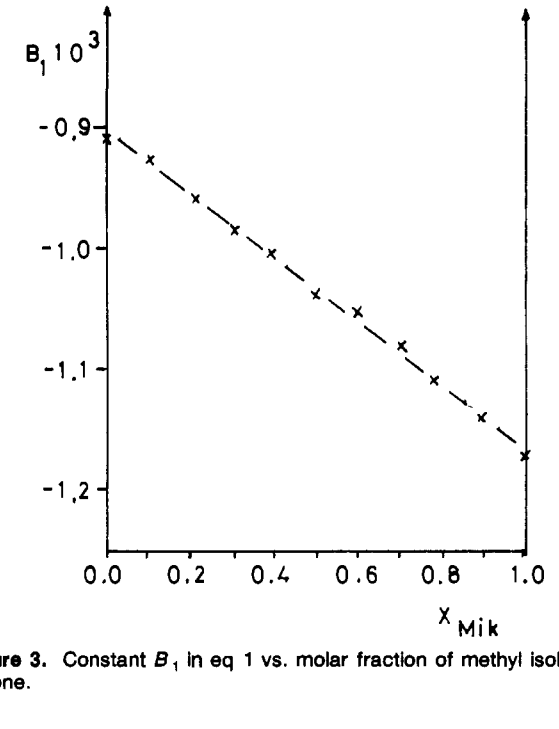

Figure 3. Constant B_1 in eq 1 vs. molar fraction of methyl isobutyl ketone.

listed in Table VI. By means of eq 4-15, density, viscosity, and refractive index data for the studied systems in this paper at any temperature and composition, within the experimental ranges, can be predicted. The calculated values through these equations compared well with the experimental data, and the average percent deviation (D) for each property and system is also listed in Table VI.

Glossary

A_1, B_1	constants in eq 1
A_2, B_2	constants in eq 2
A_3, B_3	constants in eq 3
ρ	density of the mixture, g cm^{-3}
η	viscosity of the mixture, cP
n_D	refractive index of the mixture for the sodium D line.
X_{MIK}, X	molar fraction of the MIK
T	temperature, K
t	temperature, °C
D	average percent deviation

Registry No. MIBK, 108-10-1; P_1, 71-41-0; P_2, 6032-29-7; IA, 123-51-3; TA, 75-85-4.

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Isentropic Compressibilities of Binary Liquid Mixtures at 303.15 and 313.15 K

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Isentropic compressibilities for the binary mixtures of methyl ethyl ketone with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene have been determined at 303.15 and 313.15 K, using ultrasonic velocity and density data. Excess isentropic compressibility, k_s^E, values are negative over the entire range of composition for all the systems and at both temperatures. The behavior of k_s^E as a function of composition and temperature has been studied. The results have been discussed in terms of dipole-induced dipole and dipole-dipole interactions between dissimilar components.

Excess isentropic compressibilities have been determined for binary mixtures of methyl ethyl ketone with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene in order to study the effect that group substitution on a benzene ring has on the molecular interaction in the presence of a polar component. A literature survey revealed that the excess isentropic compressibilities for these systems have not been reported.

Table I. Pure Component Parameters

component	T/K	V/(cm^3 mol^{-1})	K_s/TPa^{-1}	$10^3\,\alpha$/K^{-1}	C_p/(J K^{-1} mol^{-1})
MEK	303.15	90.77	915	1.256	162.2
	313.15	91.72	1002	1.271	169.1
C_6H_6	303.15	89.81	707	1.242	137.4
	313.15	91.08	770	1.258	140.6
$C_6H_5CH_3$	303.15	107.44	699	1.079	159.9
	313.15	108.61	757	1.091	163.4
C_6H_5Cl	303.15	102.75	589	0.985	150.6
	313.15	103.76	634	1.005	152.2
C_6H_5Br	303.15	105.98	514	0.896	155.9
	313.15	106.95	554	0.992	157.3
$C_6H_5NO_2$	303.15	103.16	395	0.818	177.3
	313.15	104.01	426	0.865	173.6

Experimental Section

Ultrasonic velocities were measured by using a single-crystal interferometer at a frequency of 2 MHz, and the values were accurate to ±0.1%. Density data for the pure components were measured by using a bicapillary pycnometer, and in the

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Table II. Mole Fraction, x_1, of Methyl Ethyl Ketone, Density, ρ, Sound Velocity, u, Isentropic Compressibility, k_s, and Excess Isentropic Compressibility, k_s^E

303.15 K					313.15 K				
x_1	ρ/(g cm^3)	u/ms^{-1}	k_s/TPa^{-1}	k_s^E/TPa^{-1}	x_1	ρ/(g cm^{-3})	u/ms^{-1}	k_s/TPa^{-1}	k_s^E/TPa^{-1}
Methyl Ethyl Ketone + Benzene									
0.0000	0.868 51	1276	707		0.0000	0.857 99	1230	770	
0.1126	0.860 43	1269	722	−9	0.1126	0.850 15	1226	783	−14
0.2249	0.852 36	1260	739	−16	0.2249	0.842 23	1217	802	−22
0.3113	0.846 12	1253	753	−20	0.3113	0.836 09	1210	817	−27
0.4163	0.838 41	1244	771	−25	0.4163	0.828 59	1201	837	−32
0.5232	0.830 42	1234	791	−27	0.5232	0.820 84	1191	859	−35
0.6045	0.824 23	1225	809	−26	0.6045	0.814 96	1182	878	−35
0.7148	0.815 65	1212	835	−22	0.7148	0.806 33	1169	908	−30
0.8265	0.806 92	1197	865	−15	0.8265	0.797 71	1154	941	−22
1.0000	0.794 39	1173	915		1.0000	0.784 41	1128	1002	
Methyl Ethyl Ketone + Toluene									
0.0000	0.857 70	1291	699		0.0000	0.848 44	1248	757	
0.1367	0.850 93	1281	716	−9	0.1367	0.841 66	1240	773	−14
0.2214	0.846 43	1274	728	−13	0.2214	0.837 09	1233	786	−19
0.3435	0.839 68	1263	746	−19	0.3435	0.830 33	1222	807	−25
0.4318	0.834 42	1255	761	−23	0.4318	0.825 15	1214	822	−31
0.5406	0.827 67	1243	782	−25	0.5406	0.818 47	1202	846	−33
0.6267	0.821 94	1232	801	−25	0.6267	0.812 82	1191	867	−34
0.7122	0.816 06	1219	824	−21	0.7122	0.806 86	1178	893	−30
0.8178	0.808 15	1203	855	−15	0.8178	0.799 06	1162	927	−24
1.0000	0.794 39	1173	915		0.0000	0.784 41	1128	1002	
Methyl Ethyl Ketone + Chlorobenzene									
0.0000	1.095 50	1245	589		0.0000	1.084 68	1206	634	
0.1068	1.067 31	1238	611	−9	0.1068	1.057 11	1197	660	−9
0.1972	1.043 19	1235	629	−19	0.1972	1.033 14	1194	679	−21
0.3202	1.009 03	1229	656	−28	0.3202	0.999 33	1188	709	−33
0.4174	0.981 14	1224	680	−35	0.4174	0.971 49	1183	736	−41
0.5576	0.939 45	1218	718	−41	0.5576	0.929 81	1177	776	−52
0.6242	0.919 87	1213	740	−43	0.6242	0.909 51	1172	801	−52
0.7288	0.885 76	1201	782	−37	0.7288	0.876 23	1160	848	−45
0.8531	0.844 70	1187	840	−22	0.8531	0.835 38	1146	911	−31
1.0000	0.794 39	1173	915		1.0000	0.784 41	1128	1002	
Methyl Ethyl Ketone + Bromobenzene									
0.0000	1.481 50	1146	514		0.0000	1.468 03	1109	554	
0.1221	1.409 17	1144	542	−14	0.1221	1.396 87	1104	587	−15
0.1917	1.367 04	1141	562	−20	0.1917	1.354 69	1101	609	−21
0.2946	1.303 23	1139	591	−30	0.2946	1.291 03	1099	641	−32
0.4069	1.230 75	1142	623	−41	0.4069	1.218 99	1102	676	−44
0.5335	1.145 12	1146	665	−48	0.5335	1.134 02	1106	721	−55
0.6748	1.044 72	1152	721	−50	0.6748	1.034 19	1112	782	−59
0.8126	0.941 60	1155	796	−35	0.8126	0.931 72	1115	863	−44
1.0000	0.794 39	1173	915		1.0000	0.784 41	1128	1002	
Methyl Ethyl Ketone + Nitrobenzene									
0.0000	1.193 41	1456	395		0.0000	1.183 52	1408	426	
0.0986	1.159 09	1426	424	−19	0.0986	1.150 66	1386	452	−24
0.2098	1.120 39	1388	463	−35	0.2098	1.111 94	1348	494	−44
0.3268	1.077 87	1354	506	−50	0.3268	1.069 04	1314	542	−63
0.4182	1.043 39	1336	537	−66	0.4182	1.034 46	1296	575	−79
0.5212	1.003 11	1312	579	−77	0.5212	0.994 51	1272	621	−92
0.6458	0.952 65	1277	642	−80	0.6458	0.943 13	1239	691	−94
0.7512	0.907 51	1241	715	−63	0.7512	0.898 94	1201	771	−77
0.8119	0.880 61	1223	759	−52	0.8119	0.871 93	1183	819	−66
1.0000	0.794 39	1173	915		1.0000	0.784 41	1128	1002	

case of mixtures the data were obtained from excess volumes (*1*) by using the relation

$$\rho = \frac{x_1M_1 + x_2M_2}{x_1V_1 + x_2V_2 + V^E} \quad (1)$$

Density values obtained from both methods were accurate to $\pm 5 \times 10^{-5}$ g cm^{-3}. All the analytical grade chemicals were further purified by the methods described earlier (*1–3*). The purity of the samples was checked by comparing the values of density, boiling point, and refractive index with those reported in the literature (*4*).

Results

The isentropic compressibilities were calculated indirectly by using the ultrasonic velocity, u, and density, ρ, with the relation

$$k_s = 1/u^2\rho \quad (2)$$

The values of k_s were accurate to ± 2 TPa^{-1}. The excess isentropic compressibilities were computed by using the equation

$$k_s^E = k_s^{mix} - k_s^{id} \quad (3)$$

where k_s^{mix} and k_s^{id} are isentropic compressibilities of the actual mixture and ideal mixture. The values of k_s^{id} were obtained by using the equation (*5*, *6*)

$$k_s^{id} = \sum\phi_i[k_{s,i} + TV_i\alpha_i^2/C_{p,i}] - T(\sum x_iV_i)(\sum\phi_i\alpha_i^2)/(\sum x_iC_{p,i}) \quad (4)$$

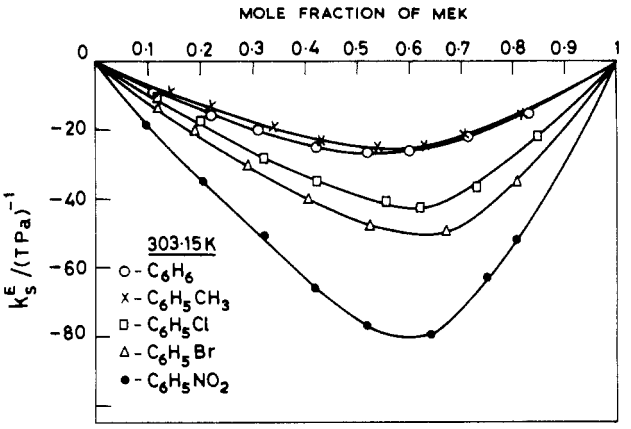

Figure 1. Mole fraction vs. excess isentropic compressibility at 303.15 K.

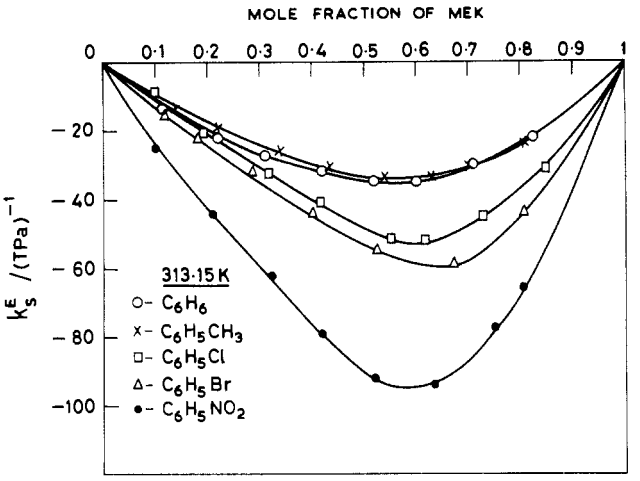

Figure 2. Mole fraction vs. excess isentropic compressibility at 313.15 K.

where ϕ_i, $k_{s,i}$, V_i, α_i, and $C_{p,i}$ are volume fraction calculated on the basis of ideal density, isentropic compressibility, molar volume, thermal expansivity, and heat capacity of component i, respectively. The values of these parameters are given in Table I. The values of ultrasonic velocity, density, isentropic compressibility, and excess isentropic compressibility at both the temperatures are given in Table II. The graphs of k_s^E vs. composition are also presented in Figures 1 and 2. The dependence of k_s^E on mole fraction has been represented by an empirical equation of the form

$$k_s^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (5)$$

The parameters a_0, a_1, and a_2 are obtained by the method of least squares and are given in Table III along with the standard deviation $\sigma(k_s^E)$.

Discussion

Excess isentropic compressibilities are negative for all the systems over the entire range of composition. The results are attributed to the induced dipole and dipole interaction between π electrons of the benzene ring and carbonyl group of methyl ethyl ketone in the systems methyl ethyl ketone with benzene and toluene. In addition to the above effect a dipole–dipole interaction between the groups $\rangle$CO with –Cl, –Br, and $-NO_2$ may be responsible for the large negative values of k_s^E in the other three systems. The algebraic values of k_s^E fall in the order benzene ≈ toluene < chlorobenzene < bromobenzene < nitrobenzene, at both temperatures.

This order is parallel to the dielectric constant values of the noncommon components. A similar trend is also observed with respect to excess volumes, reported in our earlier paper (*1*). The two properties are compared in Table IV and a remarkable similarity has been observed in their behavior with respect to these systems and at both temperatures. A negative temperature coefficient is observed in all the systems.

Table III. Values of the Parameters in Eq 5 and Standard Deviation $\sigma(k_s^E)$

methyl ethyl ketone +	T/K	a_0/ TPa^{-1}	a_1/ TPa^{-1}	a_2/ TPa^{-1}	$\sigma(k_s^E)$/ TPa^{-1}
benzene	303.15	−109.8	−9.4	25.5	1.2
	313.15	−137.6	−10.6	0.6	1.2
toluene	303.15	−99.1	−15.2	11.6	0.8
	313.15	−137.5	−26.9	17.4	1.4
chlorobenzene	303.15	−163.7	−46.8	59.1	1.9
	313.15	−197.2	−86.7	56.3	1.7
bromobenzene	303.15	−194.6	−65.6	46.3	2.6
	313.15	−222.7	−99.1	23.5	2.9
nitrobenzene	303.15	−302.4	−92.8	67.6	3.9
	313.15	−363.8	−110.9	58.8	4.1

Table IV. Comparison of the Maximum Values of Excess Isentropic Compressibilities k_s^E and Excess Volumes V^E, at 303.15 and 313.15 K

	303.15 K		313.15 K	
methyl ethyl ketone +	k_s^E/TPa^{-1}	V^E/ (cm^3 mol^{-1})	k_s^E/TPa^{-1}	V^E/ (cm^3 mol^{-1})
benzene	−27	−0.161	−35	−0.168
toluene	−26	−0.256	−34	−0.245
chlorobenzene	−43	−0.362	−52	−0.376
bromobenzene	−50	−0.405	−59	−0.419
nitrobenzene	−80	−0.601	−94	−0.644

Registry No. MEK, 78-93-3; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; C_6H_5Cl, 108-90-7; C_6H_5Br, 108-86-1; $C_6H_5NO_2$, 98-95-3.

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