1012 *J. Chem. Eng. Data* **1996,** *41,* 1012−1014

Densities, Speeds of Sound, and Viscosities of Mixtures of Oxolane with Chloroethanes and Chloroethenes

Abburi Krishnaiah* and Korikani N. Surendranath

Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India

---

Data on density, speed of sound, and viscosity for mixtures of oxolane with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene at 303.15 K are reported. The results are used to derive isentropic compressibility (k_s), deviations in isentropic compressibility (Δk_s), and deviations in viscosity ($\Delta \ln \eta$). Values of Δk_s are positive in mixtures of oxolane with 1,2-dichloroethane and tetrachloroethene and negative in the systems oxolane + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, and + trichloroethene. All the systems exhibit positive deviation in viscosity. The results are interpreted in terms of electron−donor−acceptor interactions between unlike molecules.

Introduction

The present work forms a part of our investigation on organic solvent mixtures containing cyclic mono- and diethers in order to characterize the behavior of the ether group with respect to chloro-substituted alkanes and alkenes. We have reported excess enthalpies of oxolane and 1,4-dioxane (Surendranath et al., 1992) and excess volumes of oxolane (Surendranath et al., 1992) and of 1,4-dioxane (Krishnaiah et al., 1994) with chlorinated ethanes and ethenes. In this work we report density data computed from excess volumes, experimental data on speed of sound and viscosity for mixtures of oxolane with 1,2-dichloro-, 1,1,1-trichloro-, and 1,1,2,2-tetrachloroethanes and trichloro- and tetrachloroethenes at 303.15 K and atmospheric pressure. Isentropic compressibilities, deviations in isentropic compressibility, and viscosity are calculated from experimental data. The behavior of these mixtures are discussed on the basis of the deviations in isentropic compressibility and viscosity. The primary aim of the present investigation is to characterize the type and magnitude of molecular interactions in these mixtures. The secondary aspect is to study the effect of number of chlorine atoms and unsaturation in the ethane molecule on deviations in isentropic compressibility and viscosity of these mixtures.

Experimental Section

Materials. Oxolane (BDH) was kept over sodium hydroxide for 24 h, then refluxed for three times for 10 h over sodium metal and distilled. 1,2-Dichloroethane (BDH), 1,1,1-trichloroethane (Koch-light), 1,1,2,2-tetrachloroethane (Riedel), trichloroethene (BDH), and tetrachloroethene (BDH) were purified as described by Surendranath (1989). The purity of the samples was checked by comparing the measured densities, viscosities at 303.15 K, and boiling points with those reported in the literature (Riddick et al., 1986). The measured values of density, viscosity, and boiling point are included in Table 1 along with the literature values.

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 ±0.15%. The temperature of the liquid in the interferometer cell was maintained at 303.15 ± 0.01 K.

Table 1. Densities (ρ), Viscosities (η) at 303.15 K, and Normal Boiling Points (T_b) of Pure Components and Comparison with Literature Data (Riddick et al., 1986; Timmermans, 1962)

	ρ/kg m^{-3}		η/mP$_a$ s		T_b/K	
component	exptl	lit.	exptl	lit.	exptl	lit.
oxolane	879.14	879.10	0.4656	0.550[a]	339.05	339.15
1,2-dichloroethane	1238.28	1238.31	0.7295	0.730	356.70	356.63
1,1,1-trichloroethane	1320.92	1320.96	0.7243	0.725	347.00	347.15
1,1,2,2-tetrachloroethane	1578.57	1578.60	1.4554	1.456	419.25	419.35
trichloroethene	1451.34	1451.40	0.5230	0.532[b]	360.40	360.34
tetrachloroethene	1606.36	1606.40	0.7976	0.798	394.45	394.35

[a] At 293.15 K. [b] 298.15 K.

Viscosity. Viscosities of pure liquids and liquid mixtures were measured using a suspended-level Ubbelohde viscometer. The viscometer was calibrated at 303.15 ± 0.01 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 $k = \eta_w/\rho_w t_w$. An average of 10 measurements that do not differ by more than 0.0005 cm^2 s^{-2} was taken as the k value. An electronic stopwatch capable of measuring time to ± 0.01 s was used for flow time measurement. Capillary-end kinetic energy corrections were applied and found to be negligible. The estimated error in viscosity is ±0.0005 mPa s. The performance of the viscometer was ascertained by measuring and comparing the viscosity of pure components with those reported in the literature (Riddick et al., 1986; Timmermans, 1962).

Density. Densities of pure components were measured using a bicapillay pycnometer. In case of mixtures densities were computed from excess volume (V^E) data reported earlier (Surendranath et al., 1992) using the relation

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

where x_1 and x_2 are mole fractions, M_1 and M_2 are molecular weights, and V_1 and V_2 are molar volumes of oxolane (1) and chloroethane or ethene (2). The values of density are reproducible to ±5 parts in 10^5.

Results and Discussion

Data on density (ρ) and speed of sound (U) are used to compute isentropic compressibilities (k_s) and deviations in

---

* To whom correspondence should be addressed.

S0021-9568(95)00304-9 CCC: $12.00 © 1996 American Chemical Society

Table 2. Mole Fraction (x_1), Volume Fraction (ϕ_1), Density (ρ), Speed of Sound (U), Isentropic Compressibility (k_s), and Viscosity (η) at 303.15 K

x_1	ϕ_1	ρ/kg m^{-3}	U/m s^{-1}	k_s/TPa^{-1}	η/mPa s
Oxolane (1) + 1,2-Dichloroethane (2)					
0.0000	0.0000	1238.28	1173.3	586.6	0.7295
0.0815	0.0835	1207.73	1175.4	599.3	0.7038
0.1436	0.1468	1184.66	1177.8	608.5	0.6852
0.2414	0.2462	1148.83	1181.7	623.3	0.6571
0.3055	0.3110	1125.56	1184.7	633.0	0.6394
0.4137	0.4200	1086.61	1191.0	648.8	0.6105
0.5015	0.5080	1055.31	1197.6	660.7	0.5879
0.6095	0.6157	1016.92	1206.9	675.1	0.5606
0.7289	0.7340	974.70	1281.6	690.9	0.5307
0.8142	0.8181	944.65	1228.5	701.4	0.5097
0.9176	0.9195	908.20	1242.0	713.8	0.4850
1.0000	1.0000	879.14	1253.7	723.7	0.4656
Oxolane (1) + 1,1,1-Trichloroethane (2)					
0.0000	0.0000	1320.92	942.6	852.1	0.7243
0.0731	0.0602	1295.97	962.8	832.4	0.7289
0.1213	0.1008	1278.81	975.3	822.1	0.7262
0.2262	0.1919	1239.93	1002.9	801.8	0.7112
0.3894	0.3412	1174.90	1047.0	776.8	0.6687
0.4716	0.4202	1140.13	1069.5	766.8	0.6424
0.5677	0.5161	1097.67	1097.1	756.9	0.6104
0.6475	0.5987	1060.83	1121.1	750.0	0.5834
0.7415	0.6997	1015.51	1151.7	742.4	0.5513
0.8139	0.7803	979.00	1177.5	736.7	0.5271
0.8660	0.8400	952.02	1197.3	732.7	0.5100
1.0000	1.0000	879.14	1253.7	723.7	0.4656
Oxolane (1) + 1,1,2,2-Tetrachloroethane (2)					
0.0000	0.0000	1578.57	1133.1	493.4	1.4554
0.0912	0.0718	1530.58	1135.1	506.5	1.4033
0.1846	0.1487	1479.00	1139.4	520.8	1.3473
0.2753	0.2266	1426.14	1143.3	536.4	1.2832
0.3389	0.2834	1387.61	1148.1	546.7	1.2301
0.4617	0.3982	1308.45	1156.5	571.4	1.1077
0.5426	0.4778	1252.94	1164.3	588.8	1.0145
0.6763	0.6171	1154.79	1178.7	623.3	0.8466
0.7791	0.7312	1073.18	1195.2	652.3	0.7155
0.8994	0.8734	970.82	1222.2	689.6	0.5718
0.9513	0.9378	924.29	1236.9	707.2	0.5150
1.0000	1.0000	879.14	1253.7	723.7	0.4656
Oxolane (1) + Trichloroethene (2)					
0.0000	0.0000	1451.35	1013.7	670.5	0.5230
0.0614	0.0560	1420.76	1023.0	672.6	0.5484
0.1057	0.0967	1398.18	1029.6	674.3	0.5631
0.2281	0.2112	1334.34	1050.6	679.0	0.5879
0.3529	0.3307	1266.90	1073.7	684.7	0.5932
0.4929	0.4683	1188.35	1103.1	691.6	0.5817
0.5166	0.4919	1174.72	1108.5	692.8	0.5781
0.6400	0.6170	1102.39	1138.5	699.8	0.5560
0.7608	0.7424	1029.63	1171.5	707.7	0.5289
0.8813	0.8706	954.77	1209.6	715.8	0.4983
0.9421	0.9365	916.30	1231.2	720.0	0.4822
1.0000	1.0000	879.14	1253.7	723.7	0.4656
Oxolane (1) + Tetrachloroethene (2)					
0.0000	0.0000	1606.36	1027.8	589.3	0.7976
0.0667	0.0537	1567.70	1033.5	597.2	0.7821
0.1429	0.1170	1522.13	1041.0	606.2	0.7630
0.2457	0.2056	1458.11	1052.7	618.9	0.7362
0.3692	0.3174	1377.27	1069.8	634.4	0.7008
0.4384	0.3828	1329.92	1081.2	643.2	0.6795
0.5309	0.4735	1264.08	1098.9	655.1	0.6487
0.6897	0.6385	1143.99	1136.7	676.5	0.5914
0.7605	0.7161	1087.29	1157.7	686.2	0.5641
0.8435	0.8107	1018.17	1185.9	698.4	0.5312
0.9213	0.9029	950.54	1216.8	710.5	0.4988
1.0000	1.0000	879.14	1253.7	723.7	0.4656

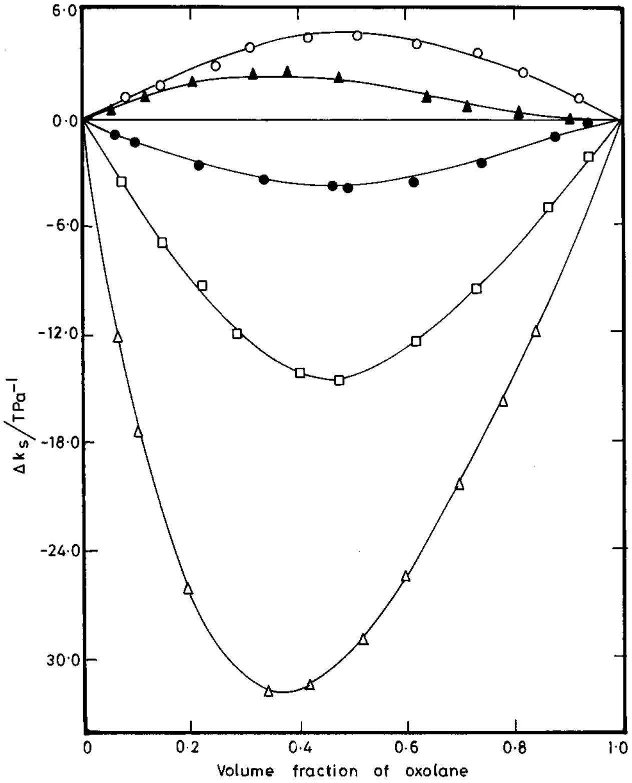

Figure 1. Deviations in isentropic compressibilities (Δk_s) for oxolane + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (△), + 1,1,2,2-tetrachloroethane (□), + trichloroethene (●), and + tetrachloroethene (▲) at 303.15 K.

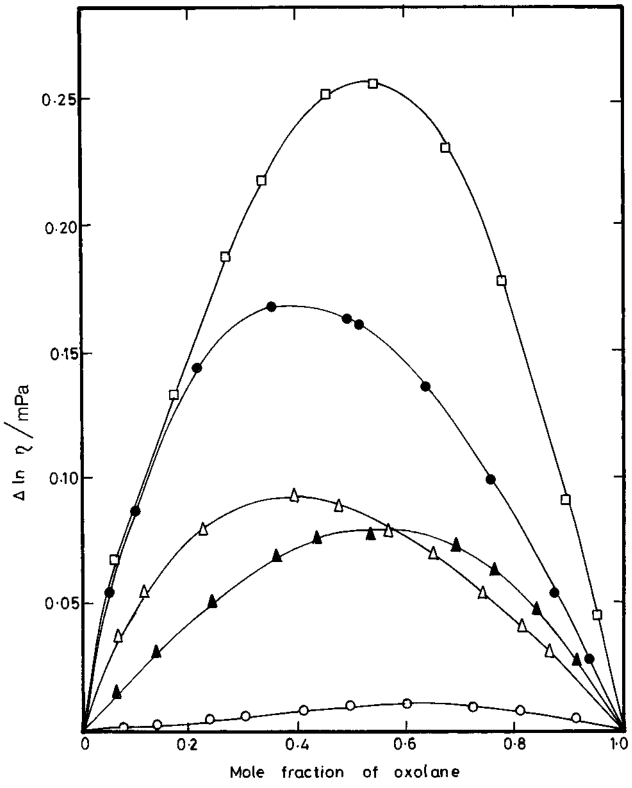

Figure 2. Deviations in viscosities ($\Delta \ln \eta$) for oxolane + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (△), + 1,1,2,2-tetrachloroethane (□), + trichloroethene (●), and + tetrachloroethene (▲) at 303.15 K.

isentropic compressibility (Δk_s) using the equations

$$k_s = 1/U^2\rho \tag{2}$$

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

where k_s, $k_{s,1}$, and $k_{s,2}$ are the isentropic compressibilities of the mixture and pure components 1 and 2, respectively. ϕ_1 and ϕ_2 are the ideal volume fractions of components 1 and 2.

Table 3. Values of the Parameters of Eqs 5 and 6 along with the Standard Deviations

system	a_0/TPa^{-1}	a_1/TPa^{-1}	a_2/TPa^{-1}	$\sigma(\Delta k_s)$/TPa^{-1}	b_0/mPa s	b_1/mPa s	b_2/mPa s	$\sigma(\Delta \ln \eta)$/mPa s
oxolane + 1,2-dichloroethane	18.2	0.5	−3.9	0.2	0.0371	0.0240	−0.0101	0.0002
oxolane + 1,1,1-trichloroethane	−115.8	68.1	−36.9	0.5	0.3440	−0.1702	0.1033	0.0005
oxolane + 1,1,2,2-tetrachloroethane	−56.5	7.0	16.0	0.4	1.0294	0.1120	−0.1843	0.0001
oxolane + trichloroethene	−15.4	5.3	5.8	0.2	0.6492	−0.2482	0.1070	0.0003
oxolane + tetrachloroethene	8.4	−9.0	−4.2	0.1	0.3140	0.0632	0.0012	0.0003

Deviations in viscosity are estimated using the relation

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

where η_{mix}, η_1, and η_2 are the viscosities of the mixture and pure components 1 and 2, respectively. Data on density, speed of sound, isentropic compressibility, and viscosity are included in Table 2. The dependence of Δk_s on volume fraction and of $\Delta \ln \eta$ on mole fraction are shown in Figures 1 and 2, respectively.

The variation of Δk_s and $\Delta \ln \eta$ with compositions are correlated by the polynomial equations of the form

$$\Delta k_s = \phi_1\phi_2[a_0 + a_1(\phi_1 - \phi_2) + a_2(\phi_1 - \phi_2)^2] \tag{5}$$

$$\Delta \ln \eta = x_1x_2[b_0 + b_1(x_1 - x_2) + b_2(x_1 - x_2)^2] \tag{6}$$

The values of the parameters a_i and b_i are obtained by a least-squares method and are included in Table 3 along with the standard deviation, σ.

The deviations in isentropic compressibility are negative in mixtures of oxolane with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethene and positive in mixtures containing 1,2-dichloroethane and tetrachloroethene as noncommon components. Deviations in viscosity are positive in all the systems. These observed deviations are mainly attributed to the dominant nature of specific n−σ type interaction between oxygen (n-donor) and chloro (σ-acceptor) over the dispersion forces in all the systems except in mixtures consisting of 1,2-dichloroethane and tetrachloroethene. The existence of electron−donor−acceptor interaction between a cyclic ether and 1,1,1-trichloroethane is reported by Inglese et al. (1981). In mixtures containing chloroethanes as noncommon components, the deviations in compressibility decrease except in the case of 1,1,1-trichloroethane and the deviations in viscosity increase with increase in number of chlorine atoms on ethane molecule indicating that the strength of interaction increases with increase in the number of chlorine atoms in ethane molecule. On the other hand, in mixtures containing chloroethenes deviations in compressibility increase and deviations in viscosity decrease as the number of chlorine atoms increases. This may be attributed to a partial saturation of the electron accepting capacity of the chlorine atoms by the π-electrons of the alkene bond.

Literature Cited

Inglese, A.; Castagnolo, M.; Dell'atti, A. Excess Heat Capacities and Excess Volumes of Binary Liquid Mixtures of 1,1,1-Trichloroethane with Cyclic Ethers at 298.15 K. *Thermochim. Acta* **1981**, *47*, 165−177.

Krishnaiah, A.; Surendranath, K. N.; Viswanath, D. S. Excess Volumes and Viscosities of 1,4-Dioxane + Chlorinated Ethanes or + Chlorinated Ethenes at 303.15 K. *J. Chem. Eng. Data* **1994**, *39*, 756−758.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents—Physical Properties and Methods of Purification*; Wiley: New York, 1986.

Surendranath, K. N. Ph.D. Thesis, S. V. University, Tirupati, India, 1989.

Surendranath, K. N.; Chandrasekhar, A. C. H.; Krishnaiah, A. *Phys. Chem. Liq.* **1992**, *24*, 255−259.

Surendranath, K. N.; Krishnaiah, A.; Ramakrishna, M. *Fluid Phase Equilib.* **1992**, *71*, 169−176.

Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1962.

Received for review November 30, 1995. Revised manuscript received April 2, 1996. Accepted May 1, 1996.⊗

JE950304E

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.