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Volume of Mixing, Speed of Sound, and Viscosity of Methyl Cellosolve with Aliphatic Alcohols at 308.15 K

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The volume of mixing, speed of sound, and viscosity of binary liquid mixtures composed of methyl cellosolve (1) and aliphatic alcohols (2), namely, methanol, propan-1-ol, butan-1-ol, 2-methyl-propan-1-ol, 2-methyl-propan-2-ol, and pentan-1-ol are measured at 308.15 K. The results are used to derive densities and isentropic compressibilities. The excess volumes and deviations in compressibility and viscosity are discussed in terms of molecular interaction between like and unlike components.

Introduction

The thermodynamic properties of binary mixtures containing self-associated components exhibit significant deviation from ideality, arising ont only from differences in molecular size but also from the changes in the hydrogen-bonding interaction between like and unlike molecules. Methyl cellosolve is widely used for various industrial processes (*1*) and has unique solvating properties associated with its quasi-aprotic character (*2*). Mixtures containing methyl cellosolve as one of the components have been studied (*3−9*) extensively. However, no systematic effort has been made to study the interaction between methyl cellosolve with aliphatic alcohols at 308.15 K. We report excess volumes, isentropic compressibilities, and viscosities of methyl cellosolve with methanol, propan-1-ol, butan-1-ol, 2-methyl-propan-1-ol, 2-methyl-propan-2-ol, and pentan-1-ol. The methyl cellosolve is an ether alcohol and shows physicochemical properties midway between protic and dipolar aprotic solvents. It is a toxic solvent, a weak narcotic, and a systemic poison (*10*) and must be handled with care. The relative influence of the ether group in methyl cellosolve on molecular interactions has been investigated. The aim of this work is to provide information on the molecular interactions between alcohols and methyl cellosolve from measurements of excess volumes and deviations in isentropic compressibility and viscosity.

Experimental Section

Materials. The alcohols (Fluka Puriss) were dried by refluxing the fused calcium oxide for 5 h and then distilled using a fractionating column containing 30 theoretical plates. 2-Methoxyethanol was dried over Drierite for 1 day and fractionally distilled. The purity of all substances was better than 99.95 mass % as found by GLC analysis. The purity of the chemicals was checked by comparing the density and the boiling temperature of the components with those reported in the literature (*10, 11*). The densities were measured using a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. The boiling temperature was measured using a Swietoslawski-type ebulliometer (*12*), which gave an accuracy of ±0.2 K. The measured values are included in Table 1 along with the literature values.

Table 1. Boiling Points and Densities of Pure Components at 25 °C

	T_b/K		ϱ/(g·cm^{-3})	
component	exptl	lit. (*10, 11*)	exptl	lit. (*10, 11*)
methyl cellosolve	397.5	397.8	0.960 20	0.960 24
methanol	337.5	337.7	0.786 50	0.786 37
propan-1-ol	370.2	370.3	0.799 72	0.799 60
butan-1-ol	390.7	390.9	0.805 80	0.805 75
2-methylpropan-1-ol	380.9	381.0	0.797 90	0.797 80
2-methylpropan-2-ol	355.3	355.5	0.781 12	0.781 20
pentan-1-ol	411.0	411.1	0.810 91	0.810 80

Excess volumes were measured using a single composition per loading type dilatometer as in earlier work (*13*). The dilatometer consisted of a U-tube with mercury at the bottom to separate the two components. One arm of the U-tube was fitted with a ground-glass stopper and the other arm with a capillary that can be replaced by another with a thicker (or thinner) bore. Mixing was carried out by tilting the dilatometer, thereby breaking the mercury seal. Four dilatometers with different capacities were used to cover the entire composition range. A thermostatically controlled, well-stirred water bath with temperature controlled to ±0.01 K was used for all the measurements. The composition of the mixture was obtained from the mass of the components, and the uncertainty of the excess volume is estimated to be less than ±0.003 cm^3·mol^{-1}.

Preparation of Mixtures. Mixtures were prepared in air-tight bottles on a mass basis using an analytical balance reproducible to ±0.1 mg. Precautions were taken to ensure that components were not exposed to the atmosphere during the preparation of the mixtures and subsequent measurements. The bottles were fitted with air-tight septa, evacuated, and filled with 2-methoxyethanol, the low-volatile component. The space above the liquid was evacuated while cooling the contents and again weighed to make certain that the residual air was removed. The second component, an alcohol, was injected into the bottle through the septa and its mass determined. In all cases care was taken to have minimal space above the liquid; if any space was left, it was filled with nitrogen gas. This procedure eliminates loss due to evaporation, and the error is minimized. Thus, the possible error in the mole fraction is estimated to be less than $\pm 5 \times 10^{-4}$.

Speed of Sound. Speeds of sound in liquids and liquid mixtures were measured with a single crystal ultrasonic interferometer at a fixed frequency of 2 MHz, and the values are reproducible to ±0.1%.

Viscosity. Viscosities were measured using a suspended-level Ubbelohde-type viscometer. The viscometer was calibrated at 308.15 K using distilled water. The viscometer constant K was calculated from the viscosity, η_w, density, ϱ_w, and flow time, t_w, of water using the relation

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Table 2. Excess Volumes at 308.15 K at Mole Fraction x

x_1	$V^E/(cm^3 \cdot mol^{-1})$	x_1	$V^E/(cm^3 \cdot mol^{-1})$
Methyl Cellosolve (1) + Methanol (2)			
0.1120	−0.185	0.6190	−0.274
0.1430	−0.220	0.7634	−0.185
0.3160	−0.340	0.8295	−0.140
0.4840	−0.335	0.9122	−0.070
Methyl Cellosolve (1) + Propan-1-ol (2)			
0.1599	0.029	0.5181	0.056
0.1821	0.041	0.6944	0.044
0.3016	0.056	0.7980	0.030
0.4608	0.057	0.8727	0.021
Methyl Cellosolve (1) + Butan-1-ol (2)			
0.1257	0.113	0.5789	0.168
0.2313	0.150	0.6536	0.165
0.3419	0.162	0.7411	0.155
0.4522	0.173	0.9091	0.099
Methyl Cellosolve (1) + 2-Methylpropan-1-ol (2)			
0.1398	0.125	0.6567	0.170
0.2781	0.173	0.7219	0.155
0.3352	0.180	0.7957	0.132
0.5061	0.189	0.8797	0.098
Methyl Cellosolve (1) + 2-Methylpropan-2-ol (2)			
0.1422	−0.018	0.5208	−0.032
0.2512	−0.026	0.6434	−0.026
0.3161	−0.033	0.7559	−0.020
0.4346	−0.037	0.8705	−0.012
Methyl Cellosolve (1) + Pentan-1-ol (2)			
0.1245	0.180	0.6223	0.420
0.2318	0.300	0.6908	0.379
0.3174	0.380	0.7786	0.308
0.4711	0.440	0.9037	0.160

$k = \eta_w / \varrho_w t_w$. An average of 10 measurements which do not differ by more than 0.0005 $cm^2 \cdot s^{-2}$ was taken as the k value. An electronic stopwatch capable of measuring time to ±0.015 s was used for the time measurement. Kinetic energy corrections were applied and found to be negligible. The estimated error in viscosity is $\pm 5 \times 10^{-4}$ mPa·s. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature.

Results

Experimental excess volumes (V^E) are given in Table 2 and graphically represented in Figure 1. The V^E values are used to compute the density (ϱ) of mixtures from the equation

$$\varrho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \tag{1}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molecular weights, and V_1 and V_2 are the molar volumes of 2-methoxyethanol (1) and alcohols (2), respectively. Speeds of sound (u) along with the density data are used to calculate isentropic compressibilities (k_s) and deviations in isentropic compressibility (Δk_s):

$$k_s = 1/u^2 \varrho \tag{2}$$

$$\Delta k_s = k_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \tag{3}$$

where ϕ_1 and ϕ_2 are the ideal volume fractions of components 1 and 2, respectively, and k_s, $k_{s,1}$, and $k_{s,2}$ are the isentropic compressibilities of the mixture and components 1 and 2, respectively. Deviations in viscosity ($\Delta \ln \eta$) are estimated using the equation

$$\Delta \ln \eta = \ln \eta_{mix} - x_1 \ln \eta_1 - x_2 \ln \eta_2 \tag{4}$$

where η_{mix}, η_1, and η_2 are the viscosities of the mixture and pure components 1 and 2, respectively. Values of ϱ, u, k_s, and η are included in Table 3. The variations of Δk_s with volume fraction and $\Delta \ln \eta$ with mole fraction are illustrated in Figures 2 and 3, respectively.

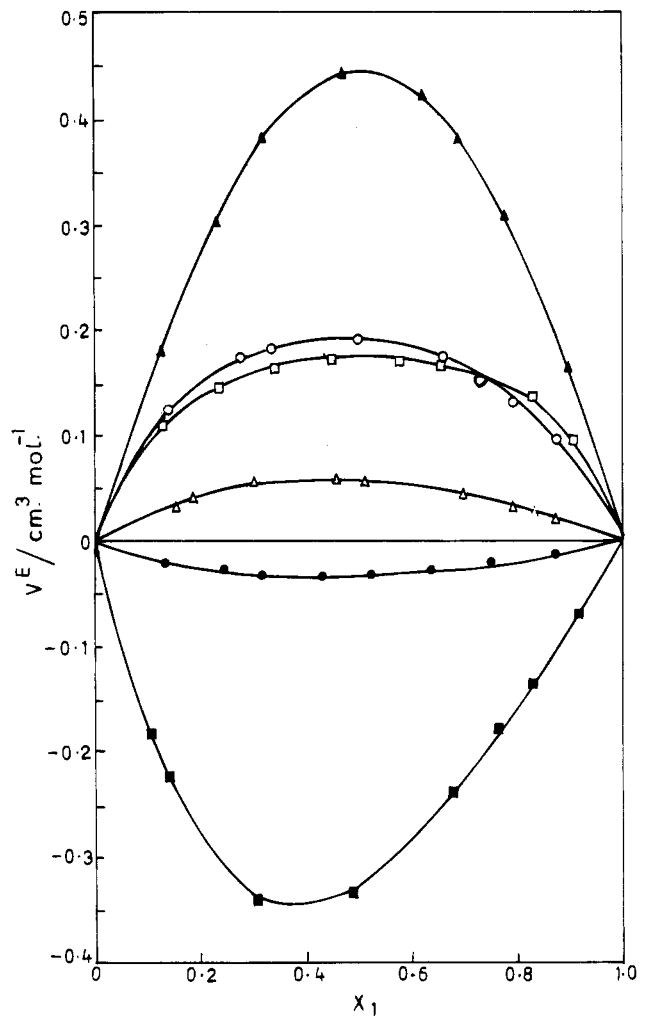

Figure 1. Mole fraction of methyl cellosolve versus excess volumes for methyl cellosolve + methanol (■), + propan-1-ol (△), + butan-1-ol (□), + 2-methyl-propan-1-ol (○), + 2-methylpropan-2-ol (●), and + pentan-1-ol (▲) at 308.15 K.

Discussion

The composition dependence of the excess volume, deviation in isentropic compressibility, and deviation in viscosity are correlated by the Redlich−Kister polynomial

$$X = x_1 x_2 \sum_{i=0}^{2} a_i (x_1 - x_2)^i \tag{5}$$

where X is the excess volume or deviation in viscosity, the composition is in mole fraction, and if X is the deviation in compressibility, the volume fraction should be taken as the composition variable. a_i's are the adjustable parameters and are evaluated by a least-squares method. The values of the parameters along with the standard deviation are given in Table 4. Values of σ are obtained from the equation

$$\sigma = \left[\frac{\sum (X_{expt} - X_{calc})^2}{(n - p)} \right]^{1/2} \tag{6}$$

Table 3. Density, ρ, Speed of Sound, u, Isentropic Compressibility, k_s, and Viscosity, η, at 308.15 K at Volume fraction ϕ

ϕ_1	x_1	ρ/(g·cm^{-3})	u/ms^{-1}	k_s/TPa^{-1}	η/(mPa·s)
Methyl Cellosolve (1) + Methanol (2)					
0.0000	0.0000	0.777 71	1079	1104	0.479
0.2051	0.1175	0.816 98	1139	943	0.569
0.3358	0.2098	0.842 07	1174	862	0.640
0.4705	0.3143	0.865 59	1209	790	0.717
0.6475	0.4866	0.896 14	1251	713	0.844
0.7540	0.6126	0.913 77	1276	672	0.930
0.8612	0.7620	0.931 05	1301	635	1.036
0.8913	0.8201	0.936 93	1308	624	1.074
0.9515	0.9101	0.945 30	1322	605	1.130
1.0000	1.0000	0.952 90	1327	596	1.189
Methyl Cellosolve (1) + Propan-1-ol (2)					
0.0000	0.0000	0.792 65	1184	900	1.466
0.1225	0.1170	0.812 00	1200	856	1.362
0.1873	0.1795	0.822 27	1208	833	1.319
0.3135	0.3024	0.842 31	1224	793	1.260
0.4655	0.4526	0.866 59	1245	744	1.207
0.5394	0.5265	0.878 45	1257	721	1.192
0.6557	0.6439	0.897 16	1276	685	1.185
0.7999	0.7915	0.920 47	1300	643	1.182
0.8751	0.8693	0.932 64	1312	623	1.174
1.0000	1.0000	0.952 90	1327	596	1.189
Methyl Cellosolve (1) + Butan-1-ol (2)					
0.0000	0.0000	0.798 85	1211	854	1.911
0.1036	0.1184	0.813 83	1221	824	1.694
0.2086	0.2345	0.829 59	1231	795	1.551
0.3050	0.3377	0.844 29	1241	769	1.443
0.4116	0.4484	0.860 64	1252	741	1.361
0.5102	0.5476	0.875 75	1264	715	1.305
0.5956	0.6312	0.888 84	1274	693	1.265
0.7062	0.7363	0.905 82	1288	666	1.229
0.8974	0.9104	0.935 98	1312	621	1.195
1.0000	1.0000	0.952 90	1327	596	1.189
Methyl Cellosolve (1) + 2-Methylpropan-1-ol (2)					
0.0000	0.0000	0.790 95	1168	927	2.247
0.1252	0.1438	0.810 11	1186	878	1.902
0.2448	0.2792	0.829 53	1202	834	1.664
0.2984	0.3329	0.837 56	1212	813	1.595
0.4650	0.5050	0.864 43	1239	753	1.422
0.6283	0.6648	0.891 09	1271	695	1.320
0.6919	0.7249	0.901 32	1285	672	1.292
0.7762	0.7936	0.913 53	1297	650	1.264
0.8820	0.8977	0.932 81	1312	622	1.231
1.0000	1.0000	0.952 90	1327	596	1.189
Methyl Cellosolve (1) + 2-Methylpropan-2-ol (2)					
0.0000	0.0000	0.770 60	1083	1106	2.546
0.1008	0.1190	0.789 11	1112	1025	2.241
0.2171	0.2504	0.810 42	1141	948	1.929
0.3265	0.3687	0.830 43	1166	886	1.713
0.4630	0.5096	0.855 36	1194	820	1.527
0.6004	0.6441	0.880 34	1223	759	1.402
0.6829	0.7218	0.895 35	1242	724	1.350
0.7725	0.8035	0.911 60	1264	687	1.298
0.8850	0.9026	0.932 03	1295	640	1.242
1.0000	1.0000	0.952 90	1327	596	1.189
Methyl Cellosolve (1) + Pentan-1-ol (2)					
0.0000	0.0000	0.804 40	1244	803	2.534
0.1331	0.1741	0.822 27	1247	782	1.966
0.2042	0.2604	0.832 04	1249	770	1.804
0.2778	0.3455	0.842 34	1254	755	1.665
0.4108	0.4796	0.860 09	1260	732	1.511
0.5329	0.6102	0.879 45	1275	699	1.385
0.6571	0.7245	0.898 31	1291	668	1.309
0.7210	0.7800	0.908 20	1299	653	1.284
0.8695	0.9014	0.931 70	1316	620	1.230
1.0000	1.0000	0.952 90	1327	596	1.189

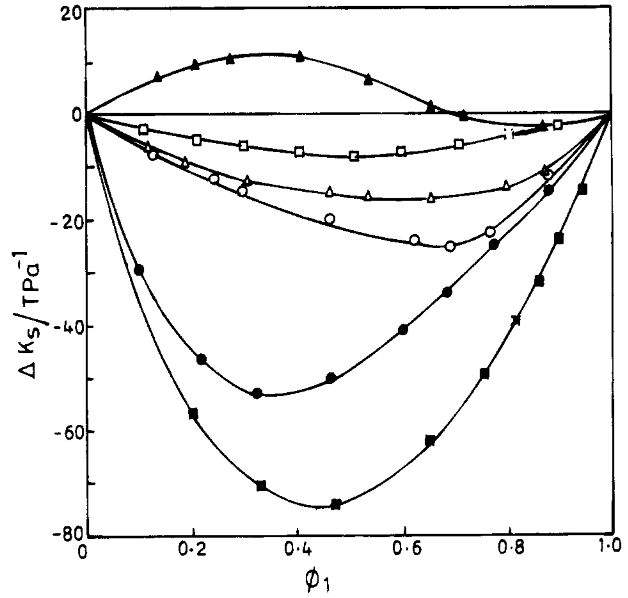

Figure 2. Volume fraction of methyl cellosolve versus deviation in isentropic compressibility of methyl cellosolve + methanol (■), + propan-1-ol (△), + butan-1-ol (□), + 2-methylpropan-1-ol (○), + 2-methylpropan-2-ol (●), and + pentan-1-ol (▲) at 308.15 K.

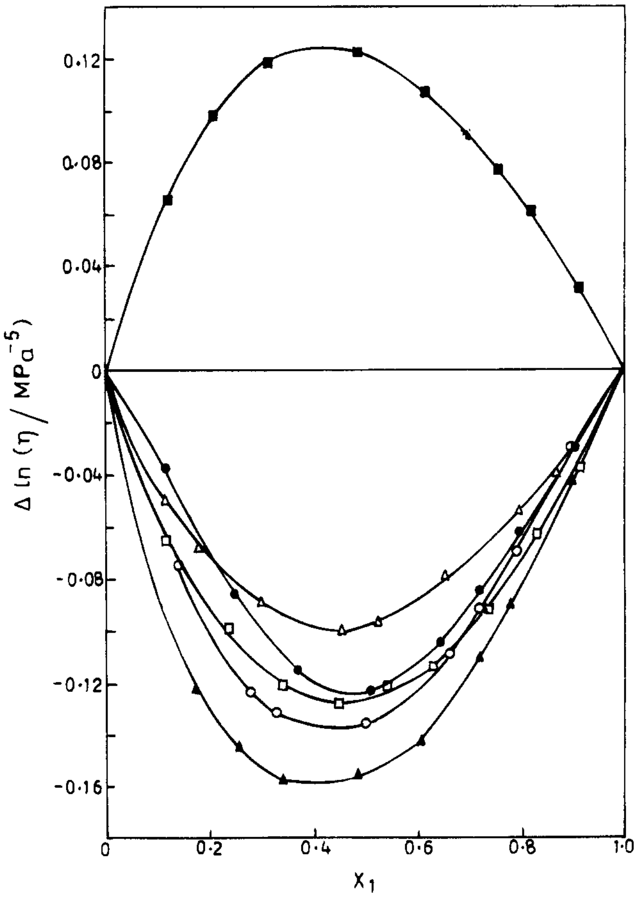

Figure 3. Mole fraction of methyl cellosolve versus deviations in viscosity for methyl cellosolve + methanol (■), + propan-1-ol (△), + butan-1-ol (□), + 2-methylpropan-1-ol (○), + 2-methylpropan-2-ol (●), and + pentan-1-ol (▲) at 308.15 K.

where n is the number of experimental points and p is the number of parameters in eq 5.

The excess volumes are positive in all the systems except for 2-methoxyethanol + methanol and + 2-methylpropan-2-ol at 308.15 K. Further, V^E becomes more positive with an increase in the chain length of the 1-alkanol. For isomeric butanols, V^E values follow the order butan-1-ol > 2-methyl-propan-1-ol > 2-methyl-propan-2-ol. Figure 2 indicates that deviations in isentropic compressibility are negative in all the systems and increase with the chain

Table 4. Values of the Parameters of Eq 5 and Standard Deviation at 308.15 K

X^E	a_0	a_1	a_2	$\sigma(X)$
Methyl Cellosolve (1) + Methanol (2)				
$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$	−1.321	0.610	−0.102	0.003
$\Delta k_s/\mathrm{TPa^{-1}}$	−277.10	69.93	−95.95	2.4
$\Delta \ln (\eta/(\mathrm{mPa{\cdot}s}))$	0.499	−0.153	−0.003	0.002
Methyl Cellosolve (1) + Propan-1-ol (2)				
$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$	0.232	−0.048	−0.033	0.003
$\Delta k_s/\mathrm{TPa^{-1}}$	−58.30	−22.34	−45.99	0.3
$\Delta \ln (\eta/(\mathrm{mPa{\cdot}s}))$	−0.379	0.094	−0.046	0.003
Methyl Cellosolve (1) + Butan-1-ol (2)				
$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$	0.661	0.042	0.722	0.005
$\Delta k_s/\mathrm{TPa^{-1}}$	−30.15	4.52	5.83	0.4
$\Delta \ln(\eta/(\mathrm{mPa{\cdot}s}))$	−0.504	0.109	−0.029	0.003
Methyl Cellosolve (1) + 2-Methylpropan-1-ol (2)				
$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$	0.738	−0.100	0.435	0.003
$\Delta k_s/\mathrm{TPa^{-1}}$	−91.89	−42.59	−7.08	2.1
$\Delta \ln(\eta/(\mathrm{mPa{\cdot}s}))$	−0.557	0.167	0.133	0.002
Methyl Cellosolve (1) + 2-Methylpropan-2-ol				
$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$	−0.134	0.033	0.016	0.002
$\Delta k_s/\mathrm{TPa^{-1}}$	−189.97	116.69	−73.88	0.6
$\Delta \ln/(\eta/(\mathrm{mPa{\cdot}s}))$	−0.496	0.018	0.238	0.003
Methyl Cellosolve (1) + Pentan-1-ol (2)				
$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$	1.764	0.101	−0.045	0.005
$\Delta k_s/\mathrm{TPa^{-1}}$	28.70	−60.74	−23.08	0.8
$\Delta \ln(\eta/(\mathrm{mPa{\cdot}s}))$	−0.629	0.244	−0.077	0.005

length of the 1-alkanols. Deviations in viscosity are positive in the system methyl cellosolve + methanol and negative over the entire range of composition for all the remaining systems, and the negative values decrease with an increase in the chain length of 1-alkanols. The variation of V^E, Δk_s, and $\Delta \ln \eta$ with composition is symmetrical, with the maximum values being at around 0.5 mole fraction/volume fraction. The properties observed for the mixtures studied are influenced by the dissociation of the associated alcohols and alkoxyalkanol. Hydrogen bond formation occurs between the unlike molecules during the deletion process. The actual value of the property depends on the balance of the two effects.

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