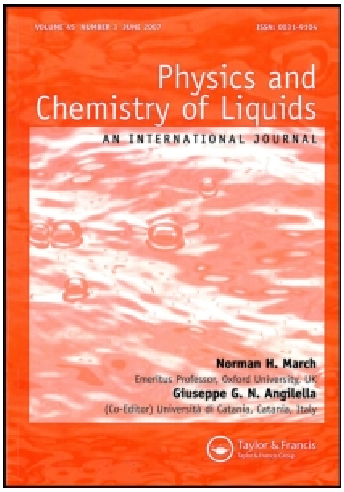

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Viscosity of aqueous solutions of 2-propyne-1-ol, 2-methyl-3-butyne-2-ol and 3-butene-2-ol

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VISCOSITY OF AQUEOUS SOLUTIONS OF 2-PROPYNE-1-OL, 2-METHYL-3-BUTYNE-2-OL AND 3-BUTENE-2-OL

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Viscosities of aqueous solutions of 2-propyne-1-ol (propargyl alcohol), 2-methyl-3-butyne-2-ol and 3-butene-2-ol have been measured at temperatures 308.15, 313.15, 318.15, 323.15 and 328.15 K over the entire composition range. Viscosity of the aqueous solutions of 2-methyl-3-butyne-2-ol and 3-butene-2-ol increases up to a maximum value and then starts decreasing almost linearly as the mole fraction of alcohol increases. 2-Methyl-3-butyne-2-ol + water and 3-butene-2-ol + water systems exhibit maxima around 0.5 and 0.2 mole fraction, respectively. Conversely, 2-propyne-1-ol + water system shows a rapid initial increase in viscosity up to 0.3 mole fraction followed by a slow steady increase as the mole fraction of alcohol increases to its pure state. Plots of excess viscosities against mole fraction of organic solutes for all the systems exhibit a sharp increase in η^E to reach a well defined maxima, after which the curves show a descending trend. The variations of viscosity and excess viscosity with the composition of the mixtures have been interpreted in terms of hydrophobic and hydrophilic interactions between the species forming the mixtures.

Keywords: Aqueous alcohol solutions; Excess viscosity; Hydrophobic and hydrophilic interaction; Organic solutes

1. INTRODUCTION

Interaction between water and alcohol are extremely complex. Both alcohols and water are self-associated liquids through H-bonding. 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 through hydrophobic hydration. A better understanding of water–alcohol interaction is of vital importance in the field of solution chemistry, as it can provide

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with important information regarding hydrophilic and hydrophobic interactions. Thermodynamic and transport studies of aqueous solution of alcohols, therefore, attracted considerable interest and some works have been reported in the literature [1–5]. Such studies with alcohols having different hydrophobic chain may provide more information about hydrophobic interaction.

With this in view and as a part of our systematic study on volumetric and viscometric properties of binary liquid mixtures, we have undertaken the viscometric study of aqueous solution of alcohols with different hydrophobic chain. Viscometric studies of aqueous solutions of 2-propyne-1-ol (propargyl alcohol) ($CH{\equiv}C{-}CH_2OH$), 2-methyl-3-butyne-2-ol [$CH{\equiv}C{-}C(CH_3)_2OH$] and 3-butene-2-ol [$CH_2{=}CH{-}CH(CH_3)OH$] have been undertaken and form the subject matter of our present communication. The selection of these alcohols enables us to study the dependence of viscosity on the factors like size and branching of alkyl group and degree of unsaturation in hydrocarbon chains in alcohols.

2. EXPERIMENTAL

The alcohols with quoted purities, 2-propyne-1-ol (GC, 99%) and 3-butene-2-ol (GC, 98%) were procured from Merck-Schuchardt Company and 2-methyl-3-butyne-2-ol (GC > 99%) was procured from Fluka chemical company. The alcohols were used without further purification. The water used was first distilled, then deionized and finally redistilled in alkaline $KMnO_4$ medium. The densities and viscosities of pure liquids corresponded well with literature values. The density was measured by previously calibrated pycnometer. An electronic balance with an accuracy of ± 0.0001 g was used. The viscosity was measured by using U-tube Ostwald viscometer of the British standard Institution with sufficiently long efflux time, so that, no kinetic energy correction was necessary. The viscometer was calibrated previously. The flow time of liquids was recorded using an electronic stopwatch, capable of reading up to 0.01 s. The temperature was controlled by a thermostatic water bath fluctuating to ± 0.01 K.

3. RESULTS AND DISCUSSION

Viscosities of 2-propyne-1-ol (propargyl alcohol), 2-methyl-3-butyne-2-ol, 3-butene-2-ol in their pure state and their aqueous solutions were measured at 308.15, 313.15, 318.15, 323.15 and 328.15 K over the entire composition range. The values are listed in Table I. The variation of viscosities at these temperatures as a function of the mole fraction of the alcohols is shown in Figs. 1–3. For comparison, viscosity *vs* composition curves for all the alcohol solutions are drawn on the same scale and are shown in Fig. 4. The following characteristic features of viscosity are observed:

(a) Viscosities increase rapidly with alcohol concentration and show maxima at 0.5004 and 0.2 mole fraction for 2-methyl-3-butyne-2-ol and 3-butene-2-ol respectively. The position of maxima virtually does not change remarkably with the variation of temperature. Lower members of alcohols, like methanol, and ethanol, are also found to show such maxima [6,7].

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

Mole fraction of alcohol (x_2)	*Viscosities, η and excess viscosities, η^E in millipoise at temperatures*									
	308.15 K		*313.15* K		*318.15* K		*323.15* K		*328.15* K	
	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
Water (x_1) + *2-methyl-3-butyne-2-ol* (x_2) *system*										
0.0000	7.195	–	6.532	–	5.963	–	5.471	–	5.042	–
0.1001	16.124	8.118	14.034	6.814	12.399	5.837	11.045	5.058	9.846	4.357
0.2003	20.202	11.294	17.801	9.821	15.602	8.380	13.686	7.133	12.159	6.183
0.3009	22.001	12.084	19.199	10.374	16.703	8.752	14.501	7.326	12.881	6.373
0.4001	22.891	11.867	19.731	9.986	17.002	8.260	14.832	6.986	13.002	5.923
0.5004	23.082	10.813	19.855	9.082	17.191	7.560	14.981	6.393	13.197	5.489
0.6020	22.968	9.295	19.682	7.758	17.122	6.518	14.862	5.451	13.117	4.716
0.7044	22.538	7.288	19.283	6.073	16.693	4.999	14.493	4.172	12.739	3.574
0.8017	22.101	5.183	18.976	4.417	16.427	3.593	14.242	2.975	12.526	2.574
0.9005	21.519	2.721	18.378	2.307	15.818	1.712	13.758	1.442	12.046	1.224
1.0000	20.902	–	17.752	–	15.514	–	13.471	–	11.775	–
Water (x_1) + *3-butene-2-ol* (x_2) *system*										
0.1003	15.533	7.902	13.473	6.564	11.892	5.602	10.489	4.736	9.399	4.114
0.2000	18.585	10.494	16.174	8.868	14.052	7.420	12.429	6.381	11.048	5.509
0.3004	18.543	9.961	16.116	8.387	14.042	7.047	12.404	6.044	11.016	5.209
0.4000	17.654	8.555	15.351	7.179	13.451	6.075	11.868	5.182	10.587	4.502
0.5013	16.817	7.161	14.605	5.956	12.812	5.028	11.377	4.343	10.107	3.725
0.6010	15.665	5.427	13.687	4.541	12.088	3.881	10.775	3.380	9.599	2.911
0.7012	14.567	3.709	12.798	3.124	11.303	2.647	10.066	2.290	9.049	2.038
0.8046	13.871	2.334	12.309	2.058	10.802	1.657	9.691	1.502	8.776	1.416
0.9031	13.309	1.085	11.711	0.879	10.437	0.800	9.323	0.719	8.361	0.652
1.0000	12.939	–	11.436	–	10.146	–	9.032	–	8.068	–
Water (x_1) + *2-propyne-1-ol* (*propargyl alcohol*) (x_2) *system*										
0.1138	9.894	2.253	8.862	1.916	7.991	1.656	7.267	1.453	6.618	1.264
0.2351	11.051	2.903	9.927	2.512	8.936	2.179	8.222	2.019	7.501	1.794
0.3145	11.494	2.997	10.342	2.602	9.365	2.317	8.508	2.037	7.832	1.881
0.4174	11.711	2.738	10.589	2.408	9.551	2.107	8.741	1.904	8.036	1.753
0.5002	11.864	2.490	10.693	2.138	9.676	1.897	8.856	1.710	8.131	1.568
0.6100	11.939	2.004	10.766	1.689	9.877	1.630	8.958	1.381	8.241	1.287
0.7185	11.997	1.475	10.852	1.226	9.924	1.188	9.072	0.998	8.323	0.960
0.8223	12.087	0.971	10.951	0.773	10.002	0.770	9.191	0.705	8.433	0.656
0.9000	12.162	0.580	11.068	0.454	10.068	0.447	9.223	0.377	8.461	0.359
1.0000	12.211	–	11.202	–	10.172	–	9.331	–	8.541	–

(b) Unlike the above mentioned alcohols, 2-propyne-1-ol (propargyl alcohol) does not show any maximum (Fig. 3). For this alcohol the viscosity also increases rapidly up to about ~0.3 mole fraction of alcohol beyond which the viscosity increases slowly but regularly till its pure state is reached. Similar observations have also been reported [1] for the same system.

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

$$\eta^E = \eta_{\mathrm{obs}} - \exp(x_1 \ell n \eta_1 + x_2 \ell n \eta_2) \qquad (1)$$

where, η_{obs} is the measured viscosity of the mixtures, η_1 and η_2 are the viscosities of water and alcohol respectively, x_1 and x_2 are the respective mole fractions.

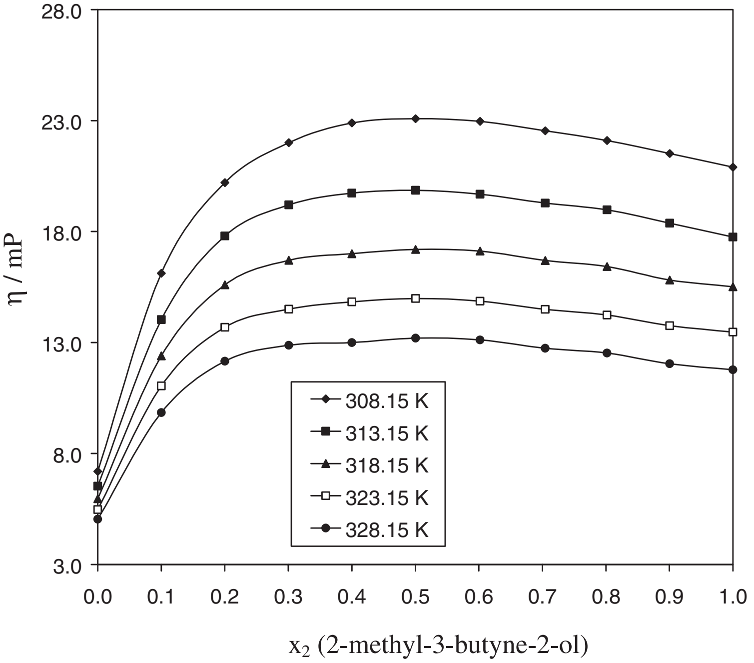

FIGURE 1 Viscosity against mole fraction of 2-methyl-3-butyne-2-ol (x_2).

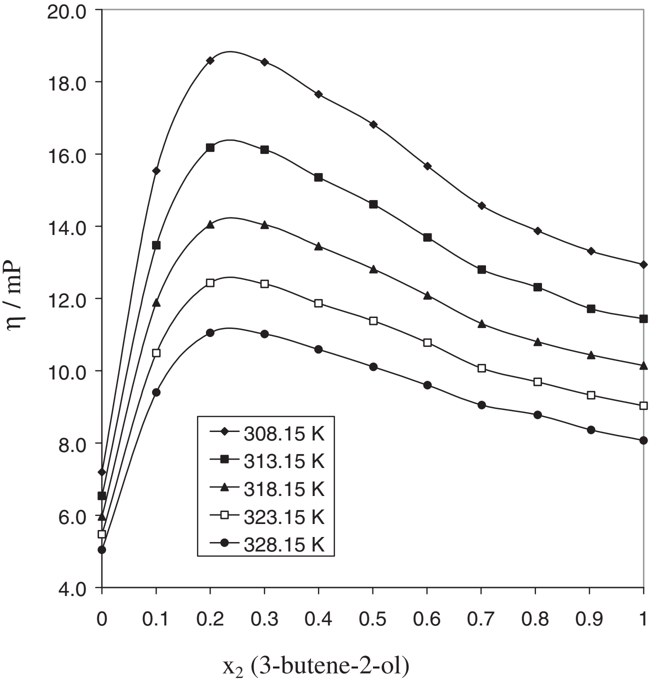

FIGURE 2 Viscosity against mole fraction of 3-butene-2-ol (x_2).

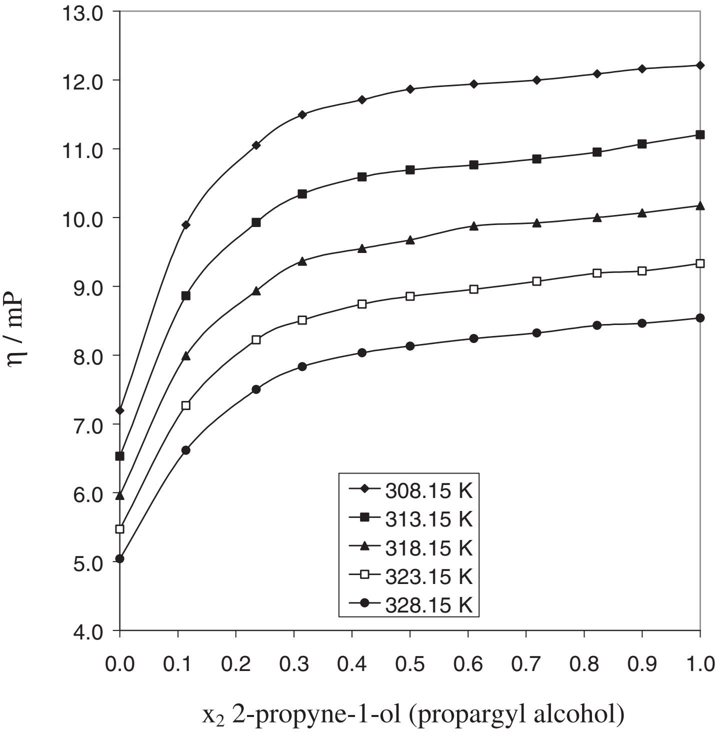

FIGURE 3 Viscosity against mole fraction of 2-propyne-1-ol (x_2).

The values are shown in Table I. The excess viscosities were fitted by least squares method to a polynomial of the form,

$$\eta^E = x_2(1 - x_2)\sum_{i=0}^{3} A_i(2x_2 - 1)^i \tag{2}$$

The values of the fitting parameters along with the standard deviation are presented in Table II. The variation of η^E against mole fraction of alcohol (x_2) is shown in Figs. 5–7.

The η^E values are positive and large in magnitude, which demonstrate that the aqueous solutions of alcohols are highly non-ideal. The height and sharpness of maxima are in the order, 2-methyl-3-butyne-2-ol > 3-butene-2-ol > 2-propyne-1-ol (propargyl alcohol).

The viscosities and excess viscosities can be interpreted on the basis of various interactions between the components of the mixture.

The rapidly ascending portion of the viscosity curves (Figs. 1 and 2) in the dilute region of alcohol can be explained primarily in terms of the phenomenon called hydrophobic hydration. It can be assumed that, in water-rich region, the water molecule forms highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohol. 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,

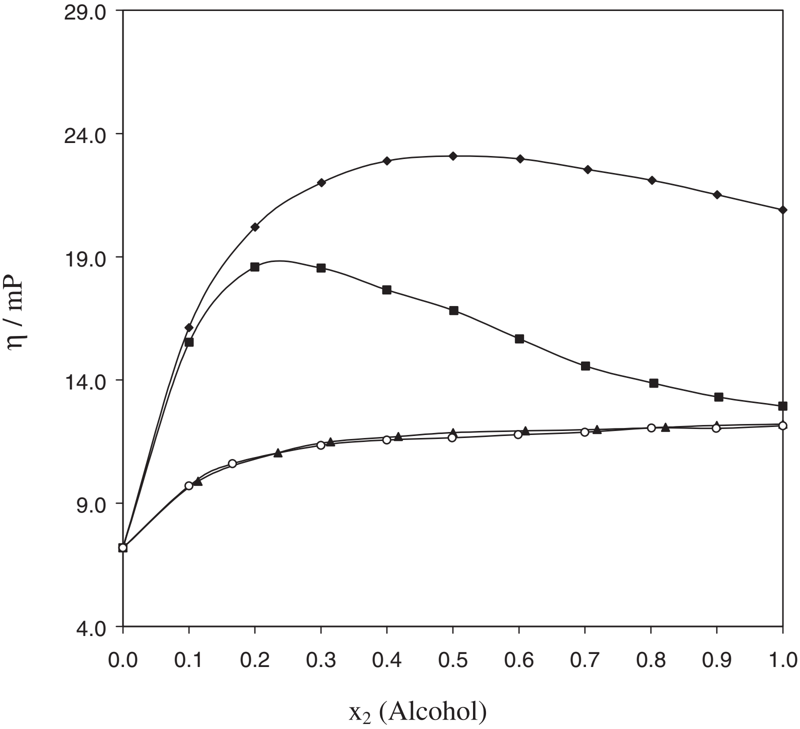

FIGURE 4 Viscosity against mole fraction of alcohols (x_2) at 308.15 K. ◆ 2-methyl-3-butyne-2-ol, ■ 3-butene-2-ol, ▲ 2-propyne-1-ol (propargyl alcohol), ○ reference data of 2-propyne-1-ol (propargyl alcohol [1].

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

System	*Temperature* (K)	A_0	A_1	A_2	A_3	σ
Water + 2-methyl-3-butyne-2-ol	308.15	42.9247	−25.0657	25.0383	−18.8144	0.1172
	313.15	36.0830	−22.9815	22.8142	−13.1911	0.0656
	318.15	30.1040	−18.9526	19.2177	−15.5470	0.0844
	323.15	25.2560	−16.0001	16.9088	−14.5764	0.0768
	328.15	21.6786	−13.7249	14.9616	−13.0637	0.0846
Water + 3-butene-2-ol	308.15	27.9075	−33.3418	33.7334	−22.4608	0.1455
	313.15	23.3867	−28.1467	28.7138	−18.0810	0.1163
	318.15	19.7581	−23.4581	24.0767	−15.9477	0.0959
	323.15	17.0306	−19.9173	20.6802	−13.0825	0.0991
	328.15	14.6878	−16.8636	18.6731	−11.2764	0.0694
Water + 2-propyne-1-ol	308.15	9.8036	−7.6576	7.1174	−4.1959	0.0405
	313.15	8.4793	−7.2042	5.4846	−2.8325	0.0311
	318.15	7.6800	−5.3903	4.8435	−3.2797	0.0365
	323.15	6.6693	−0.4035	−2.0409	−4.3250	0.0387
	328.15	6.3139	−4.8970	3.4669	−0.8612	0.0131

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 are available. Simultaneously, the hydroxyl groups of alcohol from hydrogen bonds with the surrounding water molecules.

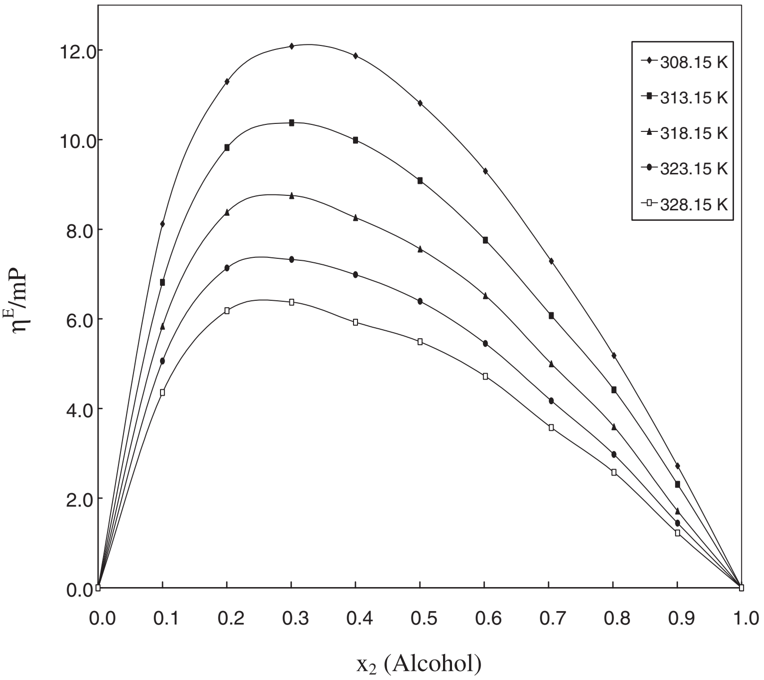

FIGURE 5 Excess viscosity against mole fraction of 2-methyl-3-butyne-2-ol.

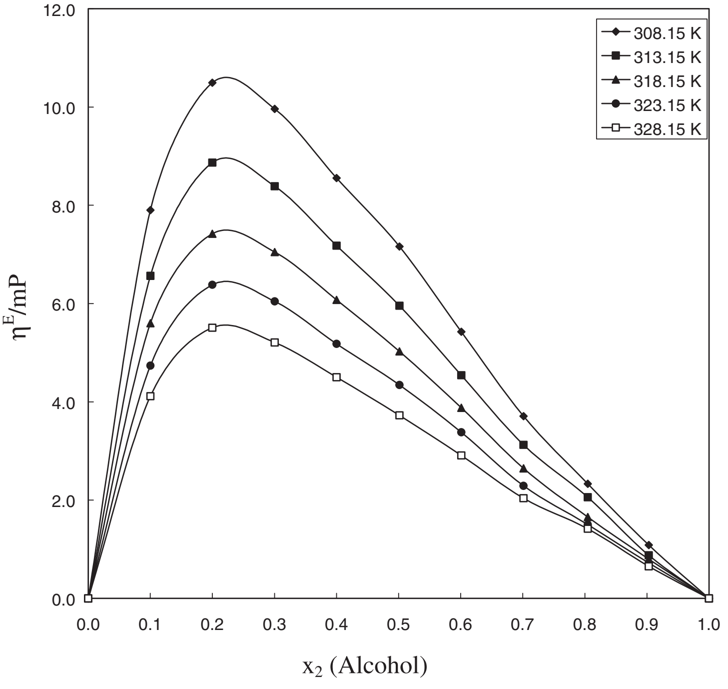

FIGURE 6 Excess viscosity against mole fraction of 3-butene-2-ol.

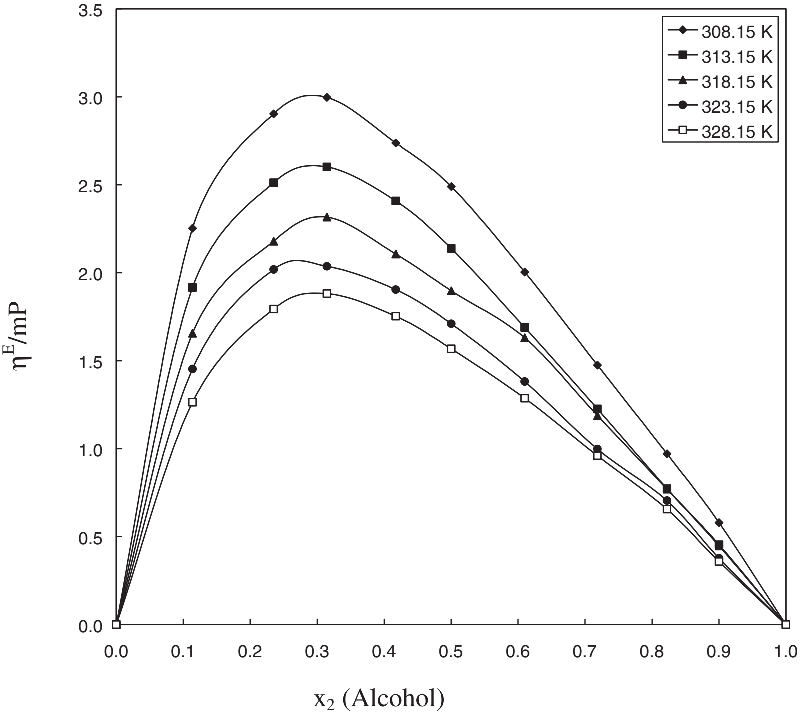

FIGURE 7 Excess viscosity against mole fraction of 2-propyne-1-ol.

The increase in viscosity with mole fraction of alcohol in water rich region may be attributed to these two effects collectively. After attaining the state of maximum viscosity 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 2-propyne-1-ol (propargyl alcohol), for which a separate treatment is given for the interpretation of the viscosity behaviour of its aqueous solution.

The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols, while the hydrophilic effect is expected to be the same for all the studied alcohols. 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 of the dependence of hydrophobicity 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 and their hydrophobicity 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 viscosity should be in the order, 2-methyl-3-butyne-2-ol > 3-butene-2-ol > 2-propyne-1-ol (propargyl alcohol). This order is in good agreement with experimental observation.

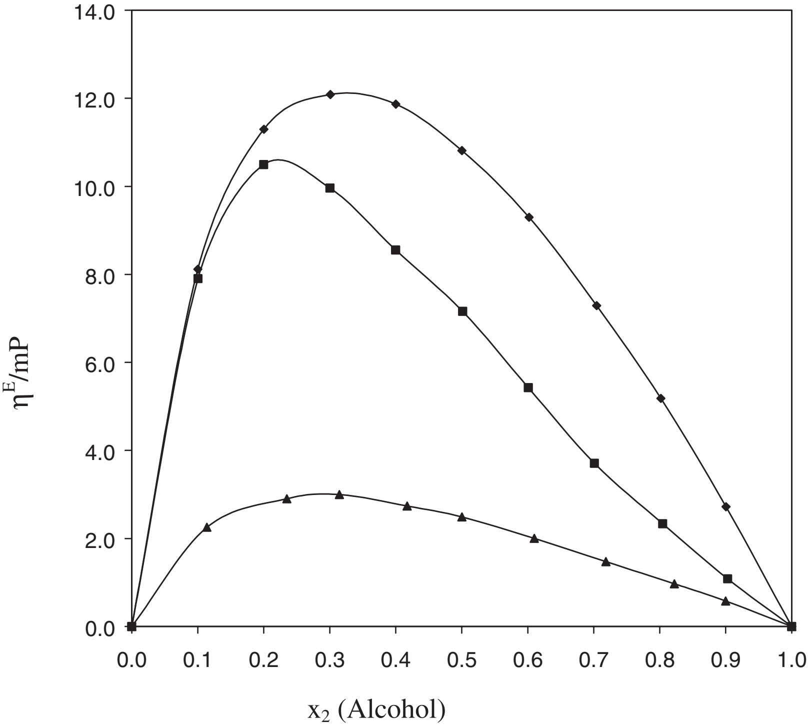

FIGURE 8 Excess viscosity against mole fraction of alcohols (x_2) at 308.15 K. ◆ 2-methyl-3-butyne-2-ol, ■ 3-butene-2-ol, ▲ 2-propyne-1-ol (propargyl alcohol).

Turning our attention again to 2-propyne-1-ol (propargyl alcohol), we notice that this alcohol exhibits quite dissimilar viscosity behaviour from rest of the alcohols as shown in Fig. 3. At the initial stage, the rate of increase of viscosity is more pronounced though this rate is much less compared to those of other alcohols of this study. 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 predominant 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 due to increased alcohol–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.

The difference in maxima of viscosity over the temperature range ($\Delta\eta_{\mathrm{max}}$) of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison 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 and 2) shows that $\Delta\eta_{\mathrm{max}}$ varies in the order, 2-methyl-3-butyne-2-ol (9.9 mp) > 3-butene-2-ol (7.5 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 chain of alcohols are also assumed to be thermally unstable than water–water association in normal water [12,13].

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