Viscosity of Aqueous Solutions of Some Alcohols

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VISCOSITY OF AQUEOUS SOLUTIONS OF SOME ALCOHOLS

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Viscosities of aqueous solutions of 1-Propanol, 2-Propanol, *t*-Butanol, allyl alcohol and propargyl alcohol were measured at temperatures 30°, 35°, 40°, 45° and 50°C covering the whole range of composition. On addition of alcohols to water, viscosity increases rapidly. Except for propargyl alcohol, viscosities pass through maxima and then decline continuously as the addition of alcohol is continued. The heights of the maxima occuring between 0.2 and 0.3 mole fraction of alcohols are in the order, *t*-Butanol > 2-Propanol > 1-Propanol > allyl alcohol. Contrary to this, propargyl alcohol shows no such maximum. After the fast initial rise, the viscosity rises slowly and monotonically up to its pure state for this alcohol. The excess viscosities are found to be positive and large in magnitude. For all alcohols, excess viscosities show maxima in water-rich region. Shallow minima are observed for 2-Propanol and *t*-Butanol, each at the alcohol-rich end of viscosity curves, which disappear gradually with the rise of temperature. The viscosity and excess viscosity vs. composition curves of all the systems were interpreted mainly in terms of hydrophobic hydration and hydrophilic interaction.

Keywords: Aqueous alcohol solutions; viscosity; hydrophobic hydration; hydrophilic interaction

1. INTRODUCTION

Interactions between water and alcohols are extremely complex. Both alcohols and water are self-associated liquids through H-bonding.

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Alcohols possess hydrophilic OH group(s) as well as hydrophobic alkyl group(s). The mode of interaction of these two groups towards water is completely different. The hydrophilic OH group of an alcohol forms H-bond with water through hydrophilic interaction and disrupts normal water structure, while the alkyl group promotes the structure of water molecules surrounding this group – the phenomenon is known as hydrophobic hydration. It is believed that both these effects, hydrophilic and hydrophobic, take place in water-rich region of aqueous alcohol solutions and are the main cause of the fast rise of viscosity. The interactions are sensitive to the following factors:

(a) Size and branching of alkyl groups in alcohols.
(b) Degree of unsaturation in hydrocarbon chains of alcohols.
(c) Composition of alcohol solutions.

For viscosity studies we have chosen 1-Propanol (CH_3-CH_2-CH_2OH), 2-Propanol (($CH_3)_2CHOH$), *t*-Butanol (($CH_3)_3COH$), allyl alcohol ($CH_2 = CH$-CH_2OH) and propargyl alcohol ($CH \equiv C$-CH_2OH). Since all these alcohols are soluble in water in all proportions, it was possible to measure viscosities covering the whole range of composition. As viscosity is an indirect measure of these interactions, we attempted to understand the extent and nature of these interactions through viscosity measurements. The selectin of these alcohols enabled us to study the dependence of viscosity on the factors mentioned above. Although some viscosity results on aqueous solutions of 1-Propanol, 2-Propanol and *t*-Butanol are available [1 – 4], as far as we know, no systematic viscosity data yet are available for allyl alcohol and propargyl alcohol and their aqueous solutions. We, therefore, are interested to report the data on these two alcoholic systems particularly, which are *hitherto* not known.

2. EXPERIMENTAL

The alcohols with quoted purities, 1-Propanol (99.7%), 2-Propanol (99.9%), *t*-Butanol (99.5%), allyl alcohol (99 + %) and propargyl alcohol (99%) were procured from Aldrich. The alcohols were used without further purification, except that they were allowed to stand

over molecular sieves (4A) about two weeks before measurements. The water used was redistilled. The densities and viscosities of pure liquids corresponded well with literature values. The density was measured by a 25 ml density bottle previously calibrated. An analytical balance with an accuracy of ± 0.1 mg was used. The viscosity was measured by U-tube Ostwald viscometers of the British Standard Institution with sufficiently long efflux, times, so that, no kinetic energy correction was necessary. The viscometers were also previously calibrated. The flow time of liquids was recorded by a timer to ± 0.1 sec. The temperature was controlled by a thermostatic water bath fluctuating to ± 0.05 K. The average accuracy in measured viscosity was above 1.7×10^{-3} mp.

3. RESULTS AND DISCUSSION

Viscosities of pure alcohols, 1-Propanol, 2-Propanol, t-Butanol, allyl alcohol and propargyl alcohol and their aqueous solutions were measured at 30°, 35°, 40°, 45° and 50°C over the whole range of composition. The values are shown in Table I. Viscosities at these temperatures are represented in Figures 1 – 5 as a function of the mole fraction of the alcohols. For comparison, viscosity-composition curves for all alcohol solutions are drawn on the same scale and are shown in

TABLE I Experimental viscosities, η, and excess viscosities, η^E, in millipise of aqueous alcohol systems for different molar ratios at different temperatures

$t/°C$	30		35		40		45		50	
x_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
				Water (x_1) + 1-Propanol (x_2) system						
0.000	8.007	–	7.225	–	6.560	–	5.989	–	5.494	–
0.100	17.914	9.263	15.351	7.554	13.329	6.260	11.690	5.246	10.344	4.444
0.200	21.996	12.649	18.869	10.454	16.357	8.739	14.310	7.377	12.600	6.264
0.300	22.833	12.735	19.645	10.564	17.049	8.839	14.922	7.462	13.149	6.345
0.400	22.282	11.372	19.317	9.516	16.812	7.964	14.740	6.713	13.045	5.738
0.500	21.343	9.555	18.569	7.992	16.261	6.726	14.294	5.657	12.682	4.835
0.600	20.381	7.645	17.800	6.385	15.663	5.388	13.829	4.536	12.303	3.876
0.700	19.391	5.361	17.031	4.712	15.040	3.967	13.342	3.343	11.896	2.846
0.800	18.616	3.749	16.440	3.145	14.574	2.641	12.978	2.220	11.607	1.888
0.900	17.959	1.897	15.941	1.593	14.196	1.336	12.679	1.103	11.381	0.944
1.000	17.354	–	15.484	–	13.859	–	12.455	–	11.208	–

TABLE I   (Continued)

| $t/°C$	30		35		40		45		50	
x_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
			Water (x_1) + 2 – Propanol (x_2) system							
0.100	20.473	11.793	17.179	9.377	14.658	7.602	12.682	6.268	11.081	5.221
0.200	25.322	15.913	21.274	12.850	18.108	10.519	15.600	8.730	13.548	7.298
0.300	25.789	15.589	21.763	12.667	18.594	10.431	16.029	8.671	13.916	7.250
0.400	24.579	13.521	20.895	11.073	17.932	9.152	15.500	7.619	13.563	6.453
0.500	22.849	10.862	19.545	8.939	16.832	7.388	14.622	6.182	12.794	5.210
0.600	21.127	8.133	18.169	6.716	15.704	5.546	13.677	4.637	12.013	3.924
0.700	19.601	5.515	16.959	4.592	14.765	3.840	12.905	3.223	11.369	2.742
0.800	18.540	3.270	16.088	2.734	14.034	2.283	12.302	1.932	10.848	1.646
0.900	17.901	1.347	15.578	1.159	13.617	0.977	11.945	0.839	10.530	0.716
1.000	17.945	–	15.570	–	13.595	–	11.895	–	10.468	–
			Water (x_1) + t – Butanol (x_2) system							
0.098	24.815	15.619	21.477	13.302	18.348	11.177	15.700	9.061	13.638	7.607
0.217	35.806	24.927	29.636	20.138	24.780	16.347	20.996	13.472	17.964	11.210
0.301	38.937	26.688	32.095	21.536	25.655	17.362	22.591	14.372	19.274	11.958
0.445	39.150	24.139	31.849	19.189	26.265	15.287	22.037	12.474	18.559	10.168
0.500	38.110	21.886	31.118	17.549	25.684	13.984	21.563	11.431	18.132	9.290
0.592	36.458	17.983	29.551	14.313	24.305	11.291	20.341	9.180	17.128	7.477
0.694	34.884	13.546	28.411	11.083	23.273	8.628	19.291	6.866	16.233	5.599
0.790	33.302	8.866	27.053	7.495	22.149	5.784	18.344	4.599	15.401	3.749
0.905	32.576	3.831	26.331	3.723	21.406	2.711	17.770	2.259	14.818	1.819
1.000	32.873	–	25.484	–	20.867	–	17.141	–	14.229	–
			Water (x_1) + Allyl alcohol (x_2) system							
0.100	14.147	5.865	12.310	4.835	10.824	4.038	9.613	3.417	8.601	2.918
0.199	16.042	7.479	13.988	6.256	12.297	5.279	10.905	4.496	9.754	3.878
0.299	16.027	7.171	14.036	6.037	12.384	5.124	11.028	4.397	9.907	3.829
0.400	15.314	6.151	13.531	5.252	12.024	4.511	10.723	3.860	9.622	3.333
0.500	14.397	4.920	12.795	4.229	11.431	3.659	10.313	3.212	9.263	2.758
0.600	13.689	3.887	12.225	3.362	10.956	2.916	9.910	2.563	8.973	2.244
0.696	12.968	2.844	11.628	2.471	10.452	2.146	9.463	1.872	8.586	1.635
0.795	12.326	1.858	11.092	1.621	10.018	1.428	9.099	1.248	8.284	1.097
0.896	11.764	0.933	10.606	0.803	9.616	0.727	8.760	0.634	8.008	0.571
1.000	11.217	–	10.156	–	9.208	··	8.419	–	7.703	–
			Water (x_1) + Propargyl alcohol (x_2) system							
0.100	10.940	2.508	9.708	2.100	8.728	1.820	7.923	1.614	7.208	1.420
0.166	11.910	3.185	10.604	2.730	9.534	2.384	8.633	2.102	7.845	1.853
0.300	12.748	3.395	11.352	2.910	10.227	2.561	9.273	2.269	8.450	2.022
0.400	12.910	3.056	11.566	2.671	10.479	2.402	9.513	2.130	8.707	1.930
0.499	12.962	2.591	11.653	2.292	10.542	2.040	9.624	1.851	8.802	1.666
0.599	13.087	2.162	11.786	1.943	10.691	1.735	9.758	1.568	8.933	1.413
0.700	13.127	1.618	11.878	1.488	10.787	1.350	9.844	1.212	9.020	1.093
0.801	13.266	1.138	12.021	1.071	10.915	0.971	9.977	0.877	9.169	0.811
0.899	13.297	0.538	12.037	1.517	10.946	0.482	10.000	0.422	9.179	0.382
1.000	13.447	–	12.143	–	11.030	–	10.099	–	9.277	–
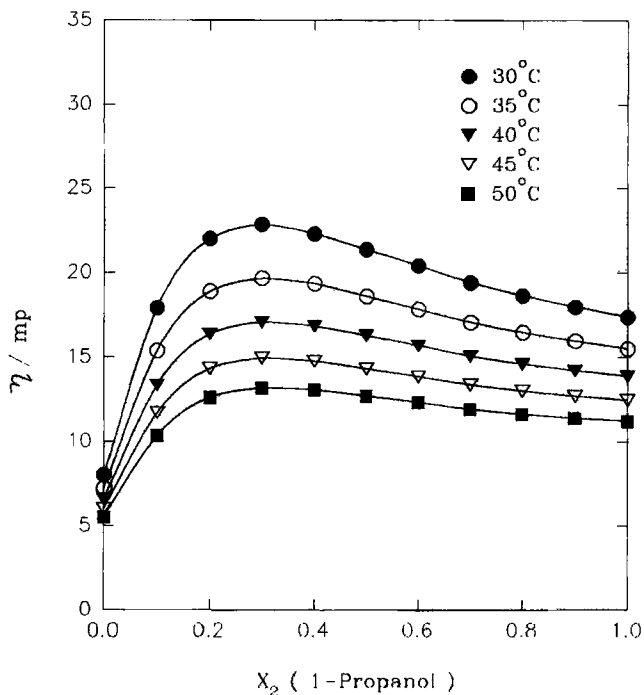
FIGURE 1   Viscosity against mole fraction of 1-Propanol (x_2).

Figure 6. The following characteristic features of viscosity are observed:

(a) Viscosities increase rapidly with the alcohol concentration and show maxima in the water-rich region (0.2 - 0.3 mole fractin of alcohol) for 1-Propanol, 2-Propanol, t-Butanol and allyl alcohol, the position of the maxima virtually does not change with the variation of temperature. Lower members of alcohols, methanol and ethanol, are also found to show such maxima [5, 6].

(b) Unlike the above alcohols, propargyl alcohol does not show any maximum (Fig. 5). For this alcohol the viscosity also increases rapidly up to about 0.3 mole fraction of alcohol. Beyond this concentration, the viscosity increases slowly but regularly until that of pure alcohol is reached.

(c) At the alcohol-rich region shallow minima are observed for 2-Propanol and t-Butanol ($\sim$0.9 mole fraction of alcohol), and it is
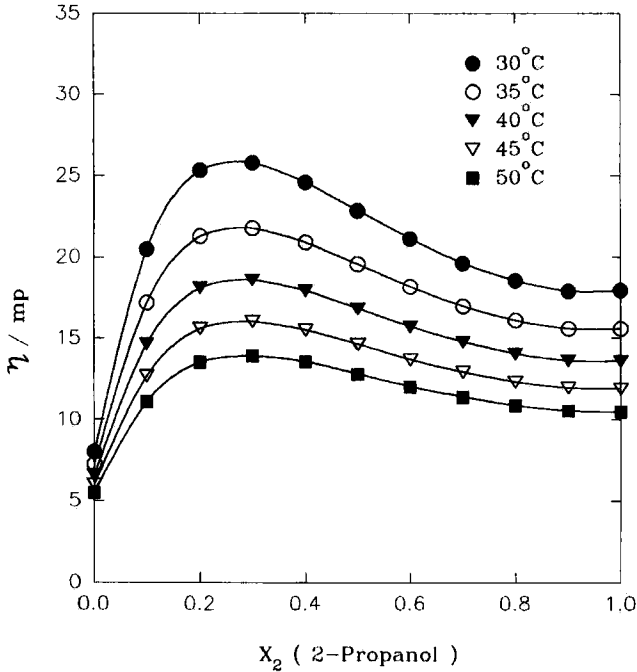
FIGURE 2   Viscosity against mole fraction of 2-Propanol (x_2).

deeper for the latter than the former alcohol (Figs. 2 – 3). The minima seem to disappear with the rise of temperature. Such minima were also observed by Tanaka *et al.* [2] for 2-Propanol and *t*-Butanol, and separately by Senanayake *et al.* [3] and Kipkemboi *et al.* [4] for *t*-Butanol aqueous solutions.

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

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

where, η is the measured viscosity of the mixtures, and η_1 and η_2 are the viscosities of water and alcohol, respectively, and x_1 and x_2 are the respective mole fractions. The values are shown in Table I. The excess viscosities were fitted to a polynomial of the form,

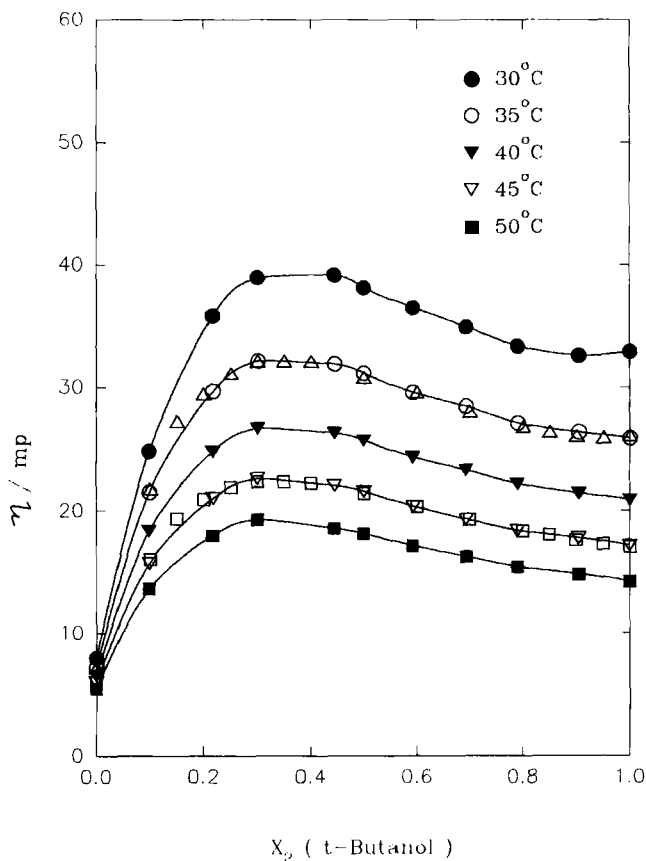$$\eta^E = x_1 x_2 \sum_{i=0}^{n} A_i (2x_1 - 1)^i \qquad (2)$$

FIGURE 3   Viscosity against mole fraction of t-Butanol (x_2). $\triangle$ and $\square$ represent the data of Ref. [4] at 35°C and 45°C respectively.

where, A_i is the fitting coefficient. Using $n = 3$, at each temperature, four A_i values and the standard deviation, σ, were obtained through the least squares method, which are shown in Table II. Figure 7 represents the η^E vs x_2 curves at 30°C for all systems. The η^E values are found to be positive and large in magnitude, indicating that the aqueous solutions of alcohols are highly non-ideal. All the curves pass through maxima in the water-rich region. The height and sharpness of the maxima are in the order, t-Butanol > 2-Propanol > 1-Propanol > allyl alcohol > propargyl alcohol.
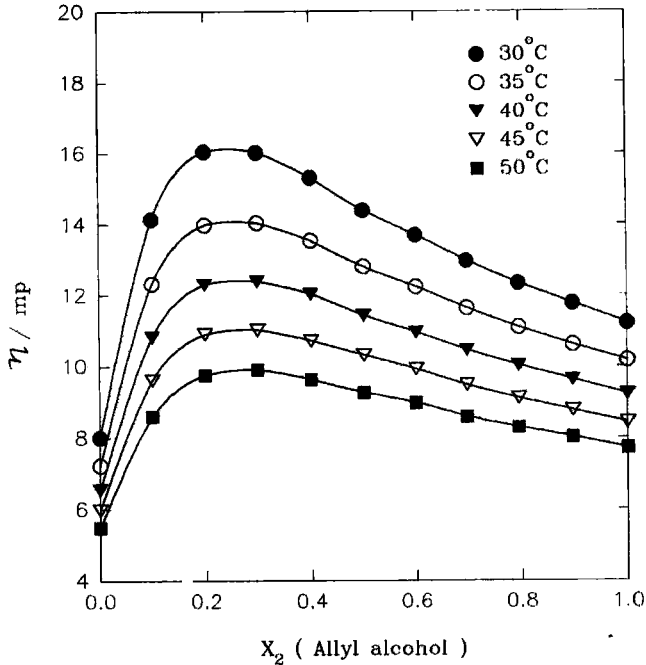
FIGURE 4   Viscosity against mole fraction of allyl alcohol (x_2).

The viscosities and excess viscosities are accounted for mainly by the following factors:

(a) Strong alcohol-water and alcohol-alcohol interactions.
(b) Hydrophobic hydration of alcohols.

The rapidly ascending part of the viscosity curves (Figs. 1 – 4) in the dilute region of alcohols can be explained primarily in terms of the phenomenon called hydrophobic hydration, which assumes that, in water-rich region, the water molecules form highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohols. These are variously known as ice-bergs, clusters or cages, though we prefer to use the term cages. There is a large body of experimental evidences which suggest the existence of such cages. On addition of alcohol to water, cages are formed continuously till the water molecules necessary to form these cages fall short. Concurrently,
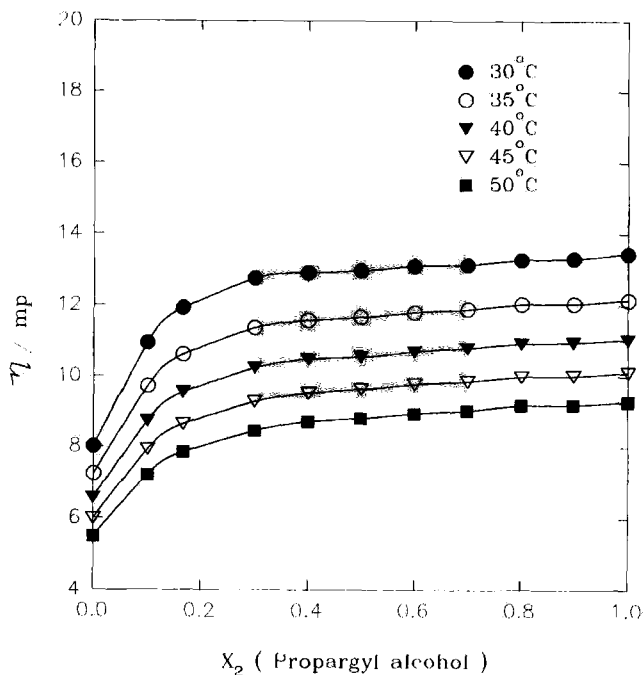
FIGURE 5   Viscosity against mole fraction of propargyl alcohol (x_2).

the hydroxyl groups of alcohols form hydrogen bonds with the surrounding water molecules. There is evidence to suggest that, at least in the case of t-Butanol, the hydroxyl group is involved in H-bonding with water solvent [7]. These two effects together cause the viscosity to rise rapidly. Further addition of alcohol continuously breaks down both cages and alcohol-water associates, and instead, alcohol-alcohol associates are preferentially formed, which result in the regular decrease in viscosity. The appearance of viscosity maxima is therefore expected as a result of these competing processes. This interpretation seems to explain well the viscosity-composition curves for all the alcohols studied, except propargyl alcohol, for which a separate treatment is given for the interpretation of the viscosity behaviour of its aqueous solutions.

The hydrophobic effect obviously increases with the size of the hydrocarbon tails of alcohols, while the hydrophilic effect should vary
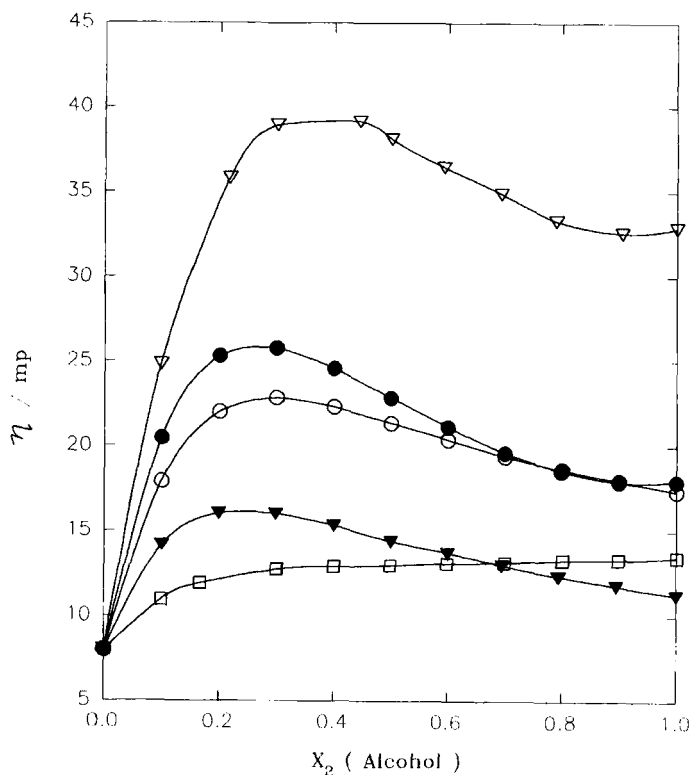
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FIGURE 6 Viscosity against mole fraction of alcohols (x_2) at 30°C. ○-1-Propanol, ●-2-Propanol, ▽-*t*-Butanol, ▼-allyl alcohol, □-propargyl alcohol.

in the reverse order. In the study of hydrophobic interactions in aqueous solutions of alkane-1, 2-diols by calorimetric and spectroscopic methods, Andini *et al.* [8] showed that hydrophobicity of hydrocarbon group varies in the order, $CH_3 > CH_2 > CH$. Further, a rough estimate as to the dependence of hydrophobocity on the saturation state of hydrocarbon part of alcohols can be made from the values of the standard thermodynamic transfer functions of ethane, ethylene and acetylene from benzene to water [9–11]. It follows from these data that the saturated alcohols should be the most hydrophobic ones and that their hydrophobocity should decrease with increasing degree of unsaturation. Having regard to these considerations, one would predict that in water-rich region the viscosity and the maxima in
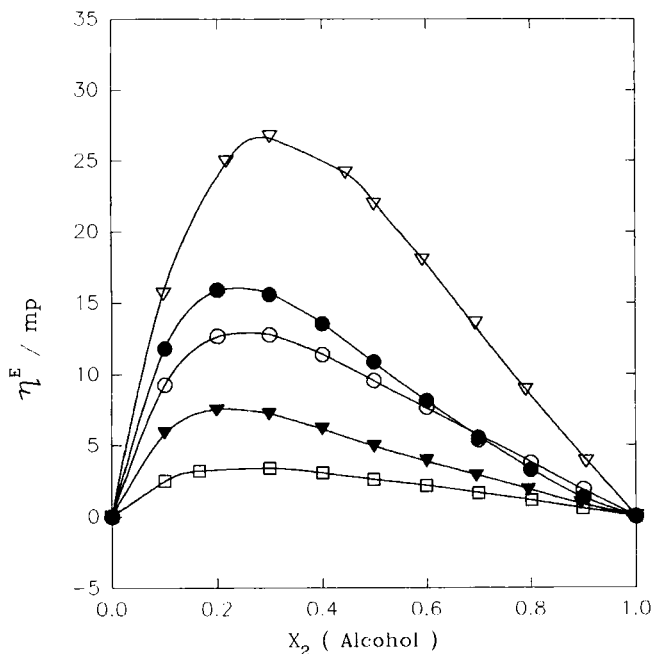
FIGURE 7   Excess viscosity against mole fraction of alcohols (x_2) at 30°C. Symbols as in Figure 6.

viscosity should be in the order, t-Butanol > 2-Propanol > 1-Propanol > allyl alcohol > propargyl alcohol. This order is in good agreement with experimental observation.

Turning our attention again to propargyl alcohol, we notice that this alcohol exhibits quite a dissimilar viscosity behaviour from the rest of alcohols as shown in Figure 6. In the initial stage, the viscosity rises at an increased rate, but comparatively much less faster than the other alcohols. Because of the existence of the maximum unsaturation and the hydrocarbon part which is least capable of causing hydrophobic hydration, the initial rise is assumed to be predominantly due to alcohol-water association through hydrogen bonding, in contrast to increased water-water association for other alcohols requiring the formation of cage structures. Following the initial rise of viscosity up to ~0.3 mole fraction of alcohol, the gradual but monotonic increase of viscosity is accounted for by increased alcohol-

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TABLE II   Coefficients A_i of Redlich-Kister equation (Eq. 2) and standard deviation, σ, in millipoise of the systems

System	Tempera-ture (°C)	A_0	A_1	A_2	A_3	σ
Water	30	37.9226	−40.1971	36.6473	−17.3673	0.13716
+	35	31.8855	−32.5927	29.3315	−14.2497	0.04458
1-Propanol	40	26.8225	−27.1440	23.9843	−11.6430	0.04785
	45	22.6161	−22.9989	20.0348	−9.6066	0.04334
	50	19.3250	−19.6247	16.7177	−7.8165	0.03777
Water	30	43.2122	−55.7203	46.1605	−26.9103	0.06883
+	35	35.6034	−45.1690	35.8497	−19.3363	0.06129
2-Propanol	40	29.4878	−37.2251	28.6951	−14.3479	0.04773
	45	24.6351	−30.8802	23.5552	−11.2540	0.04743
	50	20.8234	−25.7792	19.2822	−9.0362	0.04422
Water	30	88.3562	−80.2745	36.8677	−3.1770	0.18417
+	35	70.1186	−63.0682	40.0062	−5.1295	0.15830
t-Butanol	40	55.6301	−51.1786	34.2571	−11.0420	0.15954
	45	45.4422	−44.4911	27.8632	−4.0848	0.11920
	50	37.0661	−37.245	24.8170	−4.4168	0.11511
Water	30	19.6573	−23.0243	26.8348	−18.0324	0.06427
+	35	16.9262	−19.1567	21.4558	−14.2880	0.04821
Allyl alcohol	40	14.6225	−16.1746	17.6141	−11.0888	0.04499
	45	12.7331	−13.5590	14.4646	−9.5056	0.04146
	50	11.0407	−11.7646	12.5041	−7.6133	0.03486
Water	30	10.3942	−9.2875	10.1136	−6.7904	0.02489
+	35	9.1822	−7.5515	8.5394	−5.4379	0.02025
Propargyl	40	8.2364	−6.5776	7.2452	−4.3099	0.02468
alcohol	45	7.4018	−5.6087	6.1705	−4.1768	0.02009
	50	6.6846	−4.9953	5.2924	−3.3235	0.02700

alcohol association. In our recent study, the volumetric properties of the aqueous solutions of these alcohols have been explained in terms of hydrophobic and hydrophilic effect [12].

The difference in maxima of viscosity over the temperature range $(\Delta\eta_{max})$ of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparision with alcohol-water association, the water-water association in the cage structure is assumed to be more fragile to heat. Examination of viscosity curves of different alcohol solutions (Figs. 1–4) shows that $\Delta\eta_{max}$ varies in the order, *t*-Butanol (20.7 mp) > 2-Propanol (12.0 mp) > 1-Propanol (9.6 mp) > allyl alcohol (6.5 mp). The values, therefore, indicate the extent of the destruction of the cage structures by thermal effect which, in turn, reflects the extent of cage formation. The cages formed by the water-water association around hydrocarbon tails of alcohols are also

assumed to be thermally more unstable than water-water association in normal water [13, 14].

The shallow minima occuring at ~0.9 mole fraction of alcohol as observed in the cases of 2-Propanol (Fig. 2) and *t*-Butanol (Fig. 3) seem to be somewhat prominent at lower temperatures. This observation is in agreement with that made by Tanaka *et al.* [2]. In the study of the viscosity of aqueous solutions of isomeric butanols, Senanayake *et al.* [3] also noticed similar minima. A recent work by Kipkemboi *et al.* [4] on the viscosity of aqueous mixtures of *t*- Butanol in the temperature range 288 – 318 K also confirmed this phenomenon. The aqueous solutions of methanol and ethanol as studied by Kubota *et al.* [5] and Tanaka *et al.* [6], however, do not show this effect. Incidentally, minima of static dielectric constants of alcohol-water mixtures occur at about the same composition where the shallow minima of viscosity are observed [15]. Franks and Ives [16] explained these minima in terms of the formation of so called 'centrosymmetric' associates which are thought to be composed of one water and four alcohol molecules.

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