Excess Volumes and Speed of Sound of Ternary Mixtures of 2-Methoxyethanol (1) + Butyl Acetate (2) + Aromatic Hydrocarbons (3) at 303.15 K

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Excess volumes and the speed of sound of five ternary mixtures of 2-methoxyethanol (1) + butyl acetate (2) + benzene (3), + toluene (3), + chlorobenzene (3), + bromobenzene (3), and + nitrobenzene (3) have been measured at 303.15 K. The excess volumes exhibit positive deviation over the entire range of composition in the system 2-methoxyethanol (1) + butyl acetate (2) + benzene (3) and sigmoid behavior in the case of the remaining systems. The deviation in the isentropic compressibility exhibits a sigmoid behavior in all the mixtures. The results were compared with those predicted by empirical equations.

Introduction

A survey of the literature showed that excess molar volumes and the speed of sound of binary mixtures of butyl acetate (*1*, *2*) and 2-methoxyethanol (*3*) with aromatic hydrocarbons have been measured at 303.15 K. We report measurements on excess volumes and the speed of sound of five ternary mixtures. The mixtures included 2-methoxyethanol (1) and butylacetate (2) as common components and aromatic hydrocarbons as noncommon components (*3*). The aromatic hydrocarbons were benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene. The ternary results have been used to check the capability of predictive equations (*4*).

Experimental Section

Excess volumes for ternary systems were measured with the dilatometer described by Naidu and Naidu (*5*). The mixing cell contained three bulbs of different capacities. Mercury was used in the bottom to separate the three components. One of the three bulbs was fitted with a capillary, and the other two were fitted with ground-glass stoppers. Four dilatometers of the aforementioned type were used to cover the entire range of composition. The mixture compositions were determined within an accuracy of 0.0001 mole fraction. All the measurements were made at a constant temperature employing a thermostat that could maintain a temperature of 303.15 ± 0.01 K. Temperature was measured by using a quartz thermometer with a resolution of better than ±0.01 K. The measured V^E values were accurate to ±0.003 $cm^3 \cdot mol^{-1}$. Isentropic compressibilities were computed from the measured sound speed, and the density was derived from the excess volume.

The ultrasonic sound speed was measured with a single crystal interferometer at 3 MHz, and the results were accurate to ±0.15%. All the measurements were made at constant temperature using a thermostat that could be maintained to ±0.01 K.

Purification of Materials. All the chemicals used were of analytical grade. 2-Methoxyethanol was dried over Drierite for 1 day and fractionally distilled. Butyl acetate was purified by the standard methods described by Vogel (*6*). Benzene was purified by the method described by Naidu and Krishnan (*7*). Toluene was purified by the standard method described previously (*8*). Chlorobenzene and nitrobenzene were purified by standard methods described previously (*9*). Bromobenzene was dried with calcium chloride and fractionally distilled under reduced pressure. The purities of all substances were better than 99.95 mass % as found by GLC analysis. The purity of the chemicals was checked by comparing the densities and the boiling temperatures 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 temperatures were 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 Temperature T_b and Densities (ϱ) of Pure Components at 303.15 K

	T_b/K		ϱ/(g·cm^{-3})	
component	exptl	lit. (*10*, *11*)	exptl	lit. (*10*, *11*)
2-methoxyethanol	397.6	397.8	0.955 57	0.960 24
butyl acetate	399.2	399.3	0.871 23	0.871 29
benzene	353.0	353.2	0.868 61	0.868 63
toluene	383.6	383.8	0.857 78	0.857 76
chlorobenzene	404.6	404.8	1.095 52	1.095 50
bromobenzene	428.3	428.5	1.481 59	1.481 56
nitrobenzene	483.8	483.9	1.193 47	1.193 44

Results

The measured excess volume data and speed of sound results for the five ternary mixtures are given in Tables 2 and 3, respectively. The binary excess volumes and isentropic compressibilities for 2-methoxyethanol with the substituted benzenes (*3*), butyl acetate (*13*), and butyl acetate with substituted benzenes (*1*, *2*) are taken from the literature. The ternary excess volumes predicted by using the binary data through the empirical equations proposed by Redlich and Kister, Kohler and Tsao, and Smith are given in columns 4−6 of Table 2. The isentropic compressibilities, k_{s123}, and deviations in isentropic compressibility, K_{s123}, for the ternary mixtures are given in columns 5 and 6 of Table 3. Finally, the quantity δk_{s123} is given in column 8 of Table 3. The three emperical equations are given as follows:

Redlich−Kister expression

$$V^E_{ij} = x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2] \qquad (1)$$

where x_i and x_j are the mole fractions of the components

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Table 2. Experimental and Predicted Excess Molar Volumes for 2-Methoxyethanol (1) + Butyl Acetate (2) + Aromatic Hydrocarbons (3) at 303.15 K

			V^E_{123}/(cm³·mol⁻¹)			
x_1	x_3	V^E_{123}(exptl)/(cm³·mol⁻¹)	Redlich–Kister	Kohler	Tsao–Smith	ΔV^E_{123}[a]/(cm³·mol⁻¹)
		2-Methoxyethanol (1) + Butyl Acetate (2) + Benzene (3)				
0.0922	0.1348	0.304	0.115	0.119	0.130	0.189
0.0935	0.1968	0.388	0.119	0.127	0.141	0.269
0.0985	0.3449	0.529	0.129	0.145	0.161	0.400
0.0807	0.4275	0.488	0.118	0.134	0.146	0.370
0.0795	0.4914	0.497	0.117	0.135	0.146	0.380
0.0710	0.6603	0.401	0.111	0.126	0.133	0.290
0.1061	0.6995	0.494	0.142	0.156	0.166	0.352
0.0798	0.8140	0.293	0.120	0.127	0.131	0.173
0.0753	0.8921	0.175	0.117	0.119	0.120	0.058
		2-Methoxyethanol (1) + Butyl Acetate (2) + Toluene (3)				
0.1558	0.0457	0.196	0.150	0.153	0.158	0.046
0.1176	0.1750	0.204	0.075	0.083	0.089	0.129
0.1343	0.2746	0.253	0.056	0.049	0.070	0.197
0.0404	0.4164	0.019	−0.063	−0.055	−0.051	0.082
0.0516	0.5027	0.042	−0.054	−0.044	−0.048	0.096
0.0933	0.6570	0.126	0.024	0.036	0.033	0.102
0.0941	0.6821	0.113	0.033	0.044	0.042	0.080
0.1004	0.7996	0.105	0.085	0.093	0.092	0.020
0.1332	0.8462	0.137	0.141	0.145	0.144	−0.004
		2-Methoxyethanol (1) + Butyl Acetate (2) + Chlorobenzene (3)				
0.2095	0.0229	0.195	0.187	0.193	0.199	0.008
0.1707	0.1305	0.118	0.078	0.093	0.108	0.040
0.1988	0.2572	0.070	−0.010	−0.007	0.009	0.080
0.1111	0.3405	0.077	−0.132	−0.109	−0.116	0.055
0.0454	0.4119	−0.220	−0.243	−0.226	−0.235	0.023
0.0660	0.4814	−0.209	−0.234	−0.213	−0.226	0.025
0.1344	0.6408	−0.070	−0.065	−0.038	−0.053	−0.005
0.1292	0.6664	−0.065	−0.052	−0.025	−0.038	−0.013
0.1494	0.8061	0.113	0.140	0.153	0.150	−0.027
		2-Methoxyethanol (1) + Butyl Acetate (2) + Bromobenzene (3)				
0.1697	0.0987	0.348	0.079	0.083	0.083	0.269
0.1601	0.1736	0.386	0.009	0.016	0.010	0.377
0.1405	0.2892	0.318	−0.081	−0.069	−0.084	0.399
0.0328	0.3689	−0.138	−0.246	−0.237	−0.245	0.108
0.0130	0.5777	−0.243	−0.284	−0.281	−0.285	0.041
0.1085	0.6053	0.062	−0.104	−0.086	−0.103	0.166
0.1493	0.6478	0.071	−0.012	0.007	−0.009	0.083
0.1606	0.8145	0.140	0.157	0.161	0.159	−0.017
0.1534	0.8330	0.154	0.163	0.166	0.172	−0.009
		2-Methoxyethanol (1) + Butyl Acetate (2) + Nitrobenzene (3)				
0.1476	0.1142	0.426	−0.078	−0.083	−0.118	0.504
0.1675	0.1491	0.579	−0.108	−0.113	−0.163	0.687
0.0993	0.3060	0.141	−0.359	−0.357	−0.405	0.500
0.0777	0.3882	−0.049	−0.433	−0.428	−0.469	0.384
0.0684	0.5178	−0.156	−0.445	−0.440	−0.476	0.289
0.0490	0.6290	−0.252	−0.429	−0.426	−0.426	0.177
0.1138	0.6865	−0.083	−0.212	−0.210	−0.249	0.129
0.1386	0.8097	0.010	0.035	0.034	0.019	−0.025
0.1412	0.8430	0.092	0.106	0.106	0.100	−0.014

[a] $\Delta V^E_{123} = V^E_{123}$(exptl) − V^E_{123}(b) (Redlich–Kister).

in a ternary mixture. The binary parameters are given in Table 4.

Kohler expression

$$V^E_{123} = (x_1 + x_2)^2 V^E_{12} + (x_1 + x_3)^2 V^E_{13} + (x_2 + x_3)^2 V^E_{23} \quad (2)$$

where

$$V^E_{ij} = x_i' x_j' \sum_{s=0}^{n} (A_s)_{ij} (x_i' - x_j')^s$$

at composition (x_i', x_j'), such that

$$x_i' = (1 - x_j') = x_i/(x_i + x_j)$$

where x_i and x_j are the mole fractions of components i and j in a ternary mixture and $(A_s)_{ij}$'s are the parameters in the Kohler expression.

Tsao–Smith expression

$$V^E_{123} = x_2(1 - x)^{-1} V^E_{12} + x_3(1 - x_1)^{-1} V^E_{13} + (1 - x_1) V^E_{23} \quad (3)$$

where V^E_{12}, V^E_{13}, and V^E_{23} are the binary excess volumes at compositions (x_i, x_j).

Isentropic compressibilities of ternary mixtures, k_{s123} and the deviation in isentropic compressibility, K_{s123}, are calculated using the relations

$$k_{s123} = 1/u^2\varrho \quad (4)$$

$$K_{s123} = k_{s123} - k^{id}{}_{s123} \quad (5)$$

where k_{s123} and $k^{id}{}_{s123}$ are isentropic compressibilities of

Table 3. Experimental Values for Isentropic Compressibilities of the Ternary Systems 2-Methoxyethanol (1) + Butyl Acetate (2) + Aromatic Hydrocarbons (3) at 303.15 K

ϕ_1	ϕ_3	ρ/(g·cm^{-3})	u/(m·s^{-1})	k_{s123}/TPa^{-1}	K_{s123}/TPa^{-1}	K'_{s123}/TPa^{-1}	δK_{s123}/TPa^{-1}
			2-Methoxyethanol (1) + Butyl Acetate (2) + Benzene (3)				
0.0599	0.0989	0.873 87	1187	812	8	13	−5
0.0622	0.1478	0.873 27	1190	809	12	16	−4
0.0694	0.2743	0.872 29	1201	795	16	19	−3
0.0582	0.3481	0.871 39	1203	793	20	21	−1
0.0588	0.4102	0.871 10	1211	783	18	21	3
0.0561	0.5887	0.870 96	1231	758	15	20	5
0.0868	0.6467	0.872 45	1243	742	19	21	−2
0.0678	0.7811	0.872 19	1258	724	9	16	−7
0.0662	0.8858	0.872 82	1269	711	8	12	−4
			2-Methoxyethanol (1) + Butyl Acetate (2) + Toluene (3)				
0.1002	0.0397	0.877 78	1185	811	9	5	4
0.0765	0.1535	0.874 17	1188	811	18	8	10
0.0899	0.2479	0.873 64	1195	802	24	7	17
0.0267	0.3716	0.868 35	1204	794	16	7	9
0.0350	0.4594	0.867 70	1212	785	20	7	13
0.0667	0.6341	0.867 36	1233	758	22	10	12
0.0677	0.6625	0.867 16	1235	756	24	9	15
0.0746	0.8011	0.865 91	1254	734	21	13	8
0.1017	0.8719	0.866 96	1272	713	15	17	−2
			2-Methoxyethanol (1) + Butyl Acetate (2) + Chlorobenzene (3)				
0.1374	0.0194	0.885 77	1197	788	−5	2	−7
0.1128	0.1113	0.904 93	1203	764	−12	−1	−11
0.1387	0.2303	0.934 04	1218	722	−18	−6	−12
0.0756	0.2991	0.944 10	1200	736	−3	−8	5
0.0306	0.3578	0.955 83	1197	730	−5	−12	7
0.0457	0.4299	0.973 28	1207	705	−8	−11	3
0.1005	0.6181	1.019 04	1219	660	7	−9	16
0.0970	0.6459	1.024 93	1219	657	10	−4	14
0.1182	0.8229	1.064 59	1247	604	6	4	2
			2-Methoxyethanol (1) + Butyl Acetate (2) + Bromobenzene (3)				
0.1112	0.0861	0.930 51	1181	771	−7	−5	−2
0.1062	0.1533	0.970 68	1171	751	−8	−11	3
0.0949	0.2600	1.035 16	1155	724	−5	−17	12
0.0215	0.3218	1.070 70	1153	703	−19	−23	4
0.0089	0.5240	1.194 32	1143	641	−29	−31	2
0.0779	0.5782	1.230 03	1144	621	−16	−28	12
0.1105	0.6381	1.269 19	1152	594	−17	−25	8
0.1248	0.8427	1.394 26	1156	537	−9	−5	−4
0.1194	0.8629	1.405 88	1152	536	−5	−3	−2
			2-Methoxyethanol (1) + Butyl Acetate (2) + Nitrobenzene (3)				
0.0964	0.0966	0.907 33	1211	752	−15	−12	−3
0.1113	0.1283	0.917 56	1225	726	−23	−17	−6
0.0666	0.2658	0.961 36	1241	675	−26	−38	12
0.0527	0.3410	0.985 97	1258	641	−32	−46	14
0.0478	0.4684	1.027 61	1289	586	−33	−51	18
0.0349	0.5808	1.063 73	1316	543	−32	−46	14
0.0851	0.6649	1.093 54	1342	508	−19	−31	12
0.1088	0.8233	1.145 61	1404	443	−10	−5	−5
0.1121	0.8609	1.159 00	1412	433	−1	2	−3

Table 4. Values of the Parameters A_{ij}, B_{ij}, and C_{ij} and the Standard Deviation $\sigma(V^E)$ for Binary Systems at 303.15 K

system	A_{ij}/(cm^3·mol^{-1})	B_{ij}/(cm^3·mol^{-1})	C_{ij}/(cm^3·mol^{-1})	$\sigma(V^E)$/(cm^3·mol^{-1})
2-methoxyethanol + benzene	0.697	−0.832	0.380	0.001
2-methoxyethanol + toluene	0.739	−0.690	0.075	0.004
2-methoxyethanol + chlorobenzene	0.433	−1.163	0.580	0.003
2-methoxyethanol + bromobenzene	0.661	−0.805	0.295	0.003
2-methoxyethanol + nitrobenzene	0.958	−0.281	−0.038	0.003
2-methoxyethanol + butyl acetate	1.172	0.024	0.197	0.003
benzene + butyl acetate	0.164	−0.022	−0.028	0.001
toluene + butyl acetate	−0.484	−0.062	0.358	0.004
chlorobenzene + butyl acetate	−1.376	−0.430	0.908	0.002
bromobenzene + butyl acetate	−1.292	0.029	0.414	0.004
nitrobenzene + butyl acetate	−2.435	0.263	−0.281	0.004

the real mixture and an ideal mixture, respectively. The ideal isentropic compressibility of an ideal mixture is calculated using the expression

$$k^{id}_{s123} = \phi_1 K_{s1} + \phi_2 K_{s2} + \phi_3 K_{s3} \quad (6)$$

where ϕ_1, ϕ_2, and ϕ_3 and K_{s1}, K_{s2}, and K_{s3} are volume fractions and isentropic compressibilities of 2-methoxyethanol, butyl acetate, and the aromatic hydrocarbon, respectively. The quantity δK_{s123}, the difference between the measured value and that computed from constituent binary results, was calculated as

$$\delta K_{s123} = K_{s123} - K'_{s123} \quad (7)$$

where K_{s123} is the deviation in isentropic compressibility

Table 5. Values of the Parameters b_0, b_1, and b_2 and the Standard Deviation $\sigma(\Delta K_s)$ for Binary Systems at 303.15 K

system	b_0/TPa^{-1}	b_1/TPa^{-1}	b_2/TPa^{-1}	$\sigma(\Delta K_s)$/TPa^{-1}
2-methoxyethanol + benzene	100.988	−104.180	−68.171	1
2-methoxyethanol + toluene	87.390	−111.425	13.862	1
2-methoxyethanol + chlorobenzene	75.084	−55.348	−88.164	2
2-methoxyethanol + bromobenzene	18.931	−33.536	−80.125	1
2-methoxyethanol + nitrobenzene	−75.577	−86.365	80.081	1
2-methoxyethanol + butyl acetate	−67.776	−86.563	71.079	2
benzene + butyl acetate	80.057	−19.324	48.666	2
toluene + butyl acetate	19.727	−14.463	35.015	1
chlorobenzene + butyl acetate	−58.415	7.470	35.931	2
bromobenzene + butyl acetate	−124.415	−53.744	−35.330	3
nitrobenzene + butyl acetate	−220.308	35.847	157.166	2

Table 6. Values of the Ternary Constants A, B, and C and the Standard Deviation $\sigma(V^E)$ for Binary Systems at 303.15 K

system	A/(cm^3·mol^{-1})	B/(cm^3·mol^{-1})	C/(cm^3·mol^{-1})	$\sigma(V^E)$/(cm^3·mol^{-1})
2-methoxyethanol (1) + butyl acetate (2) + benzene (3)	21.994	46.753	198.192	0.005
2-methoxyethanol (1) + butyl acetate (2) + toluene (3)	8.332	−39.866	−434.437	0.006
2-methoxyethanol (1) + butyl acetate (2) + chlorobenzene (3)	2.021	−23.541	−217.702	0.007
2-methoxyethanol (1) + butyl acetate (2) + bromobenzene (3)	13.475	−115.546	−296.107	0.007
2-methoxyethanol (1) + butyl acetate (2) + nitrobenzene (3)	21.322	−223.690	−177.205	0.002

Table 7. Values of the Ternary Constants X, Y, and Z and the Standard Deviation $\sigma(\delta K_{s123})$ of Ternary Systems at 303.15 K

system	X/TPa^{-1}	Y/TPa^{-1}	Z/TPa^{-1}	$\sigma(\delta K_{s123})$/TPa^{-1}
2-methoxyethanol (1) + butyl acetate (2) + benzene (3)	306	−3084	−595483	3
2-methoxyethanol (1) + butyl acetate (2) + toluene (3)	1430	−7765	−178153	3
2-methoxyethanol (1) + butyl acetate (2) + chlorobenzene (3)	818	18268	−188477	5
2-methoxyethanol (1) + butyl acetate (2) + bromobenzene (3)	936	−6245	−188274	3
2-methoxyethanol (1) + butyl acetate (2) + nitrobenzene (3)	1525	−4660	−368875	4

calculated from experimental results and K'_{123} is the deviation calculated from binary data. The latter quantity was calculated using the relation

$$K'_{s123} = K_{s13} + K_{s12} + K_{s23} \quad (8)$$

where K_{s12}, K_{s13}, and K_{s23} denote deviations in isentropic compressibilities of the binary results. K_{sij} for a binary mixture was estimated using the smoothing equation

$$K_{sij} = \phi_i\phi_j[b_0 + b_1(\phi_i - \phi_j) + b_2(\phi_i - \phi_j)^2] \quad (9)$$

where b_0, b_1, and b_2 are constants obtained by the method of least squares and are given in Table 5.

Discussion

The results given in Tables 2 and 3 indicate that V^E and ΔK_s are sigmoid in all the systems except for 2-methoxyethanol (1) + butyl acetate (2) + benzene (3) where V^E is positive over the entire range of composition.

For all systems the deviations are not zero. This suggests that the ternary mixtures are not ideal in terms of constituent binaries, indicating that the third component modifies both the nature and degree of interaction between 2-methoxyethanol + butyl acetate.

The dependence of the experimental excess volume, V^E_{123}(exptl), on composition is expressed by the polynomial

$$V^E_{123}(\text{exptl}) = V^E_{123}(\text{b}) + x_1x_2x_3[A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2]$$

and

$$V^E_{123}(\text{b}) = V^E_{12} + V^E_{23} + V^E_{13}$$

where x_1, x_2, and x_3 are the ternary mole fractions of 2-methoxyethanol, butyl acetate, and the aromatic hydrocarbon. V^E_{123}(b) is the ternary excess volume computed from the binary data through the Redlich–Kister relation. V^E_{123} is the deviation from V^E_{123}(exptl) values. A, B, and C are ternary constants and are given in Table 6 along with the standard deviation $\phi(V^E)$. The δK_{s123} values are fitted to the polynomial

$$\delta K_{s123} = \phi_1\phi_2\phi_3[X + Y\phi_1(\phi_2 - \phi_3) + Z\phi_1^2(\phi_2 - \phi_3)^2]$$

where ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of components 1, 2, and 3 respectively. The values of adjustable parameters X, Y, and Z are obtained by the least-squares method and are given in Table 7 along with the standard deviation $\sigma(\delta K_{s123})$.

An examination of the results included in Table 2 shows that the Redlich–Kister, Kohler, and Tsao–Smith equations predict correctly the sign of the excess functions in all the mixtures. However, the equations give a rough estimate of the excess function in the quantitative sense. Further, the values predicted by the Kohler and Tsao–Smith equations are comparable to those of the Redlich–Kister equation.

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