

## Isentropic Compressibility for Binary Mixtures of Propylene Carbonate with Benzene and Substituted Benzene

D. S. Wankhede\*

School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, Maharashtra State, India. \*E-mail: dswchem@yahoo.co.in  
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**ABSTRACT.** Ultrasonic velocities ( $u$ ) for binary mixtures of propylene carbonate (PC) (1) with benzene and substituted benzenes (2) viz. benzene, ethylbenzene, o-xylene and p-xylene have been measured at 288.15-308.15 K over the entire range of composition. The experimental values of ultrasonic velocities ( $u$ ) have been utilized to calculate isentropic compressibility ( $K_s$ ), intermolecular free length ( $L_f$ ), acoustic impedance ( $Z$ ).

**Key words:** Ultrasonic velocities, isentropic compressibility, propylene carbonate

### INTRODUCTION

Ultrasonic techniques have been applied for long years to get information concerning molecular interaction. The review of literature on acoustical studies of solutions reveals that ultrasonic measurements are used to estimate the different elastic properties of the molecule from which the type of molecular interactions can be very well understood. Ultrasonic velocity has proved to be useful in understanding the physico-chemical behaviour of the particular system. Ultrasonic velocities have been very widely used to study binary liquid mixtures.<sup>1</sup>

The present paper is a part of our ongoing research on thermodynamic properties of liquid-liquid mixtures.<sup>2-7</sup> This paper includes ultrasonic velocities of binary mixtures of PC (1) with benzene, ethylbenzene, o-xylene and p-xylene at 288.15-308.15 K over the entire range of mole fractions. The experimental values of ultrasonic velocities along with densities<sup>6</sup> are used to calculate the values of isentropic compressibility ( $K_s$ ), intermolecular free length ( $L_f$ ), acoustic impedance ( $Z$ ). The variation of these parameters with mole fraction is used to interpret the intermolecular interactions present amongst the liquid components.

PC is an aprotic solvent and behaves as a normal polar liquid with dipole-dipole interactions, but with little or no specific associations.<sup>8</sup> The aromatic hydrocarbons viz. benzene, ethylbenzene, and xylenes are non-polar compounds with no measurable dipole moments. Thus they involve weak intermolecular interactions. The choice of these solvents was done because of their opposite nature of polarity and their wide range of applicability.

### EXPERIMENTAL

#### Chemicals

PC (Merck, >99%) was refluxed over anhydrous calcium carbonate and distilled at atmospheric pressure.<sup>9</sup> Benzene, ethylbenzene, o-xylene and p-xylene (all of S. D. Fine chem., Pvt. Ltd.) were distilled at atmospheric pressure. All the liquids were double distilled. The middle fraction collected of all the liquids was stored over 4Å molecular sieves.

#### Procedure

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles in order to minimize the evaporation losses. All measurements of mass were performed on a Mettler one pan balance (E-Mettler, Zurich) which can be read up to the fifth decimal place with an accuracy of  $\pm 0.05$  mg.

The ultrasonic velocities were measured at 1 MHz with a single crystal variable path interferometer (F-81 Mittal Enterprises, New Delhi) and the accuracy of ultrasonic measurement was  $\pm 0.1\%$ . For all the measurements, the temperature was controlled by using an ultra thermostat Julabo F-25 (made in Germany) which has an accuracy of  $\pm 0.02$  °C.

### RESULTS AND DISCUSSION

The compressibility ( $K_s$ ) is the ease with which a system can be compressed. Larger the compressibility value, larger the system can further be compressed, and also denotes that more space is available between the compo-

**Table 1.** Values of ultrasonic velocities ( $u$ ), isentropic compressibilities ( $K_s$ ), acoustic impedance ( $Z$ ), and intermolecular free length ( $L_f$ ) for the binary mixtures of PC (1)+benzene (2) at 288.15-308.15 K

$x_1$	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	
T = 288.15 K					T = 293.15 K				
0.0000	1349.2	621.60	1192.38	0.5035	1322.0	651.26	1161.48	0.5201	
0.0191	1351.6	614.94	1203.14	0.5008	1324.2	644.36	1171.97	0.5173	
0.0416	1354.4	607.29	1215.78	0.4976	1327.4	635.81	1184.87	0.5139	
0.0585	1356.5	601.65	1225.29	0.4953	1330.1	629.22	1194.84	0.5112	
0.0771	1358.8	595.54	1235.76	0.4928	1332.2	622.91	1205.06	0.5087	
0.1030	1362.1	587.11	1250.46	0.4893	1336.1	613.39	1220.18	0.5048	
0.1982	1373.9	557.94	1304.53	0.4770	1350.6	580.11	1276.33	0.4909	
0.2949	1386.0	530.46	1360.14	0.4651	1364.7	549.55	1333.39	0.4778	
0.3972	1398.7	503.69	1419.43	0.4532	1379.1	520.22	1393.85	0.4648	
0.4938	1410.8	480.20	1476.08	0.4425	1392.2	495.04	1450.97	0.4535	
0.5987	1423.9	456.58	1538.15	0.4315	1405.9	470.12	1513.00	0.4419	
0.7002	1436.5	435.44	1598.68	0.4214	1418.5	448.24	1572.76	0.4315	
0.7907	1447.8	417.79	1653.23	0.4127	1429.2	430.36	1625.84	0.4228	
0.9024	1461.7	397.49	1721.12	0.4026	1441.9	410.08	1691.20	0.4127	
1.0000	1478.4	378.54	1786.90	0.3929	1459.3	390.22	1756.09	0.4026	
T = 298.15 K					T = 303.15 K				
0.0000	1298.8	678.62	1134.57	0.5358	1278.0	705.19	1109.60	0.5512	
0.0191	1301.7	670.56	1145.65	0.5326	1280.9	696.69	1120.59	0.5478	
0.0416	1305.0	661.41	1158.57	0.5290	1284.3	686.87	1133.60	0.5440	
0.0585	1307.6	654.54	1168.39	0.5262	1286.9	679.60	1143.42	0.5411	
0.0771	1310.3	647.27	1179.08	0.5233	1289.7	671.79	1154.19	0.5380	
0.1030	1314.2	637.23	1194.10	0.5192	1293.5	661.27	1169.11	0.5337	
0.1982	1328.2	602.64	1249.34	0.5049	1307.7	624.56	1224.38	0.5187	
0.2949	1342.2	570.60	1305.72	0.4913	1322.0	590.61	1280.77	0.5044	
0.3972	1356.9	539.63	1365.71	0.4778	1337.0	557.91	1340.61	0.4903	
0.4938	1370.5	512.94	1422.51	0.4658	1350.9	529.83	1397.13	0.4778	
0.5987	1385.1	486.36	1484.45	0.4536	1365.8	501.97	1458.58	0.4650	
0.7002	1399.0	462.81	1544.49	0.4425	1380.1	477.29	1518.11	0.4534	
0.7907	1411.3	443.34	1598.26	0.4331	1392.7	456.99	1571.22	0.4437	
0.9024	1426.1	421.26	1664.56	0.4222	1408.1	433.89	1636.78	0.4323	
1.0000	1442.3	401.41	1727.27	0.4121	1421.5	414.99	1695.18	0.4228	
T = 308.15 K									
0.0000	1251.2	739.77	1080.39	0.5696					
0.0191	1254.6	729.62	1092.43	0.5657					
0.0416	1258.6	718.50	1105.82	0.5614					
0.0585	1261.6	710.23	1116.04	0.5581					
0.0771	1264.9	701.47	1127.03	0.5547					
0.1030	1269.4	689.72	1142.17	0.5500					
0.1982	1285.7	649.00	1198.43	0.5335					
0.2949	1301.8	611.78	1255.62	0.5180					
0.3972	1318.2	576.45	1316.00	0.5028					
0.4938	1333.2	546.27	1373.09	0.4895					
0.5987	1348.9	516.70	1434.77	0.4761					
0.7002	1363.5	490.81	1494.27	0.4640					
0.7907	1376.1	469.69	1547.18	0.4539					
0.9024	1390.9	446.29	1610.97	0.4424					
1.0000	1406.0	426.11	1669.15	0.4323					

**Table 2.** Values of ultrasonic velocities ( $u$ ), isentropic compressibilities ( $K_s$ ), acoustic impedance ( $Z$ ), and intermolecular free length ( $L_f$ ) for the binary mixtures of PC (1)+ethylbenzene (2) at 288.15-308.15 K

$x_1$	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	
T = 288.15 K					T = 293.15 K				
0.0000	1360.4	620.11	1185.40	0.5028	1339.2	642.98	1161.33	0.5168	
0.0294	1362.5	610.03	1203.12	0.4987	1341.3	632.48	1178.76	0.5126	
0.0420	1363.5	605.72	1210.80	0.4970	1342.4	627.90	1186.40	0.5107	
0.0729	1365.8	595.57	1229.37	0.4928	1345.0	617.04	1204.93	0.5063	
0.0821	1366.5	592.59	1234.92	0.4916	1345.6	614.03	1210.31	0.5050	
0.1013	1368.0	586.48	1246.42	0.4890	1347.2	607.57	1221.71	0.5024	
0.2023	1376.5	555.83	1307.01	0.4761	1355.8	575.58	1281.44	0.4890	
0.3008	1385.7	528.35	1365.88	0.4642	1365.5	546.57	1339.86	0.4765	
0.4012	1395.9	502.51	1425.62	0.4527	1375.8	519.63	1398.79	0.4646	
0.5001	1406.8	478.89	1484.32	0.4419	1386.9	494.94	1456.82	0.4534	
0.6001	1418.7	456.65	1543.56	0.4315	1399.4	471.42	1515.82	0.4425	
0.7001	1431.4	435.90	1602.69	0.4216	1412.5	449.63	1574.54	0.4322	
0.8009	1445.2	416.23	1662.40	0.4120	1426.2	429.29	1633.30	0.4223	
0.8992	1459.4	398.26	1720.51	0.4030	1440.9	410.37	1691.18	0.4129	
1.0000	1478.4	378.54	1786.90	0.3929	1459.3	390.22	1756.09	0.4026	
T = 298.15 K					T = 303.15 K				
0.0000	1318.4	667.05	1137.09	0.5312	1296.8	693.05	1112.65	0.5464	
0.0294	1320.7	655.87	1154.45	0.5267	1299.2	681.27	1129.81	0.5417	
0.0420	1321.8	651.08	1161.99	0.5248	1300.3	676.26	1137.22	0.5397	
0.0729	1324.2	639.93	1180.09	0.5203	1302.9	664.40	1155.20	0.5350	
0.0821	1324.8	636.78	1185.38	0.5190	1303.7	660.91	1160.58	0.5336	
0.1013	1326.6	629.85	1196.81	0.5162	1305.4	653.77	1171.74	0.5307	
0.2023	1335.9	595.82	1256.35	0.5021	1314.9	618.05	1230.51	0.5160	
0.3008	1345.6	565.58	1313.98	0.4892	1325.0	586.13	1287.62	0.5025	
0.4012	1356.4	537.12	1372.60	0.4767	1336.1	556.19	1345.66	0.4895	
0.5001	1368.2	510.91	1430.56	0.4649	1348.0	528.80	1402.87	0.4773	
0.6001	1381.5	485.92	1489.65	0.4534	1360.8	503.13	1460.57	0.4656	
0.7001	1394.6	463.33	1547.62	0.4427	1374.5	479.16	1518.35	0.4543	
0.8009	1408.3	442.25	1605.60	0.4325	1389.2	456.56	1576.65	0.4435	
0.8992	1424.0	422.05	1663.89	0.4225	1404.4	435.88	1633.59	0.4333	
1.0000	1442.3	401.41	1727.27	0.4121	1421.5	414.99	1695.18	0.4228	
T = 308.15 K									
0.0000	1277.6	717.82	1090.41	0.5611					
0.0294	1280.0	705.53	1107.32	0.5563					
0.0420	1281.1	700.30	1114.63	0.5542					
0.0729	1283.8	687.84	1132.44	0.5493					
0.0821	1284.6	684.20	1137.75	0.5478					
0.1013	1286.4	676.65	1148.84	0.5448					
0.2023	1296.1	639.24	1206.98	0.5295					
0.3008	1306.4	605.83	1263.49	0.5155					
0.4012	1317.9	574.35	1321.13	0.5019					
0.5001	1330.1	545.64	1377.88	0.4892					
0.6001	1343.3	518.69	1435.23	0.4770					
0.7001	1357.5	493.47	1492.79	0.4652					
0.8009	1372.7	469.72	1550.89	0.4539					
0.8992	1388.4	448.01	1607.68	0.4433					
1.0000	1406.0	426.11	1669.15	0.4323					

**Table 3.** Values of ultrasonic velocities ( $u$ ), isentropic compressibilities ( $K_s$ ), acoustic impedance ( $Z$ ), and intermolecular free length ( $L_f$ ) for the binary mixtures of PC (1) + o-xylene (2) at 288.15-308.15 K

$x_1$	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)
T = 288.15 K					T = 293.15 K			
0.0000	1392.8	582.97	1231.58	0.4876	1373.2	602.57	1208.54	0.5003
0.0230	1391.9	576.80	1245.58	0.4850	1372.2	596.28	1222.18	0.4977
0.0428	1391.9	571.85	1256.34	0.4829	1371.9	591.42	1232.48	0.4956
0.0618	1392.3	566.62	1267.58	0.4807	1371.8	586.43	1243.06	0.4935
0.0804	1391.6	560.71	1281.58	0.4782	1370.8	580.57	1256.52	0.4911
0.1015	1394.2	554.49	1293.54	0.4755	1372.0	575.27	1267.00	0.4888
0.2056	1396.8	527.98	1355.98	0.4640	1375.3	547.15	1328.92	0.4767
0.2993	1404.2	505.74	1408.12	0.4541	1381.6	524.84	1379.08	0.4669
0.3992	1414.6	483.99	1460.60	0.4442	1391.8	502.27	1430.48	0.4568
0.4995	1426.3	462.92	1514.55	0.4345	1402.7	480.81	1482.72	0.4469
0.5986	1439.9	443.53	1565.82	0.4253	1416.0	460.71	1532.88	0.4375
0.7001	1452.2	424.76	1621.19	0.4162	1428.1	441.19	1587.13	0.4281
0.8004	1465.3	407.84	1673.35	0.4078	1442.3	422.84	1639.73	0.4191
0.8990	1474.5	393.05	1725.49	0.4003	1452.4	406.91	1692.06	0.4111
1.0000	1478.4	378.54	1786.90	0.3929	1459.3	390.22	1756.09	0.4026
T = 298.15 K					T = 303.15 K			
0.0000	1354.0	622.83	1185.81	0.5133	1328.4	650.10	1157.95	0.5292
0.0230	1351.8	617.41	1198.15	0.5111	1326.2	644.51	1169.94	0.5269
0.0428	1351.2	612.65	1208.00	0.5091	1325.4	639.75	1179.36	0.5250
0.0618	1350.9	607.65	1218.22	0.5070	1324.8	634.82	1189.04	0.5230
0.0804	1349.2	602.20	1230.79	0.5047	1323.2	629.08	1201.35	0.5206
0.1015	1350.6	596.49	1241.29	0.5023	1324.5	623.18	1211.52	0.5181
0.2056	1353.2	567.80	1301.49	0.4901	1326.0	594.16	1269.26	0.5059
0.2993	1359.9	544.21	1351.23	0.4798	1332.8	569.25	1318.05	0.4952
0.3992	1369.8	520.87	1401.56	0.4694	1343.5	544.00	1368.24	0.4841
0.4995	1380.5	498.61	1452.78	0.4593	1354.8	520.09	1419.21	0.4733
0.5986	1393.8	477.61	1502.18	0.4495	1368.8	497.46	1468.60	0.4629
0.7001	1406.8	456.68	1556.53	0.4395	1381.8	475.45	1522.11	0.4526
0.8004	1420.8	437.69	1608.04	0.4303	1395.4	455.76	1572.40	0.4431
0.8990	1431.5	420.80	1660.08	0.4219	1408.8	436.37	1626.67	0.4336
1.0000	1442.3	401.41	1727.27	0.4121	1421.5	414.99	1695.18	0.4228
T = 308.15 K								
0.0000	1310.4	670.51	1138.13	0.5423				
0.0230	1308.2	664.95	1149.57	0.5401				
0.0428	1307.6	659.97	1158.78	0.5380				
0.0618	1306.9	655.11	1167.99	0.5360				
0.0804	1304.8	649.84	1179.37	0.5339				
0.1015	1306.5	643.42	1189.59	0.5312				
0.2056	1307.2	614.49	1244.92	0.5192				
0.2993	1314.5	588.24	1293.26	0.5079				
0.3992	1324.5	562.55	1342.11	0.4967				
0.4995	1335.4	537.88	1392.21	0.4857				
0.5986	1349.4	514.18	1441.26	0.4749				
0.7001	1362.5	491.11	1494.46	0.4641				
0.8004	1375.6	470.94	1543.61	0.4545				
0.8990	1390.5	449.85	1598.67	0.4442				
1.0000	1406.0	426.11	1669.15	0.4323				

**Table 4.** Values of ultrasonic velocities ( $u$ ), isentropic compressibilities ( $K_s$ ), acoustic impedance ( $Z$ ), and intermolecular free length ( $L_f$ ) for the binary mixtures of PC (1)+p-xylene (2) at 288.15-308.15 K

$x_1$	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	$u$ (m s <sup>-1</sup> )	$K_s$ (T Pa <sup>-1</sup> )	$Z$ (kg cm <sup>-2</sup> s <sup>-1</sup> )	$L_f$ (Å)	
T = 288.15 K					T = 293.15 K				
0.0000	1351.6	632.61	1169.54	0.5079	1328.0	658.52	1143.49	0.5230	
0.0227	1352.8	622.88	1186.76	0.5040	1329.1	648.43	1160.33	0.5190	
0.0397	1353.8	615.77	1199.58	0.5011	1330.3	640.78	1173.11	0.5159	
0.0573	1354.8	608.68	1212.65	0.4982	1331.5	633.17	1186.14	0.5128	
0.0816	1356.3	599.12	1230.64	0.4943	1333.1	623.08	1203.91	0.5087	
0.0980	1357.4	592.86	1242.63	0.4917	1334.0	616.71	1215.53	0.5061	
0.2090	1365.8	553.93	1321.77	0.4753	1343.3	575.22	1294.18	0.4888	
0.3029	1374.4	525.07	1385.70	0.4627	1352.2	544.83	1357.36	0.4757	
0.3993	1384.6	498.58	1448.57	0.4509	1363.4	516.43	1420.24	0.4632	
0.5028	1397.1	473.10	1512.95	0.4392	1376.6	489.40	1484.33	0.4509	
0.5978	1410.1	451.89	1569.36	0.4293	1390.9	466.47	1541.29	0.4402	
0.7068	1426.7	429.80	1630.82	0.4186	1407.8	443.37	1602.12	0.4291	
0.8012	1442.5	412.38	1681.09	0.4101	1424.2	424.96	1652.27	0.4201	
0.8996	1460.5	395.63	1730.63	0.4017	1441.8	407.86	1700.52	0.4116	
1.0000	1478.4	378.54	1786.90	0.3929	1459.3	390.22	1756.09	0.4026	
T = 298.15 K					T = 303.15 K				
0.0000	1309.6	680.56	1122.01	0.5366	1288.4	706.77	1098.18	0.5518	
0.0227	1311.1	669.68	1138.93	0.5323	1290.2	695.10	1115.05	0.5472	
0.0397	1312.3	661.76	1151.50	0.5291	1291.5	686.74	1127.50	0.5439	
0.0573	1313.5	653.88	1164.32	0.5259	1293.0	678.20	1140.36	0.5405	
0.0816	1315.4	643.12	1182.08	0.5216	1295.1	666.79	1158.00	0.5360	
0.0980	1316.6	636.24	1193.79	0.5188	1296.5	659.41	1169.69	0.5330	
0.2090	1326.3	592.92	1271.64	0.5008	1307.1	613.45	1247.14	0.5141	
0.3029	1335.8	560.96	1334.52	0.4871	1317.2	579.68	1309.66	0.4997	
0.3993	1346.9	531.67	1396.45	0.4743	1328.8	548.82	1371.24	0.4862	
0.5028	1360.3	503.54	1459.93	0.4615	1342.4	519.44	1434.10	0.4730	
0.5978	1374.0	480.23	1515.53	0.4507	1356.0	495.31	1488.90	0.4619	
0.7068	1391.2	456.10	1575.99	0.4393	1373.1	470.30	1548.54	0.4501	
0.8012	1407.6	437.03	1625.60	0.4300	1389.0	450.80	1597.05	0.4407	
0.8996	1426.0	418.84	1674.30	0.4209	1406.7	432.30	1644.44	0.4315	
1.0000	1442.3	401.41	1727.27	0.4121	1421.5	414.99	1695.18	0.4228	
T = 308.15 K									
0.0000	1268.4	733.05	1075.50	0.5670					
0.0227	1270.3	720.76	1092.21	0.5623					
0.0397	1271.8	711.81	1104.64	0.5588					
0.0573	1273.4	702.79	1117.40	0.5552					
0.0816	1275.7	690.67	1134.96	0.5504					
0.0980	1277.2	682.88	1146.57	0.5473					
0.2090	1288.5	634.29	1223.57	0.5275					
0.3029	1299.2	598.61	1285.81	0.5124					
0.3993	1311.1	566.29	1346.87	0.4984					
0.5028	1325.2	535.40	1409.42	0.4846					
0.5978	1339.1	510.14	1463.85	0.4730					
0.7068	1356.4	484.09	1522.94	0.4608					
0.8012	1372.5	463.77	1571.04	0.4510					
0.8996	1390.3	444.56	1617.93	0.4416					
1.0000	1406.0	426.11	1669.15	0.4323					

nents. The values of isentropic compressibility are calculated using the equation,<sup>10</sup>

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

Where  $u$  is ultrasonic velocity and  $\rho$  is density of the mixture.

Free length ( $L_f$ ), which is an intermolecular property defined as the distance between the surfaces of the molecules, are evaluated from the values of compressibility employing equation,

$$L_f = K' K_s^{1/2} \quad (2)$$

Where  $K'$  is the Jacobson's constant, which is temperature dependent and equal to  $(93.875 + 0.375T) \times 10^{-8}$ .

These two parameters basically depend on the interaction phenomenon and they represent the strength of the interaction present in the component molecules.<sup>11,12</sup>

Kinsler *et al.*<sup>13</sup> have suggested that acoustical impedance ( $Z$ ) is more significant parameter to describe the medium and the intermolecular interactions than the ultrasound velocity and density individually. The acoustical impedance is product of ultrasonic velocity and density and evaluated for all the binary mixtures using following equation,

$$Z = u\rho \quad (3)$$

Where  $u$  is ultrasonic velocity and  $\rho$  is density of the mixture.

The evaluated values of  $K_s$ ,  $L_f$  and  $Z$  along with the experimentally determined values of  $u$  are presented in Tables 1-3 and 4 for the binary mixtures at 288.15-308.15 K. Figs. 1, 2, 3 and 4 show the graphical variation of  $u$ ,  $K_s$ ,  $L_f$  and  $Z$  with increasing mole fractions of PC for all the binary systems at 298.15 K.

As can be seen from Tables 1-4 for all the binary systems studied, the values of ultrasonic velocity increase with increasing mole fraction of PC and decrease with increasing temperatures.

From Fig. 1, it can be noted that the ultrasonic velocity ( $u$ ) values follow the order benzene < p-xylene < ethylbenzene < o-xylene at lower mole fractions of PC (i.e. up to 0.2 mole fraction). But as the mole fraction of PC increases the values for ethylbenzene and benzene are observed superimposed upon each other along with the lowest values of p-xylene and highest that of o-xylene.

From Tables 1-4, the values of isentropic compressibility ( $K_s$ ), decrease with increasing mole fraction of PC and increase with increasing temperatures for all the four binary systems studied.

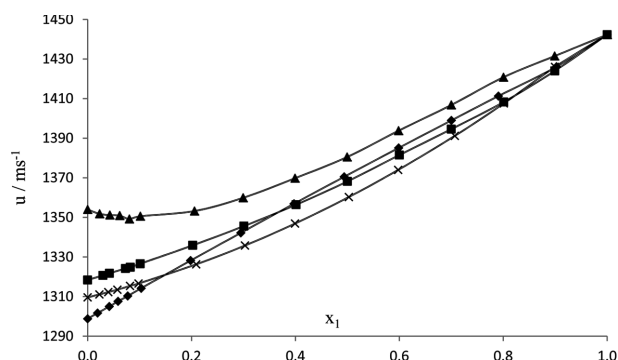


Fig. 1. Variation of ultrasonic velocities,  $u$  for binary mixtures of PC (1) + benzene (◆), ethylbenzene (■), o-xylene (▲) and p-xylene (×) at 298.15 K.

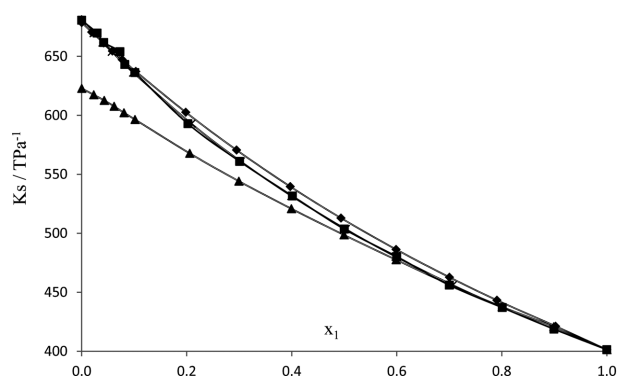


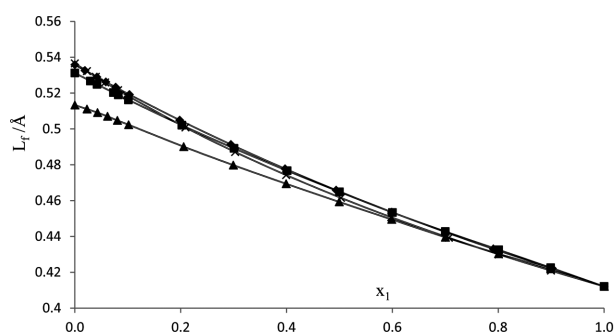
Fig. 2. Variation of isentropic compressibilities,  $K_s$  for binary mixtures of PC (1) + benzene (◆), ethylbenzene (■), o-xylene (▲) and p-xylene (×) at 298.15 K.

From Fig. 2, it can be noted that the isentropic compressibility values for benzene, ethylbenzene and p-xylene are superimposed upon each other along with the lowest values of o-xylene (up to 0.5 mole fraction of PC), which are also getting superimposed on to the other three systems at higher mole fractions of PC.

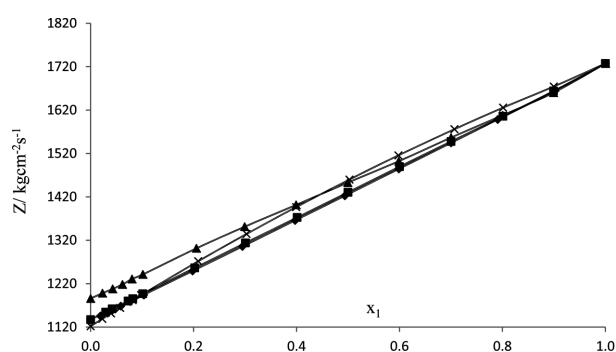
The values of intermolecular free length ( $L_f$ ) follow the same trend as isentropic compressibility. Thus the  $L_f$  values decrease with increasing mole fraction of PC and increase with increasing temperatures for all the four binary systems studied.

From Tables 1-4, the values of acoustic impedance ( $Z$ ) increase with increasing mole fraction of PC and decrease with increasing temperatures for all the four binary systems studied.

From Fig. 4, it can be noted that the acoustic impedance values are superimposed on each other for all the binary systems studied. Up to 0.4 mole fractions the values for o-xylene are higher and can be distinguished but later on with higher mole fractions these values are also getting superimposed on other system values. Hence no definite



**Fig. 3.** Variation of intermolecular free lengths,  $L_f$  for binary mixtures of PC (1) + benzene (◆), ethylbenzene (■), o-xylene (▲) and p-xylene (×) at 298.15 K.



**Fig. 4.** Plot of acoustic impedances  $Z$  for binary mixtures of propylene carbonate (1) + benzene (◆), ethylbenzene (■), o-xylene (▲) and p-xylene (×) at 298.15 K.

trend could be explained.

All the four hydrocarbons studied in the present investigation are not having much structural differences. Ethylbenzene, o- and p-xylene are in fact isomers of each other. Because of the less structural differences not much difference in the interactions is seen and the parameters studied are having superimposed values.

In the present investigation, the decrease in  $K_s$  and  $L_f$  values represent less possibility of compression of the system and less space is available between the components. PC is having less or no self association. As the mole fraction of PC increases there is no much interspaces available between two molecules.

The small interaction observed may be because of the interaction of carbonyl group in PC with the pi electron cloud of the hydrocarbon systems. The carbonyl group in PC is having n as well as pi electrons. In the present investigation the possibility of n-pi interactions between the carbonyl group of PC with the electron cloud of benzene can be predicted.

The molar volumes of the components studied at 298.15 K are  $85.25 \text{ cm}^3 \text{ mol}^{-1}$  for PC and 89.42, 123.92, 123.10,

$121.23 \text{ cm}^3 \text{ mol}^{-1}$  for benzene, p-xylene, ethylbenzene and o-xylene respectively. The interstitial accommodation because of differences between the molecular sizes of the mixing components might be another factor behind the interaction observed. The same thing is explained earlier for the same systems studying excess molar volumes and viscosity deviations by our group.<sup>6</sup>

The substitution of methyl or ethyl group increases the electron donor-acceptor interaction. With substitution of ethyl group in ethylbenzene, the inductive effect (electron donating) of ethyl groups might be increasing the electron density of the hydrocarbon and thus increasing the repulsive interaction between the pi-electrons of the carbonyl group with those of aromatic hydrocarbons, thus giving rise to weaker interactions in these systems. The same is the case in o-xylene mixtures also. The presence of two methyl groups ortho to each other have greater electron donating effect than that present in p-xylene in which the two methyl groups are in para position.

Thus electron donor-acceptor interaction, n-pi interaction and structural effects are observed for these systems but the magnitude of these effects is very small.

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