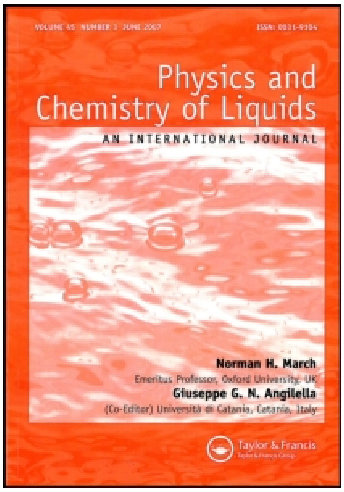

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VISCOSITY OF DILUTE AQUEOUS SOLUTIONS OF SOME DIOLS

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Viscosities of the aqueous solutions of ethane-1,2-diol, propane-1,2-diol, butane-1,2-diol, butane-1,4-diol and butane-2,3-diol up to a composition range of 0.1 mole fraction of diol have been determined at temperatures varying from 303.15 to 323.15 K, with an interval of 5 K. The viscosities and excess viscosities increase progressively with the increase of diol concentration. The free energies, excess free energies, entropies and excess entropies of activation for viscous flow also increase with diol concentration. The magnitude of all these parameters, except entropies and excess entropies, follows the order, butane-2,3-diol + water > butane-1,4-diol + water ~ butane-1,2-diol + water > propane-1,2-diol + water > ethane-1,2-diol + water. The hydrophilic and hydrophobic effects are considered for the interpretation of viscosities and the thermodynamic parameters of all aqueous diols, excepting ethane-1,2-diol + water system, for which the observed properties have been explained mainly in terms of hydrophilic effect.

Keywords: Excess viscosity; thermodynamic activation parameters; some diols

1. INTRODUCTION

This is a part of our continuing research on volumetric and viscometric properties of aqueous organic systems. Previously, we reported the volumetric and viscometric properties of acetone + water system [1] and aqueous solutions of varieties of monohydric alcohols [2, 3]. It was shown that hydrophobic hydration strongly influences the

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volumetric and viscometric properties of these systems, particularly in water-rich region. We now extend our work to aqueous systems of polyhydric alcohols, and as a first step, to dihydric alcohols. In course of our literature survey we came across some very interesting works on aqueous solutions of diols. An excellent paper on comprehensive thermodynamic investigation of ethane-1,2-diol-water was published by Huot *et al.* [4], which serves as an essential reference to the relevant fields of research. A number of other papers [5–7] that deal with excess thermodynamic properties, such as, excess free energy, excess enthalpy and excess entropy and excess partial molar volumes of the system, water + ethane-1,2-diol, seem to have some relevance with the present work. A couple of other works that deal with viscosities of the aqueous solutions of ethane-1,2-diol and propane-1,2-diol [8, 9] are directly linked with our work. The works involving aqueous solutions of higher member diols are rather scarce. A few recent studies [10–12] concerning the volumetric behaviour of aqueous solutions of higher member diols are of some significance in relation with our present work. Unfortunately, no viscometric work on aqueous butanediols, so far as we are aware, is available.

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We report in this paper the viscosities of aqueous solutions of ethane-1,2-diol, propane-1,2-diol, butane-1,2-diol, butane-1,4-diol and butane-2,3-diol up to a limited concentration range of 0.1 mole fraction of the diols. In the present investigation our main objectives are:

(a) To resolve whether hydrophobic effect exists in the systems; as the previous papers, just mentioned above, raise some controversy as to its existence. Obviously, this necessitates the measurement of physical properties in very dilute aqueous solutions of diols.
(b) To see the effect of chain length on the viscosities of the systems.
(c) To examine how the viscosities of the aqueous diol solutions are influenced by the relative position of the hydroxyl groups in butanediols.

2. EXPERIMENTAL

The diols used for experiment were procured from Aldrich, with quoted purities – ethane-1,2-diol (99 + %), propane-1,2-diol (99%),

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butane-1,2-diol (99%), butane-1,4-diol (99%) and butane-2,3-diol (99%). The chemicals were used without any further treatment except that each of them was kept over molecular sieves (4A) for at least two weeks prior to its use. The water used for preparation of solutions was twice distilled.

The density was measured by a 25 ml. specific gravity bottle previously calibrated. Ostwald viscometers of the British Standard Institution with sufficiently long efflux time were 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. The temperature was controlled by a thermostatic water bath with fluctuation of ±0.05 K.

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

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

where η is the measured viscosity, X_1 is the mole fraction of water and η_1 is its viscosity in the pure state, X_2 is the mole fraction of diol and η_2 is its viscosity in the pure state.

The enthalpy of activation, ΔH^*, and entropy of activation, ΔS^*, for viscous flow were calculated by using the Eyring equation of the form,

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

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* $1/T$ indicated by very high correlation coefficients in the range of temperature studied. ΔH^* and ΔS^* were calculated by the least squares method. By using the values of ΔH^* and ΔS^*, the free energy of activation for viscous flow, ΔG^*, was calculated by the following equation,

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

The excess thermodynamic functions, ΔG^{*E}, ΔH^{*E} and ΔS^{*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, water and diols, respectively, and X_1 and X_2 are the respective mole fractions.

3. RESULTS AND DISCUSSION

The densities and viscosities of the pure diols at different temperatures are shown in Table I. The high values of the data reveal that the diols are highly associated through intermolecular and intramolecular hydrogen bonds. Both the densities and viscosities of the pure diols are in good agreement with the literature values, except for butane-2,3-diol, for which the data differ widely from those of Sun *et al.* [14]. The extrapolated viscosity of the authors to 293.2 K is 66.56 mPa s, which is widely different from 107.9 mPa s, taken from Ref. [7] of their paper. Our extrapolated value to this temperature is 146.9 mPa s, again too far to be compared with these values. We are unable to account for this large discrepancy in the viscosity values of butane-2,3-diol, nor did Sun *et al.* [14] ascribe to the discrepancy between their data and the data referred to in their paper. At this stage we can only guess that the discrepancy of these values probably lies in the difference in the proportions of the stereoisomeric *meso* and DL forms of this diol available commercially.

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The viscosities (η) and excess viscosities (η^E) of the diol solutions at different temperatures are listed in Table II. Figure 1 shows the plots of viscosity as a function of diol concentration at 303.15 K. The viscosity is found to increase with the increase of diol concentration. At all other temperatures, the nature of the viscosity–composition curves are similar, and therefore, these are not plotted. Within the studied concentration range, it has been observed that the viscosity varies as, butane-2,3-diol + water > butane-1,4-diol + water ~ butane-1,2-diol + water > propane-1,2-diol + water > ethane-1,2-diol + water. In Figure 2 the variation of excess viscosities has been shown as a function of mole fraction of the diols at 303.15 K. The values have been found to be positive over the whole range of composition studied. The magnitude of the excess viscosities of the different diol solutions follows the same order as viscosities. Tanaka *et al.* [8] showed negative excess viscosities for ethane-1,2-diol + water and propane-1,2-diol + water systems, in

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TABLE I Density (ρ) and viscosity (η) of pure diols at different temperatures

	$\rho/g\,cm^{-3}$					$\eta/mPa\,s$				
T/K	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
Ethane-1,2-diol	1.1069 1.106512[a]	1.1031 1.103089[a]	1.0997 1.099747[a]	1.0967 1.096312[a]	1.0934 1.092946[a]	13.525 14.02[a]	11.051	9.244 9.684[a]	7.970 8.202[a]	6.713 7.032[a]
Propane-1,2-diol	1.0293	1.0256	1.0219	1.0182	1.0143	31.019	24.054	18.836	15.007	12.122
Butane-1,2-diol	0.9949 0.99544[b]	0.9912	0.9875 0.98785[b]	0.9840	0.9801	37.709 40.72[c] (303.4 K)	28.300	21.683	16.926 17.04[c] (318.5 K)	13.369
Butane-1,4-diol	1.0095 1.01011[b]	1.0067	1.0038 1.0045[b]	1.0009	0.9980	54.513 54.93[c] (303.9 K)	43.205	34.869	28.376 28.56[a] (318.5 K)	23.244
Butane-2,3-diol	0.9969 0.9849[c] (303.3 K)	0.9928	0.9893	0.9865	0.9814 0.9685[c] (322.9 K)	72.265 31.87[c] (303.3 K)	49.640	35.357	26.007 12.83[a] (318.5 K)	19.398

[a] Ref. [13]; [b] Ref. [10]; [c] Ref. [14].

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TABLE II Viscosity (η/mPa s) and excess viscosity (η^E/mPa s) of water + diols

	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
T/K	303.15		308.15		313.15		318.15		323.15	
X_2	Water (X_1) + Ethane-1,2-diol (X_2)									
0.0100	0.857	0.033	0.772	0.028	0.699	0.021	0.640	0.023	0.587	0.020
0.0200	0.929	0.082	0.836	0.071	0.756	0.060	0.690	0.056	0.630	0.048
0.0299	0.996	0.124	0.893	0.107	0.807	0.092	0.733	0.084	0.671	0.074
0.0399	1.062	0.166	0.950	0.142	0.856	0.123	0.777	0.110	0.709	0.098
0.0500	1.132	0.210	1.010	0.179	0.908	0.154	0.822	0.138	0.750	0.123
0.0600	1.212	0.263	1.079	0.226	0.969	0.196	0.876	0.174	0.795	0.152
0.0700	1.292	0.316	1.148	0.271	1.026	0.232	0.927	0.206	0.842	0.182
0.0800	1.371	0.367	1.215	0.314	1.086	0.270	0.976	0.237	0.887	0.211
0.0899	1.454	0.421	1.283	0.358	1.145	0.308	1.030	0.272	0.933	0.240
0.1001	1.534	0.471	1.354	0.402	1.205	0.345	1.083	0.304	0.978	0.267
	Water (X_1) + Propane-1,2-diol (X_2)									
0.0101	0.902	0.071	0.810	0.059	0.732	0.049	0.667	0.045	0.611	0.040
0.0200	1.022	0.161	0.910	0.133	0.820	0.114	0.743	0.102	0.678	0.089
0.0300	1.143	0.250	1.015	0.210	0.907	0.177	0.819	0.157	0.744	0.137
0.0399	1.282	0.356	1.130	0.297	1.005	0.251	0.904	0.219	0.817	0.190
0.0501	1.424	0.462	1.249	0.386	1.105	0.324	0.990	0.283	0.889	0.243
0.0598	1.568	0.572	1.373	0.479	1.213	0.406	1.078	0.349	0.967	0.301
0.0700	1.726	0.691	1.499	0.573	1.315	0.480	1.168	0.415	1.045	0.357
0.0800	1.896	0.823	1.642	0.683	1.437	0.573	1.268	0.490	1.129	0.420
0.0899	2.059	0.947	1.775	0.781	1.543	0.651	1.361	0.558	1.211	0.479
0.1000	2.246	1.091	1.927	0.898	1.671	0.748	1.466	0.636	1.299	0.544
	Water (X_1) + Butane-1,2-diol (X_2)									
0.0099	0.935	0.103	0.838	0.087	0.756	0.073	0.687	0.066	0.628	0.056
0.0200	1.099	0.235	0.976	0.197	0.874	0.166	0.789	0.146	0.716	0.126

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0.0299	1.268	0.370	1.117	0.309	0.993	0.260	0.890	0.225	0.802	0.194
0.0401	1.459	0.525	1.275	0.436	1.126	0.367	1.002	0.315	0.900	0.270
0.0496	1.639	0.669	1.422	0.553	1.247	0.462	1.104	0.395	0.986	0.337
0.0599	1.856	0.847	1.599	0.696	1.394	0.580	1.229	0.494	1.092	0.422
0.0701	2.073	1.024	1.776	0.840	1.540	0.697	1.351	0.591	1.193	0.501
0.0799	2.279	1.190	1.944	0.973	1.679	0.806	1.467	0.681	1.292	0.577
0.0899	2.493	1.360	2.120	1.113	1.823	0.919	1.587	0.775	1.395	0.657
0.0999	2.736	1.559	2.311	1.267	1.980	1.044	1.718	0.879	1.506	0.745
Water (X_1) + Butane-1,4-diol (X_2)										
0.0099	0.933	0.098	0.836	0.082	0.755	0.068	0.687	0.062	0.630	0.055
0.0201	1.090	0.218	0.971	0.184	0.871	0.156	0.788	0.138	0.718	0.121
0.0299	1.256	0.347	1.109	0.290	0.989	0.245	0.890	0.215	0.806	0.187
0.0399	1.429	0.481	1.256	0.403	1.113	0.340	0.998	0.296	0.899	0.256
0.0500	1.625	0.636	1.424	0.536	1.258	0.452	1.120	0.391	1.004	0.337
0.0599	1.838	0.807	1.595	0.669	1.400	0.563	1.243	0.485	1.110	0.418
0.0699	2.057	0.981	1.781	0.817	1.559	0.687	1.376	0.589	1.224	0.504
0.0800	2.298	1.176	1.982	0.977	1.724	0.817	1.518	0.699	1.347	0.600
0.0901	2.553	1.382	2.192	1.145	1.901	0.957	1.666	0.815	1.472	0.696
0.1000	2.818	1.597	2.404	1.314	2.079	1.097	1.817	0.933	1.602	0.797
Water (X_1) + Butane-2,3-diol (X_2)										
0.0100	0.943	0.105	0.842	0.087	0.759	0.072	0.690	0.066	0.632	0.058
0.0199	1.108	0.232	0.982	0.194	0.877	0.162	0.792	0.143	0.719	0.124
0.0300	1.294	0.378	1.138	0.316	1.010	0.266	0.905	0.231	0.816	0.200
0.0399	1.506	0.547	1.312	0.455	1.155	0.381	1.026	0.327	0.919	0.280
0.0499	1.733	0.730	1.498	0.603	1.308	0.502	1.155	0.429	1.028	0.366
0.0601	1.985	0.935	1.700	0.766	1.471	0.632	1.292	0.537	1.145	0.459
0.0699	2.242	1.145	1.910	0.936	1.649	0.776	1.436	0.654	1.264	0.554
0.0800	2.530	1.382	2.135	1.119	1.826	0.917	1.586	0.773	1.390	0.654
0.0899	2.790	1.590	2.345	1.286	1.998	1.053	1.724	0.881	1.503	0.740
0.1000	3.084	1.828	2.571	1.466	2.182	1.199	1.868	0.991	1.622	0.832

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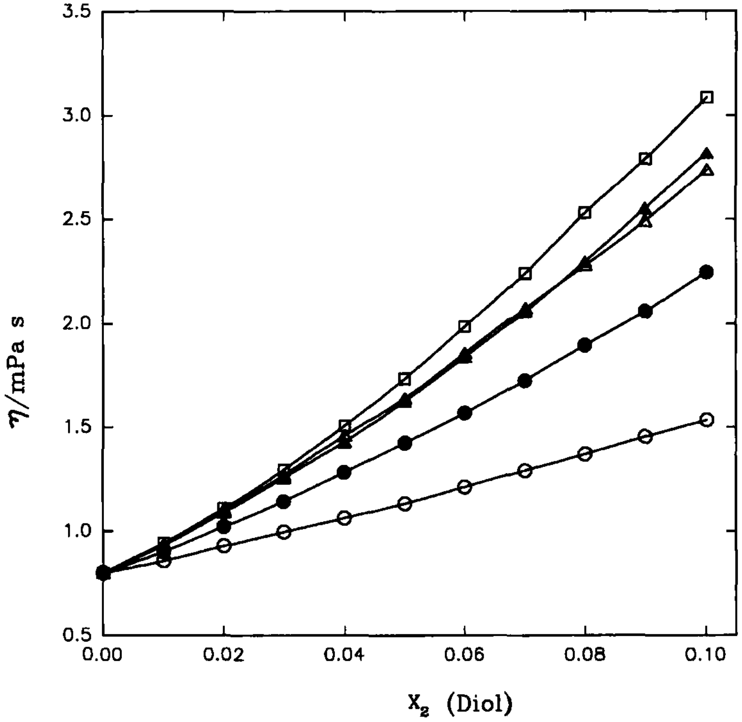

FIGURE 1 Viscosity as a function of mole fraction of diols at 303.15 K. ○ – ethane-1,2-diol, ● – propane-1,2-diol, △ – butane-1,2-diol, ▲ – butane-1,4-diol, □ – butane-2,3-diol.

contrast to our positive excess viscosities. The discrepancy has arisen, because the authors calculated excess viscosities by using the equation, $\eta^E = \eta - (X_1\eta_1 + X_2\eta_2)$, which is a different equation from Eq. (1) used by us.

The thermodynamic activation parameters for viscous flow, such as, ΔH^*, ΔG^* and ΔS^* for the pure liquids are shown in Table III. The same parameters and their excess values, ΔH^{*E}, ΔG^{*E} and ΔS^{*E} for the solutions of the different systems are shown in Table IV. Figure 3 shows the variation of ΔG^* as a function of mole fraction of diols. The values are found to increase with the increasing concentration of diols and vary in the order, butane-2,3-diol + water > butane-1,4-diol + water ~ butane-1,2-diol + water > propane-1,2-diol + water > ethane-1,2-diol + water. The variation of the excess free energies, ΔG^{*E} as

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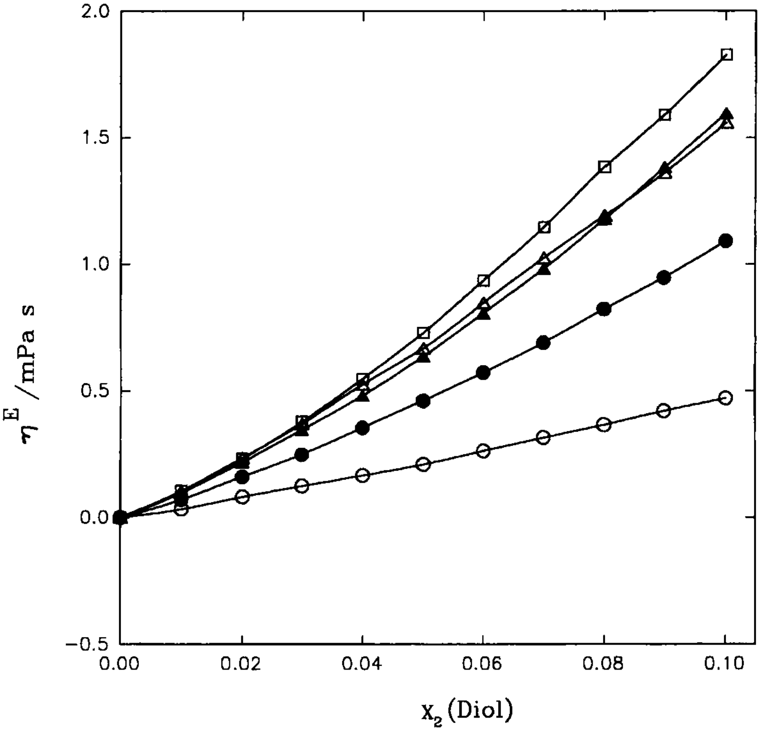

FIGURE 2 Excess viscosity as a function of mole fraction of diols at 303.15 K. Symbols as in Figure 1.

shown in Figure 4, also follows the same order as free energies. The entropies of activation for viscous flow and their excess values, ΔS^{*E}, as a function of mole fraction of diols are shown in Figures 5 and 6, respectively. The large positive η^E and the large positive ΔG^{*E} of the systems indicate strong specific interaction between the diols and water through the formation of H-bond.

The ΔS^* values of the pure liquids are found to be positive and large indicating that these liquids, which are self-associated very strongly through H-bonding, are disrupted in the activation of the flow process. The ΔS^{*E} values of the mixtures are also positive and generally large in magnitude, which suggest that in the solution systems the species formed through H-bonding are disrupted, perhaps more severely, in the flow process of the solutions.

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TABLE III Free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation for viscous flow of water and diols

	$\Delta G^*/KJ\,mol^{-1}$					$\Delta H^*/KJ\,mol^{-1}$	$\Delta S^*/J\,mol^{-1}\,K^{-1}$
T/K	303.15	308.15	313.15	318.15	323.15		
Water	9.049	8.955	8.861	8.767	8.673	14.742	18.78
Ethane-1,2-diol	19.006	18.863	18.720	18.577	18.434	27.679	28.61
Propane-1,2-diol	21.810	21.545	21.280	21.015	20.749	37.887	53.03
Butane-1,2-diol	22.791	22.489	22.187	21.884	21.582	41.129	60.49
Butane-1,4-diol	23.700	23.531	23.362	23.193	23.024	33.934	33.76
Butane-2,3-diol	24.420	23.948	23.475	23.004	22.655	53.031	94.38

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TABLE IV Free energy (ΔG^*/kJ mol^{-1}), excess free energy (ΔG^{*E}/kJ mol^{-1}), enthalpy (ΔH^{*E}/kJ mol^{-1}), excess enthalpy (ΔH^{*E}/kJ mol^{-1}), entropy (ΔS^*/J mol^{-1} K^{-1}) and excess entropy (ΔS^{*E}/J mol^{-1} K^{-1}) of activation for viscous flow of water + diols

	ΔG^*			ΔG^{*E}			ΔH^*	ΔH^{*E}	ΔS^*	ΔS^{*E}
T/K	303.15	313.15	323.15	303.15	313.15	323.15				
X_2					Water (X_1) + Ethane-1,2-diol (X_2)					
0.0100	9.257	9.066	8.875	0.118	0.115	0.112	15.046	0.200	19.09	0.27
0.0200	9.513	9.317	9.121	0.274	0.267	0.260	15.459	0.484	19.61	0.69
0.0299	9.733	9.535	9.337	0.396	0.388	0.380	15.746	0.644	19.83	0.82
0.0399	9.944	9.742	9.539	0.507	0.496	0.485	16.085	0.854	20.26	1.14
0.0500	10.150	9.944	9.738	0.613	0.599	0.585	16.395	1.034	20.60	1.39
0.0600	10.369	10.159	9.948	0.732	0.715	0.698	16.741	1.250	21.02	1.71
0.0700	10.574	10.360	10.146	0.838	0.818	0.798	17.059	1.439	21.39	1.98
0.0800	10.767	10.549	10.331	0.931	0.909	0.886	17.362	1.613	21.76	2.25
0.0899	10.955	10.735	10.514	1.021	0.997	0.973	17.636	1.760	22.04	2.43
0.1001	11.143	10.921	10.698	1.108	1.082	1.057	17.890	1.882	22.26	2.55
					Water (X_1) + Propane-1,2-diol (X_2)					
0.0101	9.409	9.207	9.005	0.241	0.229	0.218	15.534	0.584	20.20	1.13
0.0200	9.791	9.575	9.359	0.496	0.474	0.453	16.328	1.149	21.56	2.15
0.0300	10.142	9.911	9.681	0.719	0.686	0.653	17.135	1.723	23.07	3.31
0.0399	10.496	10.249	10.002	0.947	0.900	0.854	17.991	2.350	24.72	4.63
0.0501	10.826	10.565	10.303	1.147	1.090	1.033	18.754	2.877	26.15	5.71
0.0598	11.132	10.863	10.594	1.328	1.267	1.206	19.286	3.183	26.90	6.12
0.0700	11.431	11.149	10.866	1.497	1.426	1.354	20.006	3.667	28.28	7.16
0.0800	11.730	11.435	11.140	1.668	1.588	1.508	20.665	4.093	29.47	8.00
0.0899	11.993	11.690	11.386	1.806	1.720	1.634	21.202	4.403	30.38	8.57
0.1000	12.269	11.954	11.639	1.952	1.858	1.764	21.827	4.792	31.53	9.37
					Water (X_1) + Butane-1,2-diol (X_2)					
0.0099	9.522	9.312	9.101	0.345	0.327	0.308	15.893	0.910	21.02	1.86
0.0200	10.015	9.782	9.548	0.701	0.663	0.625	17.098	1.845	23.36	3.77

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TABLE IV (Continued)

	ΔG^*			ΔG^{*E}			ΔH^*	ΔH^{*E}	ΔS^*	ΔS^{*E}
T/K	303.15	313.15	323.15	303.15	313.15	323.15				
0.0299	10.460	10.204	9.948	1.009	0.953	0.897	18.229	2.709	25.63	5.61
0.0401	10.895	10.619	10.342	1.304	1.233	1.161	19.271	3.480	27.63	7.18
0.0496	11.260	10.967	10.671	1.542	1.454	1.367	20.240	4.193	29.61	8.75
0.0599	11.655	11.343	11.032	1.791	1.693	1.594	21.098	4.775	31.15	9.84
0.0701	12.012	11.684	11.355	2.009	1.899	1.788	21.958	5.364	32.81	11.06
0.0799	12.323	11.984	11.645	2.185	2.068	1.951	22.593	5.735	33.88	11.71
0.0899	12.622	12.242	11.895	2.347	2.193	2.072	23.116	5.989	34.72	12.12
0.0999	12.923	12.566	12.209	2.511	2.384	2.258	23.743	6.349	35.69	12.66
Water (X_1) + Butane-1,4-diol (X_2)										
0.0099	9.519	9.313	9.106	0.334	0.316	0.299	15.773	0.866	20.63	1.76
0.0201	9.999	9.780	9.560	0.665	0.635	0.606	16.665	1.562	21.99	2.96
0.0299	10.440	10.201	9.962	0.962	0.914	0.867	17.693	2.402	23.92	4.75
0.0399	10.850	10.598	10.346	1.225	1.167	1.108	18.489	3.005	25.20	5.87
0.0500	11.259	10.997	10.735	1.486	1.419	1.351	19.209	3.532	26.22	6.75
0.0599	11.642	11.363	11.085	1.723	1.641	1.559	20.081	4.213	27.84	8.21
0.0699	12.004	11.717	11.430	1.940	1.850	1.761	20.710	4.651	28.72	8.94
0.0800	12.358	12.062	11.766	2.145	2.048	1.952	21.322	5.068	29.57	9.64
0.0901	12.696	12.390	12.084	2.335	2.230	2.125	21.966	5.518	30.58	10.50
0.1000	13.011	12.692	12.372	2.505	2.387	2.270	22.707	6.068	31.98	11.75
Water (X_1) + Butane-2,3-diol (X_2)										
0.0100	9.538	9.324	9.111	0.345	0.326	0.307	16.016	0.917	21.37	1.89
0.0199	10.033	9.794	9.555	0.686	0.650	0.613	17.270	1.789	23.87	3.64
0.0300	10.510	10.250	9.990	1.009	0.959	0.909	18.397	2.530	26.02	5.02
0.0399	10.973	10.684	10.396	1.319	1.248	1.177	19.715	3.468	28.84	7.09
0.0499	11.405	11.093	10.781	1.597	1.510	1.423	20.853	4.222	31.17	8.66
0.0601	11.821	11.486	11.151	1.858	1.755	1.653	21.985	4.967	33.53	10.26
0.0699	12.204	11.853	11.501	2.089	1.978	1.867	22.850	5.453	35.12	11.10
0.0800	12.577	12.205	11.832	2.306	2.181	2.057	23.874	6.089	37.26	12.48
0.0899	12.897	12.509	12.120	2.475	2.342	2.209	24.661	6.501	38.81	13.28
0.1000	13.218	12.809	12.400	2.640	2.494	2.348	25.615	7.065	40.89	14.60

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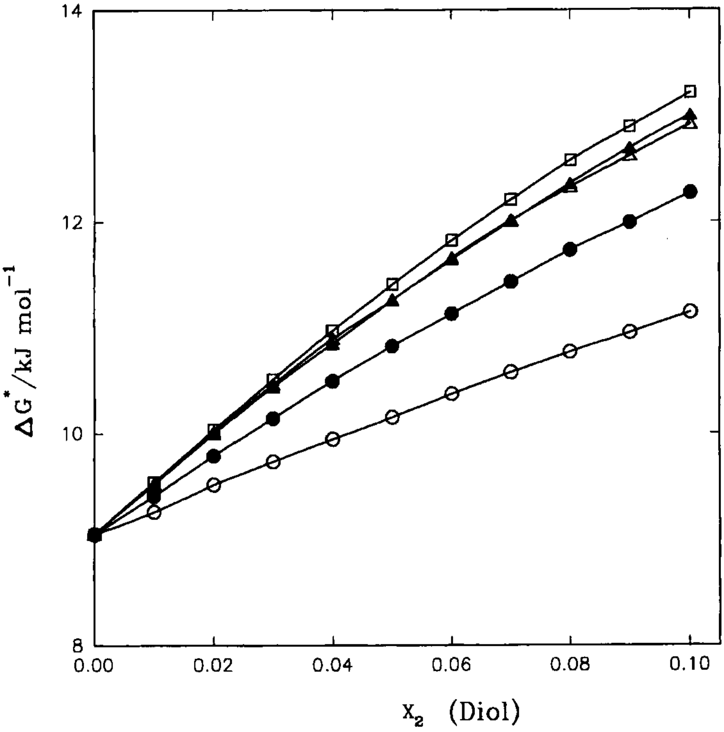

FIGURE 3 Free energy of activation for viscous flow against mole fraction of diols at 303.15 K. Symbols as in Figure 1.

In order to obtain some idea about the hydrophobic and/or hydrophilic character of diols, we wish to lay particular importance to excess entropies of the systems. At 0.1 mole fraction of diols the excess entropies are: ethane-1,2-diol (2.55 J mol^{-1} K^{-1}), propane-1,2-diol (9.37 J mol^{-1} K^{-1}), butane-1,2-diol (12.66 J mol^{-1}K^{-1}), butane-1,4-diol (11.75 J mol^{-1} K^{-1}) and butane-2,3-diol (14.60 J mol^{-1} K^{-1}). The excess entropies of the aqueous solutions of some well-known hydrophobic compounds at 0.1 mole fraction of the solutes are: 1-propanol (14.63 J mol^{-1} K^{-1}), 2-propanol (21.60 J mol^{-1} K^{-1}), *tert*-butanol (23.30 J mol^{-1} K^{-1}), the values have been taken from our unpublished results. The other hydrophobic compounds have the ΔS^{*E} values: 2-methoxyethanol (~ 12 J mol^{-1} K^{-1}) and 1,2-dimethoxyethane (~ 13 J mol^{-1} K^{-1}); the values have been estimated from the

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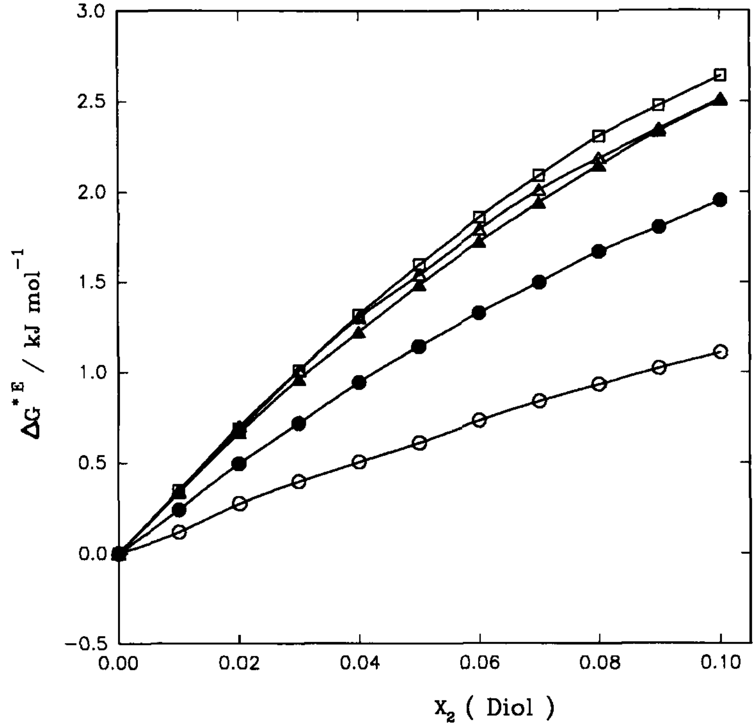

FIGURE 4 Excess free energy of activation for viscous flow against mole fraction of diols at 303.15 K. Symbols as in Figure 1.

graphs of the paper of Ref. [15]. All these compounds are characterised by the rapid increase of excess entropies in the very dilute aqueous solutions, and therefore, the values are generally large in water-rich region. Comparing these values, the diols may well be considered to be hydrophobic substances, except for ethane-1,2-diol, for which ΔS^{*E} values are too low. The viscosities of the aqueous solutions of the diols are thus influenced by both hydrophobic and hydrophilic effects. With ethane-1,2-diol, however, the effect is predominantly hydrophilic. Huot *et al.* [4], Tanaka *et al.* [8], Sakurai [5] and Corradini *et al.* [9] hold the view that ethane-1,2-diol is a weak hydrophobic substance. By hydrophilic effect, the diols form complexes with water through H-bond, while the hydrophobic effect promotes the structure of water molecules surrounding the diols in water-rich region. The two effects

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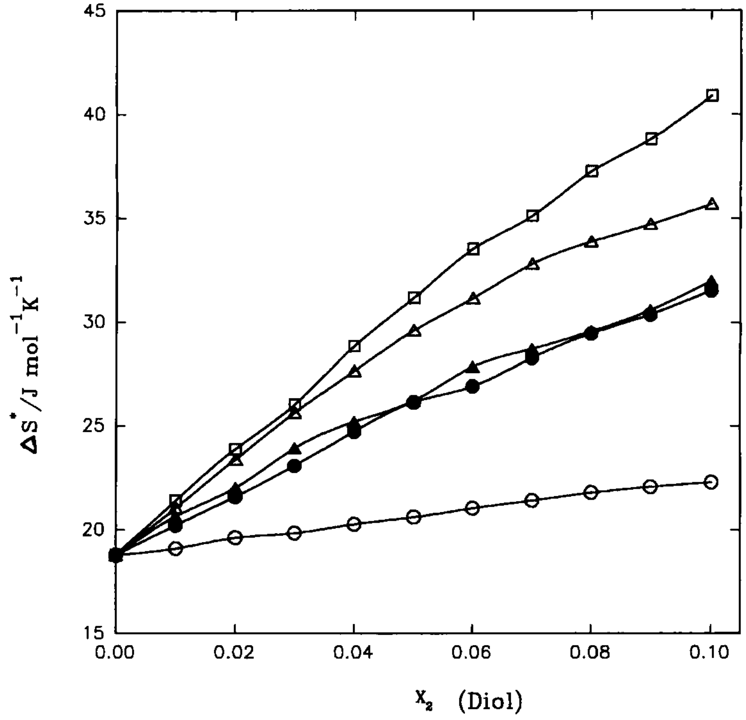

FIGURE 5 Entropy of activation for viscous flow against mole fraction of diols. Symbols as in Figure 1.

together increase the viscosity and energy of activation much more than anticipated, and hence the large positive η^E and large positive ΔG^{*E} values. In the activation of flow process the structured water molecules around the hydrophobic diols are disrupted more than the normal water giving rise to large positive excess entropies.

4. CONCLUSION

The excess viscosities and the excess thermodynamic activation parameters have been found to be positive for all the aqueous diols over the studied composition range of up to 0.1 mole fraction of diols. In order to account for the large positive excess entropies of the

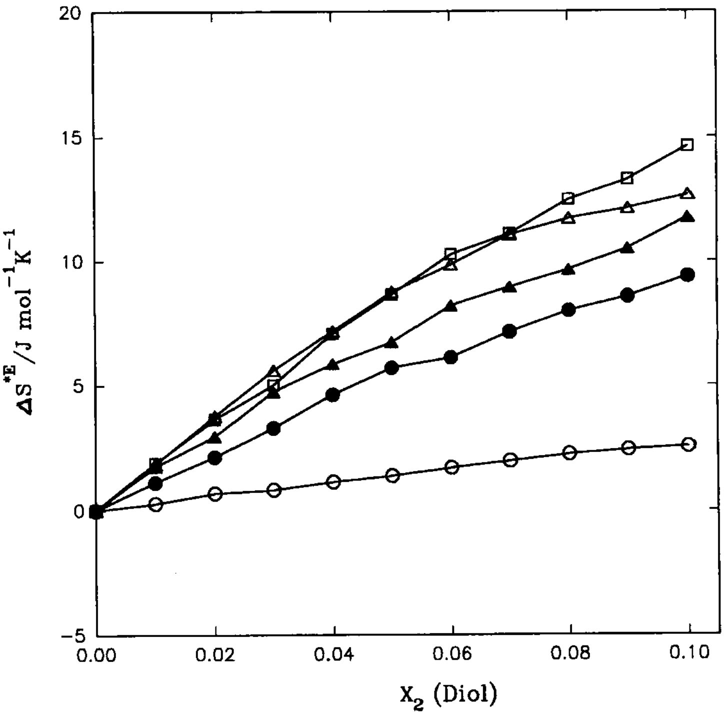

FIGURE 6 Excess entropy of activation for viscous flow against mole fraction of diols. Symbols as in Figure 1.

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mixtures, we propose that propane-1,2-diol and all other butanediols under investigation possess hydrophobic character, in addition to their hydrophilic character. However, the hydrophobic character of ethane-1,2-diol does not seem to be quite revealing, in view of the very low excess entropies of its aqueous solution. The excess viscosities, excess free energies and excess entropies of activation for viscous flow – all positive and generally large in magnitude, are accounted for by these concepts.

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