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Microheterogeniety in Aqueous Mixtures of Hydrophobic Solutes through Viscosity Studies

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Precise viscosity data for aqueous binary mixtures of ethylene glycol (EG), 2-methoxyethanol (ME), and 1,2-dimethoxyethane (DME) at different mole fractions and at various temperatures are presented. EG behaves as a structure breaker showing negative deviation in viscosity-composition curve. Hydrophobic solutes ME and DME showed typical maximum in viscosity-composition curve in water rich region; attributed to the existence of "microheterogeniety" in these mixtures.

In order to explicate the structural arrangements at molecular level, the study of physicochemical properties of solutions would be of considerable help. With the notion to gain an insight into the molecular orientations and interactions occurring between the components of the binary mixtures, viscosities at different mole fractions of ethylene glycol (EG), 2-methoxyethanol (ME), and 1,2-dimethoxyethane (DME) in water at five different temperatures, namely 25, 30, 35, 40, and 45 °C, have been determined. Of these three solutes, EG exhibits protic character due to the two hydrogen atoms of hydroxyl groups. Obviously, in the remaining two solutes, ME and DME, succinct replacement of two hydrogen atoms of EG by electron donating methyl groups, renders them to impart quasiaprotic and aprotic characters, respectively. Also IR studies indicated that intramolecular hydrogen bonding exists in EG[1,2] and ME[2,3] molecules in the liquid state. However, it is apparent that no intramolecular hydrogen bonding is feasible in pure DME. Keeping the bifunctional nature especially of these solutes, EG, ME, and DME in view, viscosity studies of their binary mixtures with water would be of interest to elucidate the structural arrangements and molecular interactions. Although the viscosity data for these aqueous binary mixtures at 25 °C were already reported,[4–6] a thorough study on the structural details has not been dealt with.

This communication presents the viscosities of aqueous binary mixtures of EG, ME, and DME at five different temperatures viz., 25, 30, 35, 40, and 45 °C.

Experimental

Materials. Ethylene glycol, (B. D. H., AnalaR) was fractionally distilled under reduced pressure; dried over anhydrous sodium sulfate for two days and decanted. This was fractionally distilled under reduced pressure and the middle cut was collected.[7]

2-Methoxyethanol (A. R.) was treated with lithium hydride until the evolution of hydrogen gas ceased. Then it was distilled twice and the middle fraction was collected.[8]

1,2-Dimethoxyethane (Riedel-De-Haenag) was kept two days over KOH and then refluxed for 24 h. This was distilled over sodium and refluxed again for 24 h. Then the sample was distilled and middle fraction was directly used for measurements.[9]

Since these three solvents are highly hygroscopic in nature, they were kept under dry nitrogen atmosphere in order to minimize atmospheric contamination before use. Aqueous mixtures of these solvents were prepared with conductivity water ($\kappa=0.2—0.5\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) obtained by triple distillation of water in the presence of alkaline $KMnO_4$.

Apparatus. Two Cannon-Ubbelohde viscometers, with flow times approximately 200 and 500 s, for water at room temperature, were calibrated[10] using pure water, methanol, carbon tetrachloride, benzene, and toluene. Viscosities of pure EG, ME, and DME so obtained at 25 °C are in excellent agreement with the literature values.[4,6,11] Thus e.g., at 25 °C $\eta_{\mathrm{EG}}{}^{4)}=16.84\times10^{-3}$, $\eta_{\mathrm{ME}}{}^{5)}=1.60\times10^{-3}$, and $\eta_{\mathrm{DME}}{}^{11)}=0.455\times10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$. Our values at 25 °C are $\eta_{\mathrm{EG}}=16.63\times10^{-3}$, $\eta_{\mathrm{ME}}=1.59\times10^{-3}$, and $\eta_{\mathrm{DME}}=0.451\times10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

During the course of measurements temperature constancy was ensured within ±0.01 °C. There was no need to incorporate corrections due to kinetic energy effects in the viscosity values calculated.[12]

Results and Discussion

Viscosity (η) values determined for aqueous binary mixtures of EG, ME, and DME, covering the whole range of composition, at 25, 30, 35, 40, and 45 °C are given in Tables 1, 2, and 3, respectively.

The monotonious increase in viscosity with the increase of EG content in the EG+water mixture (cf. Fig. 1) shows negative deviation from the ideal behavior indicating the structure breaking effect of the components on one another. Water has a well defined characteristic geometric structure.[13] However, EG, despite possessing a high degree of self-association through hydrogen bonding, does not have a defined geometric structure.[14,15] The autoprotolysis constant studies in these mixtures have also shown the absence of defined geometric structure in EG.[16] Therefore, the incompatibility which arises due to the dissimilarity in the basic geometric structures, as well as the differences in hydrogen bond energies results in the breakage of the

Table 1. Viscosities of Ethylene Glycol +Water Mixtures at Different Temperatures

No.	Mole fraction of EG	$\eta/10^{-3}$ kg m^{-1} s^{-1}				
		25 °C	30 °C	35 °C	40 °C	45 °C
1.	0.0000	0.890	0.801	0.723	0.656	0.598
2.	0.1000	1.714	1.481	1.313	1.175	1.040
3.	0.1985	2.764	2.409	2.107	1.846	1.627
4.	0.2998	4.084	3.701	2.903	2.535	2.201
5.	0.3999	5.490	4.370	3.844	3.326	2.900
6.	0.5002	6.904	5.689	4.761	4.051	3.550
7.	0.6000	8.666	7.320	5.955	5.037	4.240
8.	0.6999	10.200	8.589	6.831	5.897	4.822
9.	0.8003	11.880	9.375	7.958	6.552	5.730
10.	0.9027	13.460	11.170	9.235	7.942	6.444
11.	1.0000	16.630	13.250	10.766	9.236	7.444

Table 2. Viscosities of 2-Methoxyethanol+Water Mixtures at Different Temperatures

No.	Mole fraction of ME	$\eta/10^{-3}$ kg m^{-1} s^{-1}				
		25 °C	30 °C	35 °C	40 °C	45 °C
1.	0.0000	0.890	0.801	0.723	0.656	0.598
2.	0.1098	1.969	1.682	1.473	1.305	1.145
3.	0.2001	2.645	2.241	1.947	1.699	1.494
4.	0.3005	2.950	2.449	2.119	1.858	1.634
5.	0.4013	2.877	2.415	2.102	1.858	1.650
6.	0.5002	2.659	2.277	2.008	1.769	1.582
7.	0.5985	2.422	2.097	1.842	1.641	1.479
8.	0.7004	2.133	1.959	1.723	1.553	1.401
9.	0.7999	1.987	1.791	1.584	1.452	1.309
10.	0.9003	1.789	1.666	1.468	1.350	1.232
11.	1.0000	1.590	1.388	1.259	1.147	1.002

Table 3. Viscosities of 1,2-Dimethoxyethane+Water Mixtures at Different Temperatures

No.	Mole fraction of DME	$\eta/10^{-3}$ kg m^{-1} s^{-1}				
		25 °C	30 °C	35 °C	40 °C	45 °C
1.	0.0000	0.890	0.801	0.723	0.656	0.598
2.	0.0999	1.986	1.595	1.457	1.282	1.126
3.	0.1998	1.990	1.608	1.469	1.291	1.141
4.	0.2997	1.563	1.352	1.219	1.073	0.988
5.	0.3999	1.216	1.013	0.978	0.881	0.845
6.	0.5001	0.950	0.842	0.799	0.777	0.724
7.	0.5997	0.772	0.700	0.688	0.614	0.585
8.	0.6999	0.679	0.592	0.570	0.523	0.494
9.	0.8002	0.555	0.499	0.484	0.445	0.427
10.	0.9001	0.491	0.459	0.441	0.416	0.401
11.	1.0000	0.451	0.421	0.389	0.376	0.369

structural integrities of EG and water. Subsequently the individual water molecules will get themselves loosely associated with ethylene glycol molecules through hydrogen bonding resulting in an overall less structured solvent mixture than that expected from ideal behavior.

In case of aqueous mixtures of ME or DME, viscosity increases rapidly with the increase of solute content (ME or DME) in the mixture and reaches a maximum at a particular composition in the water-

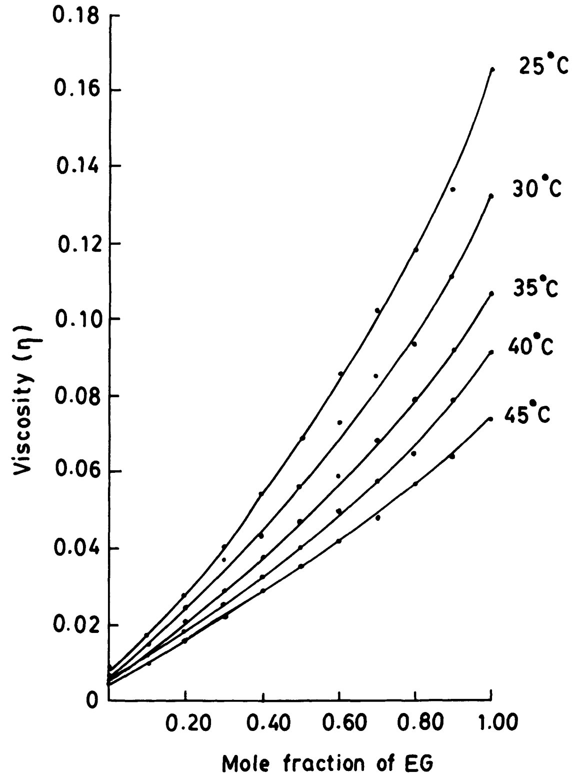

Fig. 1. Variation of viscosity (η) with the mole fraction of ethylene glycol at different temperatures.

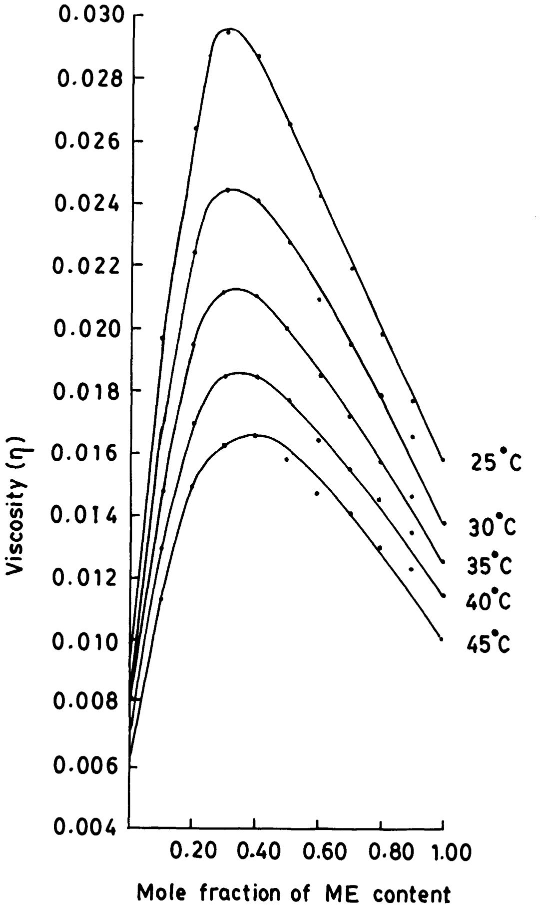

Fig. 2. Variation of viscosity (η) with the mole fraction of 2-methoxyethanol at different temperatures.

rich region (cf. Figs. 2 and 3). The viscosity maxima are nearly 2.9 and 2.0 times viscosity of water and appear around 0.30 and 0.20 mole fractions of ME and DME, respectively. Although, such a maximum, observed for aqueous mixtures of different organic solvents was attributed to the formation of an association complex,[17–20] an appropriate explanation may be given as follows. The ascending part of viscosity-composition curve (water-rich region in Figs. 2 and 3) represents structural promotion in the mixture by gradual formation of clusters of associated species. These clusters[21–27] may be formed in three different possible ways such as the association between (a) the same species (b) different species, and (c) the same species and different species simultaneously. A gradual aggregation of these different types of clusters would obviously lead to an increase in the viscosity and approach to a maximum value when aggregation is maximum. So viscosity maximum is an indication of maximum structuredness. However, the participation of different types of associated molecular species in aggregation at viscosity maximum apparently brings heterogeneity in the system (mixture). Therefore, since the observed maximum in viscosity is a consequence of aggregation of heterogeneous associated species at molecular level, this phenomenon may be termed as "microheterogeneity". The shift of viscosity maximum (Figs. 2 and 3) towards water-rich region with the addition of methyl group e.g. 0.30 mole fraction ME to 0.20 mole fraction DME in respective aqueous mixtures suggests the solvation of water into organic solute (interstitial solvation) in agreement with findings of Rohdewald and Moldner.[28]

Franks[29] has explained the structure promotion and destruction effects on the basis of the variation in $d\eta/dx$ with x (i.e. rate of change of viscosity with the change in solute content) instead of variation in η with x. The solutes, ME and DME, may be brought under the category of "structure promoters" for water-rich region, following Franks. Structural promotion 'effect' decreases with the increase in solute content and it passes through "zero structural promotion" effect (i.e. $d\eta/dx=0$) at mole fraction value corresponding to $\eta_{\max}$ (Fig. 4). This implies that at viscosity maximum no further structural promotion is possible. Further addition of solute decreases $d\eta/dx$ to a minimum value which indicates "structure breaking" in solute rich mixtures due to excess presence of solute. The mole fraction value corresponding to $d\eta/dx=0$ remains unaltered with change in temperature (Fig. 4).

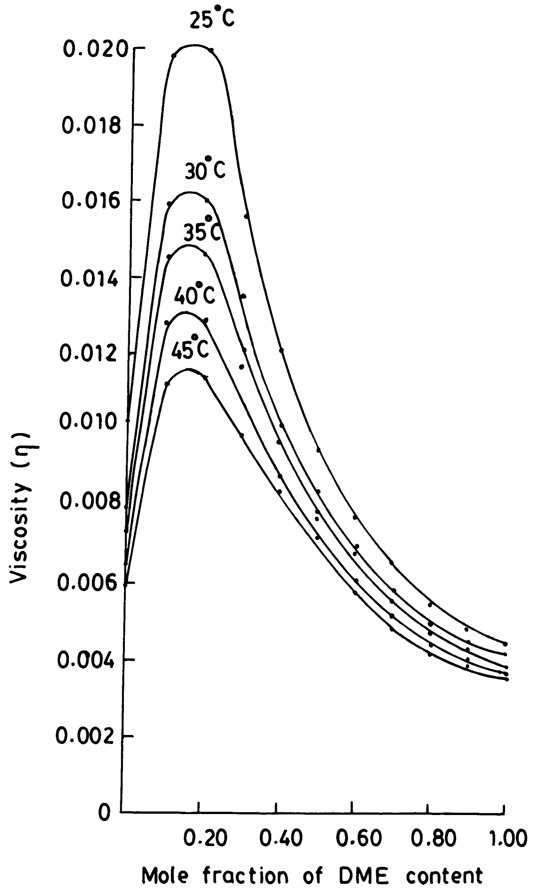

Fig. 3. Variation of viscosity (η) with the mole fraction of 1,2-dimethoxyethane at different temperatures.

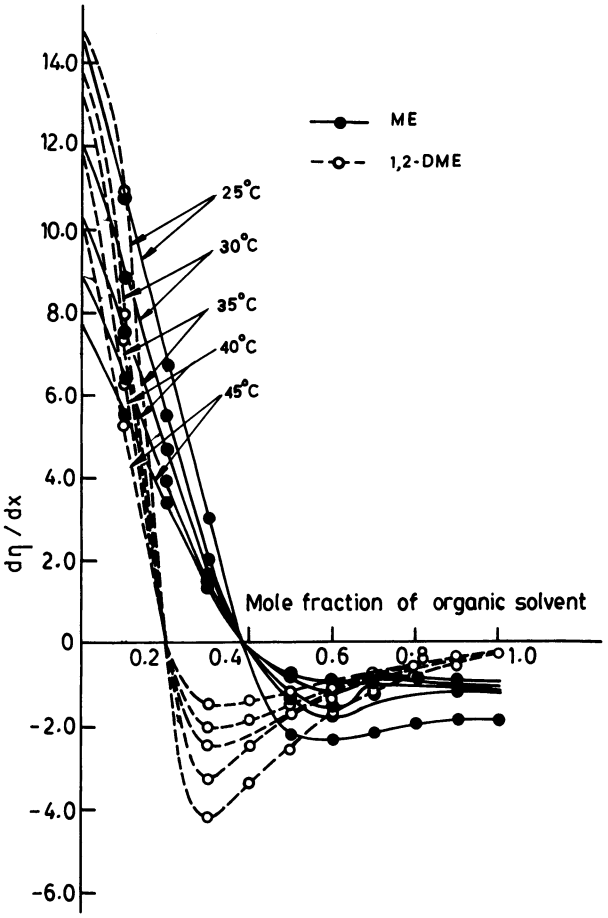

Fig. 4. Variation of first derivative ($d\eta/dx$) with mole fraction (x) of organic solvent.

These three systems have followed fairly closely the Andrade's relation[30]

$$\eta = Ae^{B/RT},$$

where B is called the "activation energy for viscous flow" and A is system specific parameter. A representative plot of variation of log η with $1/T$ for EG+water mixtures is illustrated in the Fig. 5, which clearly shows the applicability of Andrade's relation. Various other workers[31–33] also have showed that this equation is fairly applicable for several other systems.

A consideration of molecular size (S) of pure EG, ME, and DME (viz., $S_{EG}<S_{ME}<S_{DME}$) suggests that, if molecular association were not to be present the same should have been the trend in viscosity values also. A decrease in viscosity values as observed viz., $\eta_{EG}(16.63\times10^{-3}\ \mathrm{Kg\ m^{-1}\ s^{-1}})>\eta_{ME}(1.59\times10^{-3}\ \mathrm{Kg\ m^{-1}\ s^{-1}})>\eta_{DME}(0.0451\ \mathrm{Kg\ m^{-1}\ s^{-1}})$ can be explained on the basis of the gradual reduction of inter- and intramolecular association because of successive replacement of hydrogen atoms of hydroxyl groups in EG by methyl group.

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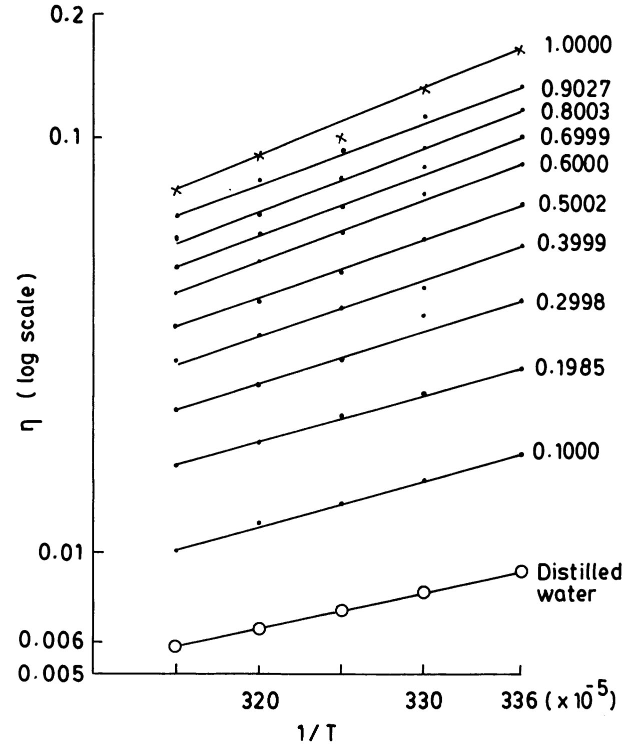

Fig. 5. log η vs. $1/T$ at different mole fractions of ethylene glycol in water.

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