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A Study on Mixing Properties of Binary Mixtures of 2-Methoxyethanol with Aromatic Hydrocarbons

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The volume of mixing, speed of sound, and viscosity of the binary mixtures of 2-methoxyethanol + benzene, + toluene, + chlorobenzene, + bromobenzene, and + nitrobenzene have been measured at 303.15 K, over the entire mole fraction range. The results are used to derive densities and isentropic compresibilities. Excess volumes are positive over the whole range of compositon, except for the mixture containing chlorobenzene in which V^E shows negative values at higher mole fractions of 2-methoxyethanol and deviations in the compressibility exhibit an inversion in sign in all the systems except for the mixture containing toluene, in which it is always positive. Deviations of the viscosity from a mole fraction overage are negative except for the mixture containing bromobenzene in which the deviation is positive at higher mole fractions. The results are fitted to the Redlich−Kister polynomial relation and are presented as a function of composition.

Introduction

Knowledge of mixing properties of binary mixtures has relevance in theoretical and applied areas of research because such results are used in design processes in the chemical and petrochemical industries. A survey of the literature shows that measurements (*1−6*) have been made on mixtures containing 2-methoxyethanol. We report experimental excess volumes, isentropic compressibilities, and viscosities of five binary mixtures. The mixtures are 2-methoxyethanol + benzene, + toluene, + chlorobenzene, + bromobenzene, and + nitrobenzene at 303.15 K. The study was undertaken to examine the effect of the addition of various functional groups on the mixture behavior with 2-methoxyethanol.

Experimental Section

Materials. AR grade samples of 2-methoxyethanol, benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene were further purified by standard methods (*7*) as their densities did not initially agree with those reported in the literature (*7*). 2-Methoxyethanol was dried over Drierite for 1 day and fractionally distilled. Benzene and toluene were shaken with concentrated H_2SO_4 until the acid developed no more color, then with water, followed by dilute NaOH solution, and finally with two portions of water. The samples were dried over anhydrous calcium chloride. The dried samples were refluxed with metallic sodium and finally fractionated. Chlorobenzene was washed with NaOH solution, followed by cold concentrated H_2SO_4, and finally with water. The sample was then dried and distilled. Bromobenzene was repeatedly washed with H_2SO_4 until the acid developed no more color. Then it was washed first with water and then with dilute potassium carbonate solution. After drying over anhydrous calcium chloride, it was fractionally distilled. Nitrobenzene was dried over anhydrous calcium chloride for 2 days, and the sample was fractionally distilled. The purities of all the substances were better than 99.95 mass % by GLC analysis. The purities of the samples were ascertained by comparing the densities, speeds of sound, viscosities, and boiling points with those reported in the literature (*1, 7−9*). The densities were measured using a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. The boiling points were measured using a Swietoslawski-type ebulliometer (*10*), which gave an accuracy of ±0.2 K. The measured values are included in Table 1 along with the literature values.

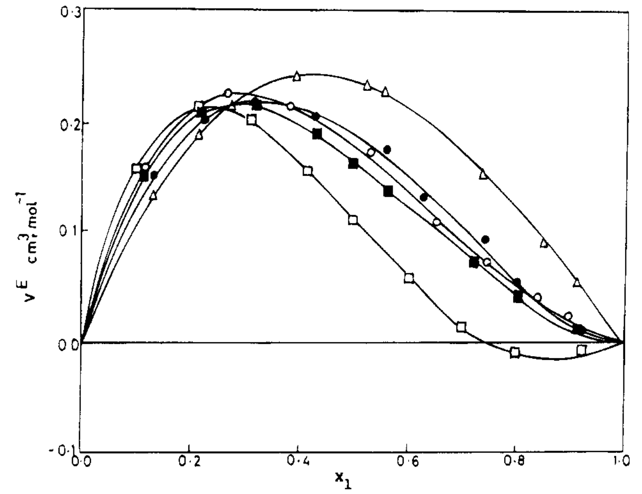

Figure 1. Mole fraction of 2-methoxyethanol versus excess volumes for 2-methoxyethanol + benzene (○), + toluene (●), + chlorobenzene (□), + bromobenzene (■) and + nitrobenzene (△) at 303.15 K.

Procedure. Excess volumes were measured directly using the batch dilatometer technique described earlier (*11*), except that three additional dilatometers having large differences in the size of the limbs were used at high mole fractions. The V^E values are reproducible to ±0.003 $cm^3 \cdot mol^{-1}$. 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 calculated from the mass of the components, and the uncertainty in the mole fraction is estimated to be less than $\pm 5 \times 10^{-4}$.

The liquid mixtures were recovered from the dilatometers using a hypodermic syringe, and used to measure the speed of sound and viscosity. Speeds of sound were measured with a single-crystal ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz. The values are reproducible to ±0.1%. The performance of the interferometer is assessed by measuring and comparing the speeds of sound of the pure components with

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Table 1. Boiling Temperatures T_b, Densities ϱ, Speeds of Sound u, and Viscosities η of Pure Components at 30 °C

	T_b/K		ϱ/(g·cm^{-3})		u/(m·s^{-1})		η/(mPa·s)	
component	exptl	lit. (*7*)	exptl	lit. (*7*)	exptl	lit. (*9*)	exptl	lit. (*7*)
2-methoxyethanol	397.6	397.8	0.955 77	0.955 85[a]	1332	1330[b]	1.376	1.600[c]
benzene	353.0	353.2	0.868 61	0.868 63	1279	1278	0.562	0.562
toluene	383.6	383.8	0.857 78	0.857 76	1285	1284	0.520	0.520
chlorobenzene	404.6	404.8	1.095 52	1.095 50	1251	1249	0.716	0.715
bromobenzene	428.3	428.5	1.481 59	1.481 56	1131	1138	0.985	0.985
nitrobenzene	483.8	483.8	1.193 47	1.193 44	1440	1439	1.635	1.634

[a] Reference 1. [b] Reference 8. [c] At 25 °C.

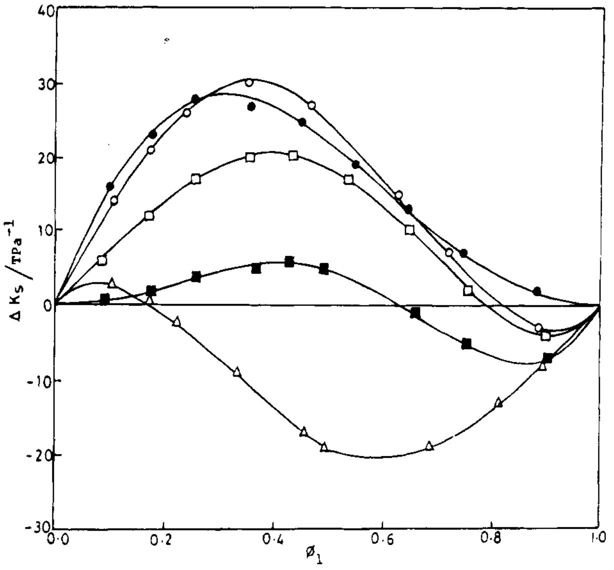

Figure 2. Volume fraction of 2-methoxyethanol versus deviation in isentropic compressibility of 2-methoxyethanol + benzene (○), + toluene (●), + chlorobenzene (box), + bromobenzene (■), and + nitrobenzene (△) at 303.15 K.

the values reported in the literature (*8*, *9*).

Viscosities are measured using a suspended level Ubbelohde viscometer. The viscometer was calibrated at 303.15 K using distilled water. The viscometer constant, K, was calculated from viscosity, η_w, density ϱ_w, and flow time, t_w, of water using the relation $K = \eta_w/(t_w\varrho_w)$. An average of 10 measurements which do not differ by more than 0.005 cm^2/s^2 is taken as the K value. An electronic stop watch capable of measuring time to ±0.015 s is used for time measurements. Kinetic energy corrections are negligible. The estimated error in viscosity is $\pm 5 \times 10^{-4}$ mPa·s. The performance of the viscometer is assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature (*7*).

Results

Experimental excess volume (V^E) data, speeds of sound (u), and viscosities (η) are given in Table 2. The V^E values are used to compute the density (ϱ) of mixtures from the equations

$$V_R^E = \frac{\pi r^2 h}{n_1 + n_2} \tag{1}$$

$$V^E = V_R^E - (x_1V_1 + x_2V_2) \tag{2}$$

$$\varrho = \frac{x_1M_1 + x_2M_2}{x_1V_1 + x_2V_2 + V^E} \tag{3}$$

where x_1 and x_2 are the mole fractoins, M_1 and M_2 are the molar masses, and V_1 and V_2 are the molar volumes of

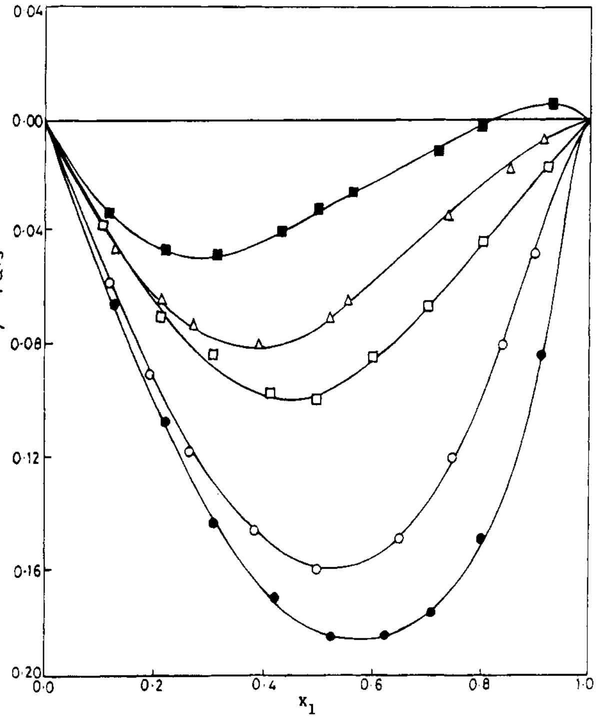

Figure 3. Mole fraction of 2-methoxyethanol versus deviations in viscosity for 2-methoxyethanol + benzene (○), + toluene (●), + chlorobenzene (□), + bromobenzene (■), and + nitrobenzene (△) at 303.15 K.

2-methoxyethanol (1) and aromatic hydrocarbons (2), respectively. The speeds of sound (u) along with the density data are used to calculate the isentropic compressibility (k_s) and the deviation in isentropic compressibility (Δk_s)

$$k_s = 1/u^2\varrho \tag{4}$$

$$\Delta k_s = k_s - \phi_1 k_{s_1} - \phi_2 k_{s_2} \tag{5}$$

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. The duration in the viscosity from a mole fraction overage

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{6}$$

where η_m is the viscosity of the mixture and η_1 and η_2 are the viscosities of 2-methoxyethanol and aromatic hydrocarbon, respectively. V^E as a function of mole fraction is shown in Figure 1. The variaton of Δk_s with volume fraction and of $\Delta\eta$ with mole fraction is given in Figures 2 and 3, respectively.

Discussion

The composition dependence of the excess volume, deviation in isentropic compressibility, and viscosity deviation

Table 2. Densities ρ, Excess Volumes V^E, Speeds of Sound u, Isentropic Compressibilities k_s, and Viscosities η at 303.15 K

x_1	ϕ_1	ρ/(g·cm^{-3})	V^E_{exptl}/(cm^3·mol^{-1})	V^E_{cubic}/(cm^3·mol^{-1})	$V^E_{Redlich}$/(cm^3·mol^{-1})	u/(m·s^{-1})	k_s/TPa^{-1}	η/(mPa·s)
2-Methoxyethanol (1) + Benzene (2)								
0.1174	0.1054	0.876 20	0.161	0.166	0.161	1271	706	0.599
0.1933	0.1750	0.881 76	0.210	0.211	0.211	1268	705	0.628
0.2642	0.2412	0.887 32	0.228	0.225	0.228	1266	703	0.659
0.3837	0.3554	0.897 34	0.215	0.211	0.215	1268	693	0.728
0.4988	0.4684	0.907 56	0.175	0.175	0.175	1275	678	0.807
0.6540	0.6260	0.921 97	0.108	0.113	0.108	1294	648	0.945
0.7474	0.7237	0.930 88	0.072	0.075	0.071	1308	628	1.049
0.8430	0.8262	0.940 15	0.041	0.039	0.040	1320	610	1.168
0.8998	0.8883	0.945 75	0.025	0.020	0.025	1328	600	1.246
2-Methoxyethanol (1) + Toluene (2)								
0.1311	0.1006	0.866 36	0.153	0.150	0.147	1275	710	0.566
0.2283	0.1798	0.873 65	0.203	0.199	0.200	1276	703	0.608
0.3137	0.2531	0.880 64	0.217	0.213	0.217	1269	705	0.645
0.4277	0.3565	0.890 79	0.206	0.203	0.206	1274	692	0.716
0.5253	0.4506	0.900 21	0.178	0.177	0.176	1279	679	0.784
0.6244	0.5520	0.910 54	0.132	0.138	0.134	1289	661	0.870
0.7116	0.6465	0.920 16	0.093	0.098	0.094	1299	644	0.954
0.8018	0.7499	0.930 68	0.053	0.056	0.056	1310	626	1.057
0.9149	0.8885	0.944 69	0.013	0.013	0.017	1323	605	1.219
2-Methoxyethanol (1) + Chlorobenzene (2)								
0.1075	0.0854	1.081 87	0.159	0.170	0.163	1252	590	0.749
0.2093	0.1702	1.069 41	0.213	0.215	0.216	1253	596	0.782
0.3086	0.2570	1.057 36	0.203	0.199	0.206	1253	602	0.836
0.4173	0.3569	1.043 88	0.157	0.151	0.156	1258	605	0.894
0.4993	0.4359	1.033 39	0.107	0.109	0.109	1264	606	0.952
0.6006	0.5382	1.019 67	0.056	0.059	0.053	1274	604	1.028
0.7032	0.6474	1.004 88	0.014	0.017	0.120	1290	598	1.113
0.8023	0.7587	0.989 58	−0.008	−0.010	−0.009	1309	590	1.201
0.9234	0.9033	0.969 35	−0.006	−0.017	−0.010	1328	585	1.309
2-Methoxyethanol (1) + Bromobenzene (2)								
0.1188	0.0920	1.431 09	0.154	0.156	0.151	1143	535	0.997
0.2190	0.1740	1.387 20	0.209	0.205	0.206	1154	541	1.024
0.3173	0.2588	1.342 50	0.218	0.211	0.215	1166	548	1.060
0.4336	0.3651	1.286 99	0.191	0.187	0.190	1182	556	1.114
0.4974	0.4265	1.255 10	0.167	0.166	0.166	1193	560	1.147
0.5621	0.4909	1.221 58	0.139	0.142	0.139	1206	563	1.179
0.7198	0.6587	1.131 68	0.071	0.077	0.073	1247	568	1.255
0.8018	0.7524	1.085 40	0.043	0.045	0.045	1271	570	1.296
0.9254	0.9031	1.006 59	0.011	0.008	0.013	1312	577	1.352
2-Methoxyethanol (1) + Nitrobenzene (2)								
0.1320	0.1051	1.166 92	0.135	0.132	0.131	1416	427	1.553
0.2148	0.1743	1.149 80	0.190	0.186	0.187	1410	437	1.514
0.2725	0.2243	1.137 60	0.217	0.213	0.214	1407	444	1.490
0.3929	0.3331	1.111 40	0.244	0.238	0.242	1403	457	1.453
0.5243	0.4597	1.081 40	0.235	0.236	0.235	1398	473	1.428
0.5584	0.4939	1.073 35	0.227	0.229	0.228	1398	477	1.425
0.7423	0.6898	1.027 67	0.154	0.157	0.156	1377	513	1.409
0.8512	0.8153	0.998 58	0.090	0.093	0.094	1358	543	1.397
0.9147	0.8922	0.980 77	0.052	0.053	0.055	1347	562	1.391

is correlated by the Redlich–Kister polynomial

$$Y = x_1 x_2 \sum_{i=0}^{2} a_i (x_1 - x_2)^i \tag{7}$$

where Y is the excess volume or deviation in viscosity and the composition is in mole fraction. If Y is the deviation in compressibility, volume fraction should be taken as the composition, a_i's are the adjustable parameters and are evaluated from the least-squares method. The values of the parameters along with the standard deviation are given in Table 3. The values of σ were obtained from the equation

$$\sigma = \left[\frac{\sum (Y_{exptl} - Y_{calcd})^2}{n - p}\right]^{1/2} \tag{8}$$

where n is the number of experimental points and p is the number of parameters in eq 7.

The V^E results were also fitted to the H^{3}M equation recently proposed by Hwang et al. (*12*)

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1 x_2 (a_0 + a_1 x_1^3 + a_2 x_2^3) \tag{9}$$

where x_1 and x_2 represent the mole fractions of components 1 and 2 and a_0, a_1, and a_2 are constants. The values of the sets of the constants are given in Table 3 along with the standard deviations. The standard deviation values in Table 3 indicate that the H^{3}M equation gives a rough agreement with the experimental data. An examination of the results included in Table 2 shows that the Hwang et al. equation correctly describes the sign of the excess volume in all mixtures. Further, the values calculated from the Hwang et al. equation are comparable to those of the Redlich–Kister relation.

The data included in Table 2 and Figure 1 indicate that the V^E values are positive in all the systems except 2-methoxyethanol (1) + chlorobenzene (2) in which V^E is

Table 3. Values of the Parameters of Eqs 7 (Redlich) and 9 (Cubic) and Standard Deviations at 303.15 K

y	a_0	a_1	a_2	$\sigma(Y)$
2-Methoxyethanol (1) + Benzene (2)				
$V^E/(cm^3 \cdot mol^{-1})$				
Redlich	0.697	−0.832	0.380	0.001
cubic	0.568	−0.472	1.499	0.004
$\Delta K_s/TPa^{-1}$	100.988	−104.180	−68.171	1
$\Delta\eta/(mPa \cdot s)$	−0.654	−0.032	0.146	0.003
2-Methoxyethanol (1) + Toluene (2)				
$V^E/(cm^3 \cdot mol^{-1})$				
Redlich	0.739	−0.690	0.075	0.004
cubic	0.714	−0.721	0.921	0.004
$\Delta k_s/TPa^{-1}$	87.390	−111.425	13.862	1
$\Delta\eta/(mPa \cdot s)$	−0.726	−9.243	−0.162	0.004
2-Methoxyethanol (1) + Chlorobenzene (2)				
$V^E/(cm^3 \cdot mol^{-1})$				
Redlich	0.433	−1.163	0.580	0.003
cubic	0.240	−0.164	2.156	0.007
$\Delta k_s/TPa^{-1}$	75.084	−55.348	−88.164	2
$\Delta\eta/(mPa \cdot s)$	−0.380	0.081	0.086	0.003
2-Methoxyethanol (1) + Bromobenzene (2)				
$V^E/cm^3\ mol^{-1}$				
Redlich	0.661	−0.805	0.295	0.003
cubic	0.563	−0.567	1.351	0.005
$\Delta k_s/TPa^{-1}$	18.931	−33.536	−80.125	1
$\Delta\eta/(mPa \cdot s)$	−0.141	0.218	−0.009	0.002
2-Methoxyethanol (1) + Nitrobenzene (2)				
$V^E/(cm^3\ mol^{-1})$				
Redlich	0.958	−0.281	−0.038	0.003
cubic	0.971	−0.385	0.284	0.004
$\Delta k_s/TPa^{-1}$	−75.577	−86.365	80.081	1
$\Delta\eta/(mPa \cdot s)$	−0.291	0.170	0.048	0.003

positive at lower x_1 and then becomes negative at high x_1. Figure 2 indicates that deviations in isentropic compressibility are positive for the toluene system over the entire range of composition, while in the remaining systems Δk_s is positive at small x_1 and then becomes negative at high x_1. Figure 3 indicates that the $\Delta\eta$ values are negative for all systems for 2-methoxyethanol (1) + bromobenzene (2) in whch $\Delta\eta$ is negative at lower x_1 and positive at high x_1. Negative Y must be due to complex formation between the π-electrons of benzene and −O− in 2-methoxyethanol. Positive Y might be due to breaking of hydrogen bonds in 2-methoxyethanol by the addition of benzene and substituted benzenes. The observed Y values are attributed to a resultant of the above two major effects.

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