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Probing the intermolecular interactions in the binary liquid mixtures of o-chlorophenol with alkoxyethanols through ultrasonic, transport and FT-IR spectroscopic studies at different temperatures

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ABSTRACT

The densities, viscosities and ultrasonic speeds of pure liquids o-chlorophenol (OCP), 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE), 2-butoxyethanol (BOE) and their binary mixtures containing OCP as a common component have been measured at 303.15, 308.15, 313.15 and 318.15 K as a function of composition of OCP. From these results, molar volume, adiabatic compressibility, intermolecular free length, and acoustic impedance are computed and their excess properties along with excess ultrasonic velocity, deviation in adiabatic compressibility, deviation in viscosity, and excess Gibb's free energy are fitted to Redlich–Kister type equation. The experimental data of viscosity is also used to test the applicability of empirical relations of Grunberg–Nissan, Katti–Chaudhri, Heric–Brewer, Hind et al. and Mc Allister four body models for the systems studied. Also, an attempt is made to use partial molar volumes and FT-IR spectral analysis of these binary mixtures to understand the interactions present and to correlate them with thermodynamic findings. The study reveals that the strength of interaction of OCP with MOE, EOE and BOE binary mixtures at all the temperatures follows the order MOE < EOE < BOE.

1. Introduction

Physico-chemical and thermodynamic investigations play an important role in understanding the nature and extent of the patterns of molecular aggregation that exist in binary liquid mixtures due to their sensitivities to variations in composition and the molecular structure of the pure components. When two or more solvent molecules are associated with one another to form a liquid mixture, it brings about a marked effect on the properties of the resulting system and differences in the intermolecular interactions of the solvents. Thermodynamic properties of fluids are required to design heat transfer machinery and chemical processes in natural gas, aerospace, environmental and other related industries. The quality and efficiency of chemical processing, including shrinking the time lines for industrial processes to maximize yields and minimize unwanted products, can be greatly enhanced through theoretical studies [1]. Studies involving density, viscosity and ultrasonic velocities of pure liquids and binary mixtures are essentially required to probe intermolecular interactions. The nature and degree of molecular interactions in different solutions depend upon the nature of the medium, the structure of the solute and also on the extent of solvation taking place in the solution. The present study is a continuation of our earlier work on molecular interactions in binary liquid mixtures of industrial importance [2–6].

From a practical point of view, alkoxyethanols are very interesting class of substances as oxygenated compounds are widely used as additives to gasoline due to their pollution-reducing and octane enhancing properties [7,8]. They have extensive use as monomers in the production of polymers and emulsion formulations. Alkoxyethanols are considered as constituted of two different functional subgroups viz., an ether subgroup (—OR), which includes an oxygen atom attached to a methylene group, and a primary alcohol subgroup (—OH). From a theoretical point of view, mixtures containing alkoxyalcohols are very important, not only because of their self association but also due to the strong intra-molecular effects which is produced by the presence of –OR and –OH groups in the same molecule [9]. In particular, the formation of the intra-molecular H-bonds leads to enhanced dipole–dipole interactions in solutions containing alkoxyethanols and alkanes relative to those present in mixtures with homomorphic alkanols [10].

A considerable amount of work has been carried out by various researchers with regard to intermolecular interactions highlighting the hydrogen bonding or dipole–dipole interactions in the binary mixtures

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Table 1
Comparison of density ρ, viscosity η and ultrasonic velocity U, of the pure liquids with literature data at 303.15 K.

Compound	U_{expt} ($m \cdot s^{-1}$)	$U_{lit.}$ ($m \cdot s^{-1}$)	$\rho_{expt.}$ ($kg \cdot m^{-3}$)	$\rho_{lit.}$ ($kg \cdot m^{-3}$)	$\eta_{expt.}$ ($m \cdot Pa\ s$)	$\eta_{lit.}$ ($m \cdot Pa\ s$)
OCP	1381.4	1376.5[a]	1255.0	1254.6[a]	2.821	2.819[a]
MOE	1356.0	1354.0[b]	953.6	952.7[b]	1.549	1.548[b]
EOE	1316.0	1314.4[b]	919.8	918.6[b]	1.612	1.572[b]
BOE	1322.0	1321.4[b]	892.6	892.1[b]	2.404	2.403[b]

[a] [12].
[b] [13].

of alkoxyethanols + diethyl carbonate [11], +2-butanone [12], + ethyl or butyl acetates [13], +2-pyrrolidone [14], + amine [15], +1-butanol [16] etc. However, no effort appears to have been made to investigate the molecular interactions of binary mixtures containing o-chlorophenol with alkoxyethanols.

The present work is focused on the volumetric, viscometric and acoustic study of properties by measuring the densities, viscosities and ultrasonic speeds of the binary mixtures of OCP with MOE, EOE and BOE over the complete composition range at temperatures of 303.15, 308.15, 313.15 & 318.15 K and atmospheric pressure. It is also aimed to study the molecular interactions between OCP and alkoxyethanols under investigation, with special reference to hydrogen bonding interactions using the FT-IR data of these mixtures. Further, the experimental data of viscosity is used to test the applicability of empirical relations of Grunberg–Nissan, Katti–Chaudhri, Heric–Brewer, Hind et al. and Mc Allister four body models for the systems studied.

2. Experimental section

2.1. Chemicals

Ortho-chlorophenol (OCP), 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE) and 2-butoxyethanol (BOE) are purchased from Merck, S.D. Fine Chemicals Ltd., India and all the chemicals are further purified as per the standard procedures [17] until their purities exceeded 99.7% as tested by gas liquid chromatography using a flame ionisation detector with a packed column, and also by comparing experimental values of density, viscosity, and ultrasound velocity with those reported in the literature [18,19] as presented in Table 1.

2.2. Apparatus and procedures

The binary mixtures are prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1 \times 10^{-7}$ kg and stored in airtight bottles. The uncertainty on mole fraction is estimated to be 1×10^{-4}. It is ensured that the mixtures are properly mixed and the measurement of the required parameters was done within one day of preparation. The viscosity, η, of the pure liquids and liquid

Table 2
Ultrasonic velocities ($u/m\ s^{-1}$), densities ($\rho/Kg\ m^{-3}$) and viscosities ($\eta/m \cdot Pa\ s$) of binary mixtures of o-chlorophenol with alkoxyethanols at temperatures of 303.15, 308.15, 313.15, and 318.15 K.

	303.15 K			308.15 K			313.15 K			318.15 K		
x_1	$u/m \cdot s^{-1}$	$\rho/kg \cdot m^{-3}$	$\eta/m \cdot Pas$	$u/m \cdot s^{-1}$	$\rho/kg \cdot m^{-3}$	$\eta/m \cdot pas$	$u/m \cdot s^{-1}$	$\rho/kg \cdot m^{-3}$	$\eta/m \cdot Pas$	$u/m \cdot s^{-1}$	$\rho/kg \cdot m^{-3}$	$\eta/m \cdot Pas$
o-Chlorophenol(1) + 2-methoxyethnanol(2)												
0.0000	1356.0	953.60	1.549	1347.0	950.80	1.492	1337.0	946.20	1.219	1314.0	943.20	1.129
0.0797	1361.2	998.78	1.925	1346.2	996.89	1.810	1330.1	992.93	1.479	1299.0	990.17	1.340
0.1630	1364.4	1043.56	2.342	1348.3	1042.49	2.126	1331.1	1039.11	1.762	1301.9	1036.52	1.572
0.2503	1367.5	1087.26	2.780	1350.3	1086.84	2.456	1332.8	1083.95	2.055	1304.4	1081.42	1.805
0.3418	1370.4	1128.85	3.204	1352.2	1128.87	2.776	1334.3	1126.32	2.335	1306.5	1123.73	2.030
0.4379	1373.2	1167.24	3.560	1353.8	1167.39	3.040	1335.4	1164.97	2.586	1308.3	1162.14	2.227
0.5388	1375.9	1200.97	3.811	1355.1	1200.85	3.212	1336.2	1198.31	2.765	1309.5	1195.03	2.370
0.6451	1378.2	1228.54	3.884	1356.2	1227.66	3.268	1336.5	1224.65	2.842	1310.1	1220.66	2.445
0.7570	1380.3	1248.06	3.735	1356.9	1245.83	3.166	1336.3	1241.97	2.785	1310.0	1236.97	2.419
0.8752	1382.0	1257.59	3.376	1357.2	1253.34	2.898	1335.5	1248.15	2.593	1309.0	1241.82	2.282
1.0000	1381.4	1255.00	2.821	1360.0	1248.00	2.491	1344.0	1241.00	2.259	1325.2	1233.00	2.038
o-Chlorophenol(1) + 2-ethoxyethnanol(2)												
0.0000	1316.0	919.80	1.612	1299.8	915.57	1.479	1274.0	911.00	1.341	1250.2	907.60	1.252
0.0961	1327.4	968.17	2.185	1310.4	964.65	1.948	1284.7	961.73	1.725	1261.0	959.74	1.567
0.1930	1337.8	1014.84	2.825	1320.1	1011.89	2.453	1294.7	1010.41	2.133	1271.2	1009.58	1.887
0.2907	1347.3	1059.20	3.450	1328.8	1056.67	2.949	1304.0	1056.30	2.524	1280.7	1056.34	2.190
0.3894	1355.7	1100.72	3.996	1336.6	1098.40	3.365	1312.4	1098.76	2.868	1289.4	1099.27	2.449
0.4889	1363.0	1138.67	4.376	1343.3	1136.33	3.660	1320.0	1136.96	3.106	1297.5	1135.20	2.630
0.5893	1369.2	1172.48	4.530	1349.0	1169.85	3.784	1326.7	1170.20	3.215	1304.7	1169.60	2.724
0.6906	1374.2	1201.56	4.410	1353.5	1198.32	3.706	1332.5	1197.82	3.170	1311.2	1196.75	2.702
0.7928	1377.9	1225.33	4.050	1356.9	1221.17	3.430	1337.4	1219.17	2.974	1316.8	1216.41	2.570
0.8959	1380.3	1243.28	3.486	1359.1	1237.88	3.005	1341.2	1233.71	2.664	1321.4	1228.64	2.341
1.0000	1381.4	1255.00	2.821	1360.0	1248.00	2.491	1344.0	1241.00	2.259	1325.2	1233.00	2.038
o-Chlorophenol(1) + 2-butoxyethnanol(2)												
0.0000	1322.0	892.60	2.404	1276.0	887.60	2.290	1269.0	883.20	2.120	1244.0	879.90	1.938
0.1256	1332.1	940.17	3.306	1288.1	936.68	2.934	1280.1	933.88	2.604	1255.2	931.63	2.282
0.2442	1341.0	985.04	4.125	1299.1	982.67	3.490	1290.2	981.02	2.992	1265.5	979.44	2.554
0.3565	1348.7	1027.28	4.745	1309.2	1025.61	3.876	1299.3	1024.68	3.267	1275.1	1023.41	2.738
0.4628	1355.6	1066.88	5.080	1318.4	1065.50	4.084	1307.6	1064.84	3.404	1283.9	1063.53	2.820
0.5638	1361.5	1103.98	5.130	1326.8	1102.51	4.093	1315.2	1101.70	3.405	1292.1	1100.00	2.833
0.6597	1366.7	1138.62	4.920	1334.6	1136.69	3.935	1322.1	1135.33	3.298	1299.7	1132.91	2.754
0.7510	1371.2	1170.95	4.500	1341.8	1168.20	3.654	1328.3	1165.91	3.106	1306.8	1162.49	2.624
0.8379	1375.1	1201.03	3.975	1348.3	1197.14	3.302	1334.0	1193.59	2.847	1313.4	1188.87	2.450
0.9208	1378.5	1229.00	3.396	1354.4	1223.69	2.895	1339.2	1218.55	2.563	1319.5	1212.30	2.254
1.0000	1381.4	1255.00	2.821	1360.0	1248.00	2.491	1344.0	1241.00	2.259	1325.2	1233.00	2.038

Standard uncertainties u are $u(x_1) = 0.0001$, $u(T) = 0.01$ K, and the combined expanded uncertainties, U_c, $U_c(\rho) = 0.2\ kg\ m^{-3}$, $U_c(\eta) = 0.005$ mPa·s and $U_c(U) = 0.8\ m\ s^{-1}$ (level of confidence = 0.95).