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Densities and viscosities of the binary aqueous mixtures of tetrahydrofuran and 1,2-dimethoxyethane at 298, 308 and 318 K

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The densities and viscosities have been determined for the binary systems of water with tetrahydrofuran and 1,2-dimethoxyethane at 298, 308 and 318 K. From the experimental results, the excess molar volumes (V^E) and the deviation of viscosity from the mole fraction average ($\Delta\eta$) have been derived. These are explained on the basis of molecular interactions between the components of the mixtures.

There has been a recent upsurge of interest[1-4] in the thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on the intermolecular interactions and geometrical effects in these systems[4]. We have presented here the densities and viscosities for tetrahydrofuran-water and 1,2-dimethoxyethane-water mixtures at 298, 308 and 318 K.

Experimental Procedure

The purification of 1,2-dimethoxyethane (Fluka, purum) has been described earlier[5]. The solvent was shaken well with $FeSO_4$ (A.R., BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and redistilled over metallic sodium. The purified solvent had a density of 861.32 kgm^{-3} and a coefficient of viscosity of 0.4236 mPa s at 298 K which agree well with the reported values[6].

Tetrahydrofuran (Merck, India) kept several days over KOH, was refluxed for 24 h and then distilled over $LiAlH_4$. The density (880.72 kgm^{-3}) and viscosity (0.4630 mPa s) at 298 K of the solvent compared well with the reported values[7]. All solutions were prepared by weight with deionized distilled water.

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298, 308 and 318 K with doubly distilled water. The temperature control had an accuracy of ±0.01 K; the reproducibility of the density measurement was $\pm 3 \times 10^{-5}$ kgm^{-3}.

The kinematic viscosities were measured by means of a suspended Ubbelohde-type viscometer with a flow time of water of about 539 s at 298 K. Temperature control during viscosity measurements was ±0.01 K. The precision of the viscosity measurements was ±0.05%. The kinematic viscosities (ν) were converted into the absolute viscosities (η) by multiplying the former with density (ρ).

Results

The experimenal results of densities and viscosities at various mole fractions of organic solvents and at three different temperatures are reported in Table 1.

Binary liquid mixture viscosities have been represented by a number of correlations in terms of their pure component properties and interaction parameters. Grunberg and Nissan[8] proposed the following equation:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \qquad \ldots (1)$$

where x_1 and x_2 are the mole fractions of tetrahydrofuran (or 1,2-dimethoxyethane) and water respectively, η, η_1 and η_2 are the respective coefficients of viscosity of the mixture, tetrahydrofuran (or 1,2-dimethoxyethane) and water, and d is a constant proportional to the interaction energy and is regarded as a measure of interaction between the components. The values of d are given in Table 1.

The excess molar volumes have been calculated by the following equation:

$$V^E = V - (x_1 V_1 + x_2 V_2) \qquad \ldots (2)$$

where V, V_1 and V_2 are the molar volumes of the mixture, tetrahydrofuran (or 1,2-dimethoxyethane)

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Table 1—Values of densities (ρ), viscosities (η) and Grunberg- Nissan parameters (d)

x_1	ρ kgm^{-3}	η mPa s	d
Tetrahydrofuran(1)-water(2)			
	298 K		
0.0000	997.07	0.890	
0.0271	992.81	1.201	12.04
0.0587	986.88	1.490	10.01
0.0967	978.33	1.680	7.99
0.1427	969.97	1.732	6.20
0.1998	958.98	1.678	4.78
0.2726	946.28	1.490	3.50
0.3682	932.19	1.224	2.40
0.4500	921.69	1.024	1.76
0.4998	915.92	0.924	1.45
0.6000	905.52	0.758	0.96
0.6921	891.12	0.656	0.69
0.7500	883.99	0.608	0.58
0.8000	880.69	0.579	0.58
0.9000	875.35	0.516	0.48
1.0000	880.72	0.463	
	308 K		
0.0000	994.06	0.722	
0.0587	983.09	1.133	8.70
0.0967	974.34	1.267	7.01
0.1427	963.34	1.323	5.56
0.1998	951.24	1.293	4.30
0.2726	938.10	1.189	3.23
0.3682	923.15	0.989	2.18
0.4500	913.08	0.852	1.62
0.4998	907.68	0.784	1.37
0.6000	896.74	0.653	0.89
0.6921	888.49	0.572	0.61
0.7500	883.80	0.539	0.53
0.8000	880.69	0.512	0.47
0.9000	875.35	0.472	0.52
1.0000	870.33	0.428	
	318 K		
0.0000	990.17	0.598	
0.0271	985.79	0.752	9.11
0.0587	977.30	0.897	7.77
0.0967	968.78	0.997	6.31
0.1427	958.52	1.045	5.06
0.1998	944.96	1.036	3.96
0.2726	929.13	0.959	2.97
0.3682	915.20	0.830	2.08
0.4500	904.06	0.714	1.49
0.4998	897.32	0.661	1.25
0.6000	886.30	0.564	0.82
0.6921	877.59	0.506	0.60
0.7500	873.84	0.473	0.45
0.8000	870.51	0.452	0.39
0.9000	865.47	0.422	0.40
1.0000	861.40	0.390	

x_1	ρ kgm^{-3}	η mPa s	d
1,2-Dimethoxyethane(1)-water(2)			
	298 K		
0.0000	997.07	0.890	
0.0399	996.72	1.502	14.43
0.1251	974.98	2.070	8.56
0.1800	963.22	2.020	6.11
0.2525	947.75	1.699	4.42
0.3124	935.11	1.413	3.23
0.3552	926.50	1.240	2.60
0.4198	915.65	1.016	1.95
0.4648	909.09	0.895	1.41
0.5088	903.10	0.800	1.08
0.5499	898.17	0.729	0.85
0.5955	892.89	0.670	0.66
0.6622	885.83	0.600	0.44
0.7199	880.31	0.558	0.33
0.7550	877.25	0.540	0.33
0.8051	872.50	0.502	0.16
0.8584	869.36	0.474	0.06
0.8999	866.80	0.460	0.09
0.9511	863.97	0.441	0.08
1.0000	861.32	0.424	
	308 K		
0.0000	994.06	0.722	
0.0399	986.81	1.200	13.90
0.1251	969.48	1.484	7.30
0.1800	957.34	1.488	5.66
0.2525	941.00	1.352	4.16
0.3124	927.26	1.185	3.22
0.3552	918.32	1.076	2.72
0.4198	901.63	0.933	2.14
0.5088	893.15	0.788	1.63
0.5499	888.12	0.732	1.45
0.5955	882.90	0.678	1.29
0.6622	876.66	0.601	1.04
0.7199	870.84	0.544	0.84
0.7550	867.87	0.513	0.72
0.8051	863.98	0.470	0.49
0.8584	860.25	0.434	0.27
0.8999	857.76	0.413	0.09
1.0000	851.29	0.385	
	318 K		
0.0000	990.17	0.598	
0.0399	982.54	0.960	12.90
0.1251	965.76	1.142	6.52
0.1800	948.61	1.152	5.09
0.2525	929.02	1.100	3.20
0.3124	915.25	1.016	3.25
0.3552	908.10	0.940	2.81
0.4198	895.56	0.834	2.29

(Contd)

Table 1—Values of densities (ρ), viscosities (η) and Grunberg- Nissan parameters (d)]—*Contd.*

x_1	ρ kgm^{-3}	η mPa s	d	x_1	ρ kgm^{-3}	η mPa s	d
0.4648	888.52	0.770	2.02	0.7550	857.66	0.456	0.73
0.5088	882.84	0.704	1.74	0.8051	853.73	0.422	0.54
0.5499	877.76	0.654	1.56	0.8584	850.05	0.400	0.48
0.5955	872.43	0.600	1.34	0.8999	846.32	0.392	0.67
0.6622	865.98	0.530	1.05	0.9511	844.01	0.378	1.09
0.7199	860.49	0.462	0.64	1.0000	840.76	0.350	

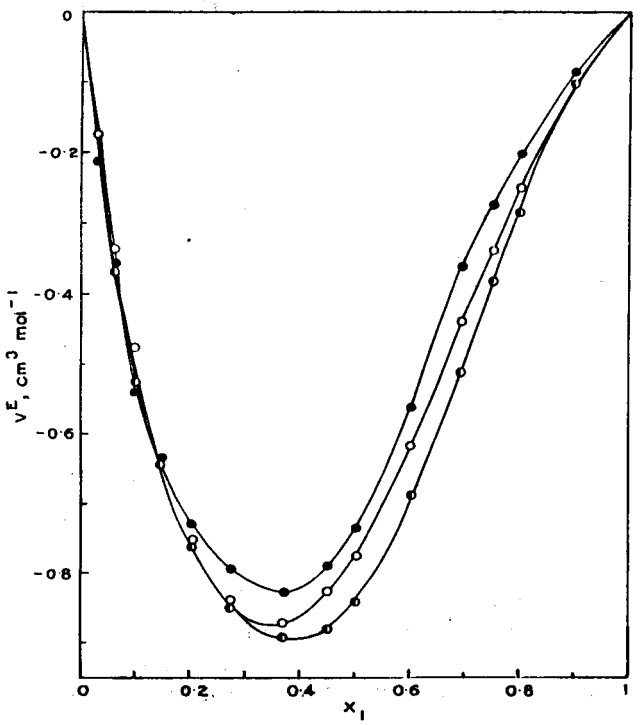

Fig. 1—Variation of V^E for the system tetrahydrofuran(1)-water(2) at 298 K (○), 308 K (◑) and 318 K (●).

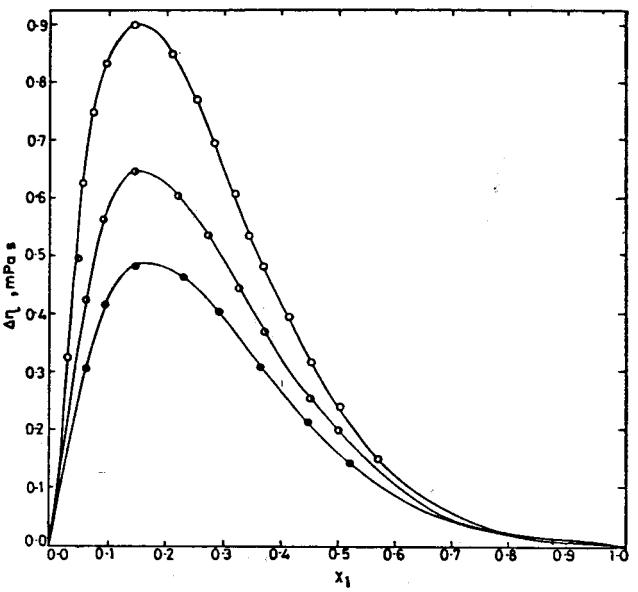

Fig. 2—Variation of $\Delta\eta$ for the system tetrahydrofuran(1)-water(2) at 298 K (○), 308 K (◑) and 318 K (●).

and water, respectively. The molar volume V is defined by

$$V=(M_1 x_1 + M_2 x_2)/\rho \quad \ldots(3)$$

here M_1 and M_2 are the molecular weights of the pure components and ρ is the density of the mixture.

The deviation of the viscosity from the mole fraction average is calculated from:

$$\Delta\eta=\eta-(x_1\eta_1+x_2\eta_2) \quad \ldots(4)$$

Graphical representations of V^E and $\Delta\eta$ as a function of x_1 are given in Figs 1-4. The properties V^E and $\Delta\eta$ were fitted to the Redlich-Kister equation[9]:

$$Y=x_1 x_2 \sum_j A_j (x_2-x_1)^j \quad \ldots(5)$$

where Y is V^E (cm^3 mol^{-1}) or $\Delta\eta$ (mPa s) and A_0, A_1, A_2, ..., etc. are adjustable parameters. These parameters were evaluated by the method of least-squares. The values of these parameters along with the standard deviations $\sigma(Y)$ of Y as defined by

$$\sigma(Y)=[\Sigma(Y_{obsd}-Y_{calcd})^2/(N-M)]^{0.5} \quad \ldots(6)$$

are given in Table 2. In Eq. (6), N is the number of parameters.

Discussion

It is well-known[10] that the sign and magnitude of V^E give a good estimate of the strength of unlike interactions in the binary mixtures. Large positive V^E values are taken as indicative of weak interactions whereas large negative values of V^E are usually found when these interactions are strong and intermolecular association "complexes" are believed to be present.

The systems tetrahydrofuran-water and 1,2-dimethoxyethane-water show negative V^E values over the entire mole fraction range and over the entire range of temperatures studied (Figs 1 and 3). Several effects may contribute to the V^E values. One of the effects which may contribute to V^E is the disruption of (i) the hydrogen bonds present in the self-associated water molecules and (ii) the intermolecular dipolar interactions in tetrahydrofuran and 1,2-dimethoxyethane. Secondly, the effect which gives a negative contribution to V^E is the difference in molecular sizes between the two components in the mixtures. The molar volumes of water, tetrahydrofuran and 1,2-dimethoxyethane at 298 K are 18.05, 81.75 and 104.65 cm^3, respectively, which might allow the components to fit into each others' structures both in tetrahydrofuran-water and 1,2-dimethoxyethane-water systems, so that a reduction in volume occurs in each case.. A third effect whose

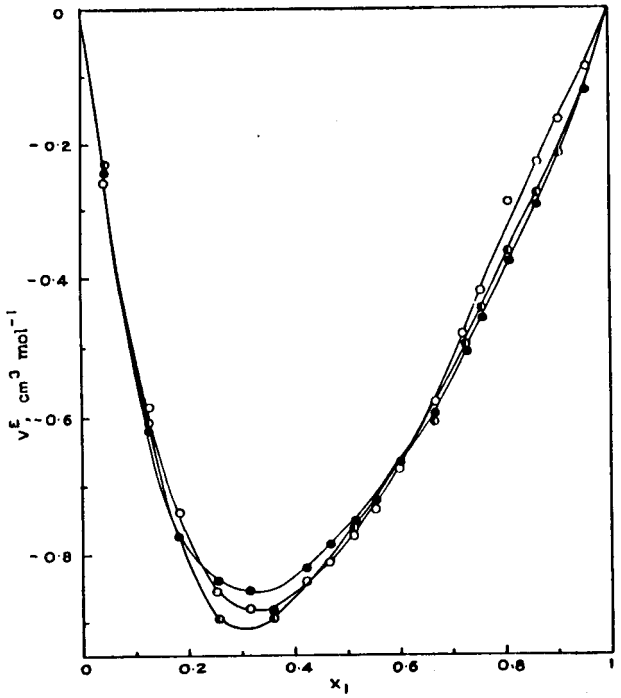

Fig. 3—Variation of V^E for 1,2-dimethoxyethane(1)-water(2) at 298 K (O), 308 K (◑) and 318 K (●).

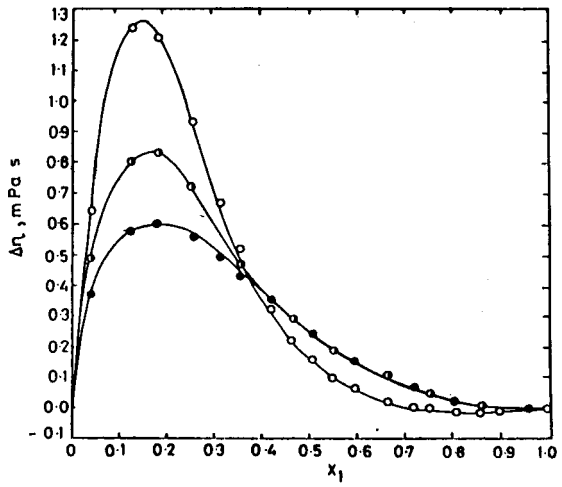

Fig. 4—Variation of $\Delta\eta$ for 1,2-dimethoxyethane(1)-water(2) at 298 K (O), 308 K (◑) and 318 K (●).

Table 2—Coefficients of Eq. 5 for V^E and $\Delta\eta$ and the standard deviations $\sigma(Y)$ at 298, 308 and 318 K

Y	Temp. K	A_0	A_1	A_2	A_3	A_4	$\sigma(Y)$
			Tetrahydrofuran-water				
	298	−3.099	−2.467	0.457	−0.510	−1.389	0.007
V^E	308	−3.354	−1.908	1.167	−1.675	−2.247	0.007
	318	−2.985	−2.410	1.882	−1.068	−4.103	0.015
	298	0.900	3.018	5.355	4.109	0.673	0.018
$\Delta\eta$	308	0.798	2.208	3.030	2.655	1.371	0.005
	318	0.628	1.841	2.675	1.573	0.106	0.007
			1,2-Dimethoxyethane-water				
	298	−6.378	−3.749	0.505	−2.439	−4.324	0.004
V^E	308	−6.239	−4.765	−4.040	0.872	2.105	0.003
	318	−6.024	−4.288	−4.611	−0.025	1.371	0.004
	298	0.552	3.497	7.945	6.751	1.304	0.003
$\Delta\eta$	308	1.147	2.495	2.248	4.861	4.783	0.007
	318	1.072	1.648	0.032	3.923	5.264	0.004

contribution to V^E is also expected to be negative is the existence of hydrogen-bond interactions between unlike molecules.

The actual value of V^E would depend upon the balance between the two opposing contributions. The experimental values indicate that the negative contributions predominate in these binaries.

For these two systems studied at three different temperatures, the values of $\Delta\eta$ are found to be positive over the entire compositional range (Figs 2 and 4). This positive deviation indicates the predominance of specific hydrogen bonding interaction between the unlike molecules (to form adducts between them) over the dissociation effects in both systems[11,12]. This results in a liquid structure where the flow is rather difficult than would be expected on the basis of the viscosities of the pure components.

The Grunberg and Nissan parameter d is found to be positive (Table 1) for both the systems. This supports the formation of intermolecular complexes between the unlike molecules through hydrogen bonding.

Thus from the present study it is clear that for both these binaries hydrogen-bonding interactions between the unlike molecules predominate over the other effects.

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