

Viscosities for binary liquid mixtures of some cellosolves with water at 298.15 K

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Viscosities (η) of three binary mixtures (cellosolve + water) have been measured as a function of mole fraction at 298.15 K using an Ubbelohde viscometer. The cellosolves were 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, and 2-[2-(2-butoxyethoxy)ethoxy]ethanol. From the experimental results, excess logarithmic viscosities ($\ln \eta^E$) and excess energies of activation for viscous flow (ΔG^{*E}) have been calculated. All the mixtures show positive excess functions over the entire concentration range and which increase as the aliphatic chain of the cellosolve increases. The results are discussed on the basis of molecular interactions between the components of the mixtures.

In continuation of our studies on binary mixtures containing the oxy(-O-) and hydroxyl (-OH) functional groups¹⁻⁸, we report here a new experimental data for viscosity of the binary mixtures of water with 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, or 2-[2-(2-butoxyethoxy)ethoxy]ethanol over the entire composition range at 298.15 K. The aim of this work is to provide a set of data for the characterization of the molecular interactions between water and cellosolves.

Experimental

Materials were of the same grade as used in earlier studies⁸. All the chemicals were stored over 4A molecular sieves to reduce water content. Water was deionized and distilled in glass. Its conductivity was always below $1.0 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Prior to the experimental measurements, all liquids were partially degassed under vacuum. The composition of each mixture was obtained with an accuracy of 1×10^{-4} from the measured masses of the components. All the masses were corrected for buoyancy.

Density (ρ) measurements of pure liquids were made using a 15 cm³ double arm pycnometer. Densities of mixtures at any composition, were

computed from the excess molar volume (V^E), reported earlier⁸, using the relation:

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V^E + x_1 V_1 + x_2 V_2} \quad \dots (1)$$

where M_1 and M_2 are the molecular weights. Density values are reproducible to $\pm 3.0 \times 10^{-4} \text{ g cm}^{-3}$. The density and viscosity of water at 298.15 K were taken from the literatures^{9,10}.

Viscosities (η) of pure liquids and liquid mixtures were measured using a modified suspended level Ubbelohde viscometer with a flow time for water of about 331s at 298.15 K. The viscometer was calibrated, and two constants, A and B, of the viscometer in the relation $\eta/\rho = At - B/t$ were obtained by measuring the flow time t with high-purity benzene, toluene and carbon tetrachloride at the working temperature. The average of four or five sets of flow time for each liquid was taken for the purpose of the calculation of viscosity. The flow-time measurements were made with an electronic stopwatch having a precision of ± 0.01 s. Viscosities were reproducible to ± 0.003 mPas. A thermostatically controlled, well-stirred water bath with temperature controlled to ± 0.01 K was used for all the measurements.

Results and discussion

The experimental results for viscosities (η) at various mole fractions of non-electrolytes at 298.15 K are reported in Table 1. Excess logarithmic viscosities, $\ln \eta^E$, were calculated from the experimental viscosities using the following relation:

$$\ln \eta^E = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad \dots (2)$$

where x_1 and x_2 are the mole fractions and η_1 and η_2 are the viscosities of components 1 and 2.

The excess energies of activation for viscous flow, ΔG^{*E} were calculated from the following relation:

$$\Delta G^{*E} = RT[\ln \eta V_1 - x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2] \quad \dots (3)$$

where V , V_1 and V_2 are the molar volumes of the binary mixtures and the pure components 1 and 2 respectively. R and T have their usual meaning. Results on $\ln \eta^E$ and ΔG^{*E} are listed in Table 1.

Table 1—Densities, ρ , viscosities, η , excess logarithmic viscosities, $\ln \eta^E$, excess activation energies of viscous flow, ΔG^{*E} and Grunberg-Nissan interaction parameter d_{12} at 298.15 K

x_2	$\rho, \text{g cm}^{-3}$	$\eta, \text{mPa s}$	$\ln \eta^E, \text{mPa s}$	$\Delta G^{*E}, \text{J mol}^{-1}$	d_{12}
<i>Water(1) + 2-[2-(2-Methoxyethoxy)ethoxy]ethanol(2)</i>					
0.0000	0.997048	0.89025			
0.0211	1.0156	1.618	0.554	1606.39	30.16
0.0490	1.0316	2.902	1.081	3162.11	23.20
0.0813	1.0427	4.466	1.446	4292.69	19.36
0.1234	1.0505	6.429	1.724	5200.79	15.93
0.1677	1.0542	7.920	1.841	5655.44	13.19
0.2255	1.0556	8.996	1.850	5812.63	10.59
0.2668	1.0555	9.333	1.802	5749.80	9.21
0.3073	1.0548	9.452	1.731	5604.19	8.13
0.3403	1.0541	9.430	1.661	5438.20	7.40
0.4018	1.0525	9.258	1.517	5061.99	6.31
0.4514	1.0513	9.041	1.391	4711.14	5.62
0.5151	1.0499	8.756	1.228	4229.56	4.92
0.5734	1.0487	8.494	1.078	3764.26	4.41
0.6295	1.0478	8.220	0.930	3290.54	3.99
0.6824	1.0470	7.975	0.791	2832.51	3.65
0.7188	1.0465	7.823	0.697	2514.88	3.45
0.7989	1.0455	7.543	0.496	1814.69	3.09
0.8449	1.0449	7.378	0.380	1401.10	2.90
0.9067	1.0441	7.185	0.226	844.46	2.68
0.9588	1.0435	7.036	0.099	371.44	2.49
1.0000	1.0430	6.9639			
<i>Water(1) + 2-[2-(2-Ethoxyethoxy)ethoxy]ethanol(2)</i>					
0.0000	0.997048	0.89025			
0.0079	1.0042	1.222	0.300	849.81	38.28
0.0173	1.0112	1.631	0.569	1633.40	33.48
0.0312	1.0193	2.350	0.906	2621.26	29.96
0.0514	1.0274	3.554	1.277	3733.96	26.18
0.0709	1.0324	4.769	1.530	4518.83	23.23
0.0947	1.0360	6.175	1.739	5195.62	20.28
0.1236	1.0381	7.595	1.885	5714.79	17.40
0.1710	1.0384	9.194	1.977	6128.52	13.95
0.2116	1.0372	9.926	1.969	6213.89	11.80
0.2564	1.0353	10.299	1.912	6146.24	10.03
0.3068	1.0329	10.350	1.812	5936.35	8.52
0.3627	1.0305	10.186	1.679	5608.04	7.26
0.4260	1.0281	9.863	1.514	5158.99	6.19
0.4653	1.0267	9.639	1.409	4854.88	5.66
0.5118	1.0253	9.362	1.282	4474.87	5.13
0.5775	1.0236	8.986	1.104	3914.56	4.52
0.6718	1.0214	3.483	0.849	3074.33	3.85
0.7243	1.0204	8.209	0.706	2588.06	3.54
0.7552	1.0198	8.069	0.625	2302.32	3.38
0.8120	1.0188	7.834	0.476	1774.22	3.12
0.8449	1.0183	7.712	0.392	1467.37	2.99
0.8987	1.0175	7.518	0.254	959.48	2.79
0.9377	1.0169	7.401	0.157	594.17	2.68
1.0000	1.0161	7.210			

Contd.

Table 1—Densities, ρ , viscosities, η , excess logarithmic viscosities, $\ln \eta^E$, excess activation energies of viscous flow, ΔG^{*E} and Grunberg-Nissan interaction parameter d_{12} at 298.15 K —

Water (1) + 2-[2-(2-Butoxyethoxy)ethoxy]ethanol (2)					
0.0000	0.997048	0.89025			
0.0047	0.9999	1.153	0.248	697.77	53.00
0.0144	1.0046	1.665	0.592	1708.76	41.71
0.0326	1.0099	2.910	1.108	3243.03	35.12
0.0520	1.0126	4.394	1.474	4375.78	29.90
0.0657	1.0134	5.440	1.655	4960.00	26.97
0.0875	1.0136	6.934	1.847	5615.96	23.13
0.1268	1.0121	9.008	2.016	6282.18	18.21
0.1594	1.0104	10.247	2.068	6556.81	15.44
0.2279	1.0067	11.662	2.036	6660.83	11.57
0.2896	1.0038	12.117	1.930	6461.28	9.38
0.3460	1.0015	12.179	1.802	6196.97	7.96
0.3819	1.0001	12.099	1.711	5900.46	7.25
0.4318	0.9983	11.959	1.582	5528.58	6.45
0.4871	0.9964	11.697	1.430	5067.55	5.72
0.5190	0.9954	11.534	1.340	4787.52	5.37
0.5516	0.9944	11.327	1.246	4485.32	5.04
0.6257	0.9925	10.939	1.036	3790.44	4.43
0.6706	0.9916	10.709	0.910	3355.28	4.12
0.7473	0.9902	10.322	0.692	2591.30	3.67
0.7897	0.9896	10.130	0.574	2163.33	3.45
0.8168	0.9892	10.021	0.499	1889.55	3.34
0.8730	0.9883	9.800	0.345	1316.03	3.11
0.9445	0.9873	9.592	0.155	590.84	2.96
1.0000	0.9868	9.361			

According to Grunberg and Nissan¹¹, the value of η for a binary mixture of components 1 and 2 is given by

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad \dots (4)$$

where d_{12} is a parameter which is regarded as a measure of the strength of interactions between dissimilar molecules. The values of d_{12} , as estimated from Eq. 4 are given in Table 1. The excess functions A^E ($= \ln \eta^E$ and ΔG^{*E}) over the whole concentration range were fitted to the Redlich-Kister¹² relation:

$$A^E = x_1 x_2 \sum_{j=1}^n a_{j-1} (x_2 - x_1)^{j-1} \quad \dots (5)$$

In each case, the optimum number of coefficients a_{j-1} was ascertained from an examination of the variation of the standard deviation with n :

$$S(A^E) = (\sum A_{\text{obsd.}}^E - A_{\text{calcd.}}^E)^2 / (n_{\text{obsd.}} - n)^{1/2} \quad \dots (6)$$

The value obtained for the coefficients a_{j-1} and the standard deviation $S(A^E)$ calculated using Eq. 6 are listed in Table 2.

The excess logarithmic viscosities, $\ln \eta^E$, and excess activation energies of viscous flow ΔG^{*E} are positive for all the mixtures studied over the entire composition range at 298.15 K. The behaviour is similar for a 2-alkoxyethanol^{13,14} and 2-(2-alkoxyethoxy)ethanol⁶ but with a high positive values in η , $\ln \eta^E$ and ΔG^{*E} here. Negative excess volumes⁸ and rather large positive η , $\ln \eta^E$ and ΔG^{*E} values may be attributed to the association between the water and the cellosolves molecules through intermolecular hydrogen bonding. The addition of cellosolve molecule, gives rise to a slight enhancement of the three-dimensional water lattice in the water-rich region, followed by a progressive destructuring. The ether functions do not seem to play a prominent role¹⁵. Since, the possibility of intramolecular hydrogen bond formation between cellosolves molecules¹⁶⁻¹⁸ may be negligible in such high concentrations of water. The presence of the etheric oxygen enhances the ability of the -OH group to form hydrogen bond. The order of strength of the hydrogen bonding owing to increased molecular weight and size is as follows: 2-[2-(2-butoxyethoxy)ethoxy]ethanol > 2-[2-(2-ethoxyethoxy)ethoxy]ethanol > 2-[2-(2-

Table 2—Values of the coefficients of Eq. 5 and the standard deviations at 298.15 K

A^E	a_0	a_1	a_2	a_3	a_4	a_5	$S(A^E)$
<i>Water(1) + 2-[2-(2-Methoxyethoxy)ethoxy]ethanol(2)</i>							
$\ln \eta^E$, mPa s	5.0968	-5.2966	4.0224	-3.1002	6.3694	-5.3260	0.010
ΔG^{*E} , J mol ⁻¹	17463.8164	-15824.6367	11425.2383	-8436.9492	16909.4531	-14160.7500	26.23
<i>Water(1) + 2-[2-(2-Ethoxyethoxy)ethoxy]ethanol(2)</i>							
$\ln \eta^E$, mPa s	5.3007	-5.7728	3.6503	-1.4903	9.0648	-9.7395	0.020
ΔG^{*E} , J mol ⁻¹	18401.9297	-17368.8672	10733.9473	-4521.9102	23880.2383	-25454.4648	52.83
<i>Water(1) + 2-[2-(2-Butoxyethoxy)ethoxy]ethanol(2)</i>							
$\ln \eta^E$, mPa s	5.6599	-6.2008	2.3115	1.4655	12.8960	-15.8827	0.039
ΔG^{*E} , J mol ⁻¹	2005.8633	-19266.5117	7918.1143	3221.5835	34124.3203	-42180.1328	102.49

methoxyethoxy)ethoxy]ethanol. The sharp changes in η , $\ln \eta^E$, and ΔG^{*E} at low mole fractions of cellosolve would imply more order and hence more structure or clustering in the water-rich region. This leads to substantial increase in the viscosities of the cellosolve+water mixtures and corresponding decrease in their apparent molar volumes⁸. Such behaviour might also arise from interstitial accommodation of cellosolve molecules occupying a void space in a more structured water lattice, thereby giving rise to a marked change in their η , $\ln \eta^E$ and ΔG^{*E} values in an aqueous environment. Also, the Grunberg-Nissan parameter d_{12} for the three systems at 298.15 K is always positive, which supports the formation of intermolecular complexes between the unlike molecules through hydrogen bonding.

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