# Excess Molar Volumes and Sound Speed in (Phenylacetonitrile + 1,2-Dichloroethane), (Phenylacetonitrile + 1,1,2-Trichloroethane), (Phenylacetonitrile + 1,1,2,2-Tetrachloroethane), (Phenylacetonitrile + Trichloroethene), and (Phenylacetonitrile + Tetrachloroethene) at Temperatures of (303.15, 308.15, and 313.15) K

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The present paper reports the experimental data for density $\rho$, viscosity $\eta$, and speed of sound $u$ in (phenylacetonitrile + 1,2-dichloroethane), (phenylacetonitrile + 1,1,2-trichloroethane), (phenylacetonitrile + 1,1,2,2-tetrachloroethane), (phenylacetonitrile + trichloroethene), and (phenylacetonitrile + tetrachloroethene) over the entire range of composition at $T$ = (303.15 to 313.15) K. These values have been used to calculate the excess molar volumes $V^E$ and deviation in isentropic compressibility $\Delta\kappa_s$. The excess molar volumes and deviation in isentropic compressibility are fitted to a Redlich−Kister-type equation to derive binary coefficients and standard deviation and to elicit the specific interactions like complex formation as well as the saturation of chlorine atoms with $\pi$ electrons.

## 1. Introduction

A deeper knowledge of the thermodynamic and transport properties of multicomponent liquid mixtures is essential in many industrial applications such as design, calculation, heat transfer, mass transfer, and fluid flow and so forth.[1] The acoustic properties of binary liquid mixtures can be quite significant and give a measure of molecular interactions and hence can provide information needed to test existing theories of solutions. Ultrasonic velocity data can be utilized to deduce some useful properties of liquid mixtures, which are not easily accessible by other means. The high precision of speed of sound measurements makes it possible to calculate many other reliable parameters which give information regarding deviations of the system from ideality. Research activities of our laboratory comprise the systematic measurements of volumetric and transport properties of mixtures of compounds.[2−11]

Chloroethanes and chloroethenes have relatively low values of dielectric constants ($\varepsilon = 2$),[12] even though they are familiar solvents in the industrial applications. The most common use of 1,2-dichloroethane is in the production of vinyl chloride which is used to make a variety of plastic and vinyl products including polyvinyl chloride (PVC). It is also used as a solvent and added to leaded gasoline to remove lead, whereas 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethene are nonflammable solvents used in fats, waxes, resins, oils, rubber, paints, varnishes, natural resins, and alkaloids. Tetrachloroethene has its importance in dry cleaning, textile processing, degreasing metals, insulating fluid, and cooling gas in electrical transformers.[12]

The aim of the present work is to analyze the changes in the thermodynamic properties, as a function of temperature and composition of mixture. For that purpose, density $\rho$, viscosity $\eta$, and speed of sound $u$ were measured within the temperature range from (303.15 to 313.15) K. The measured values were used to calculate the various properties such as excess molar volumes $V^E$ and deviations in isentropic compressibility $\Delta\kappa_s$.

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**Table 1. Experimental Density ($\rho$), Viscosity ($\eta$), and Speed of Sound ($u$) of Pure Liquids at $T$ = 298.15 K**

| | $10^{-3}\cdot\rho$ /(kg·m$^{-3}$) | | $10^3\cdot\eta$/(mPa·s) | | $u$/(m·s$^{-1}$) | |
|---|---|---|---|---|---|---|
| component | exptl | lit. | exptl | lit. | exptl | lit. |
| phenylacetonitrile | 1.00883[a] | ----- | 1.761[a] | ----- | 1519.2[a] | ----- |
| 1,2-dichloroethane | 1.2467 | 1.2468[b] | 0.776 | 0.779[d] | 1174.0[a] | 1174.0[h] |
| 1,1,2-trichloroethane | 1.4161[f] | 1.4161[g] | 1.105 | 1.100[e] | 1129.2[a] | ----- |
| 1,1,2,2-tetrachloroethane | 1.5868 | 1.5866[b] | 1.456[a] | 1.456[e] | 1134.7[a] | 1135.0[h] |
| trichloroethene | 1.4559 | 1.4558[c] | 0.527 | 0.529[c] | 1014.7[a] | 1012.4[h] |
| tetrachloroethene | 1.6148 | 1.6147[c] | 0.847 | 0.846[c] | 1028.0[a] | 1030.0[h] |

[a] Values at $T$ = 303.15 K. [b] Ref 19. [c] Ref 14. [d] Ref 20. [e] Ref 12. [f] Values at $T$ = 308.15 K. [g] Ref 16. [h] Ref 21.

## 2. Experimental Section

***2.1. Materials.*** All the solvents, phenylacetonitrile (mass fraction 0.98 determined by GC Assay, SD Fine Chemicals Ltd., India), 1,2-dichloroethane[13] (mass fraction of 0.99 supplied by Merck GR grade), 1,1,2,2-tetrachloroethane[13] (supplied by Acros Organics, USA, with cited mass fraction purity of 0.985), tetrachloroethene[14] (mass fraction of 0.99 supplied by Merck, India), trichloroethene[12] (mass fraction purity of 0.99 supplied by Merck, India), and 1,1,2-trichloroethane[12] (mass fraction of 0.98 provided by Acros Organics, USA), are purified by the standard methods. The purity of the chemicals is checked by GC which shows a single sharp peak and densities and sound speed of the pure liquids are listed in Table 1.

***2.2. Apparatus and Procedure.*** Binary mixtures were prepared by mass in airtight bottles. The mass measurements were performed on a Dhona 100 DS, India, single-pan analytical balance with a resolution of $1\cdot10^{-8}$ kg. The required properties of the mixture were measured on the same day of preparing

10.1021/je900570e 
Published on Web 08/20/2009

**Table 2. Values of Density ($\rho$), Viscosity ($\eta$), Speed of Sound ($u$), Excess Molar Volume ($V^E$), and Deviation in Isentropic Compressibility ($\Delta\kappa_s$) for the Binary Liquid Mixtures at Various Temperatures**

| $x_1$ | $10^{-3}\cdot\rho$ / (kg·m$^{-3}$) | $10^{3}\cdot\eta$ / (mPa·s) | $u$ / (m·s$^{-1}$) | $10^{6}\cdot V^E$ / (m$^3$·mol$^{-1}$) | $10^{11}\cdot\Delta\kappa_s$ / (m$^2$·N$^{-1}$) | $x_1$ | $10^{-3}\cdot\rho$ / (kg·m$^{-3}$) | $10^{3}\cdot\eta$ / (mPa·s) | $u$ / (m·s$^{-1}$) | $10^{6}\cdot V^E$ / (m$^3$·mol$^{-1}$) | $10^{11}\cdot\Delta\kappa_s$ / (m$^2$·N$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Phenylacetonitrile (1) + 1,2-Dichloroethane (2) | | | | | | | | | | | |
| $T = 303.15$ K | | | | | | | | | | | |
| 0.0000 | 1.2387 | 0.7237 | 1174.0 | 0.0000 | 0.0000 | 0.5122 | 1.1007 | 1.2130 | 1374.8 | −0.0780 | −1.0664 |
| 0.0165 | 1.2335 | 0.7352 | 1182.2 | −0.0177 | −0.1943 | 0.6480 | 1.0720 | 1.3645 | 1418.6 | −0.0608 | −0.8459 |
| 0.1059 | 1.2055 | 0.8165 | 1221.2 | −0.0382 | −0.6543 | 0.8003 | 1.0428 | 1.5359 | 1465.2 | −0.0342 | −0.5711 |
| 0.2041 | 1.1771 | 0.9029 | 1262.4 | −0.0603 | −1.0228 | 0.9705 | 1.0136 | 1.7253 | 1512.6 | −0.0103 | −0.1496 |
| 0.3088 | 1.1492 | 1.0032 | 1304.2 | −0.0751 | −1.2614 | 1.0000 | 1.0088 | 1.7613 | 1519.2 | 0.0000 | 0.0000 |
| 0.4073 | 1.1248 | 1.1034 | 1339.5 | −0.0812 | −1.2163 | | | | | | |
| $T = 308.15$ K | | | | | | | | | | | |
| 0.0000 | 1.2305 | 0.6737 | 1164.8 | 0.0000 | 0.0000 | 0.5122 | 1.0956 | 1.1167 | 1367.5 | −0.1600 | −1.1980 |
| 0.0165 | 1.2253 | 0.6821 | 1171.9 | −0.0138 | −0.0846 | 0.6480 | 1.0672 | 1.2481 | 1411.8 | −0.1406 | −0.9655 |
| 0.1059 | 1.1989 | 0.7512 | 1211.5 | −0.1103 | −0.6657 | 0.8003 | 1.0382 | 1.3981 | 1458.9 | −0.0922 | −0.6617 |
| 0.2041 | 1.1710 | 0.8313 | 1252.3 | −0.1436 | −1.0035 | 0.9705 | 1.0088 | 1.5678 | 1505.4 | −0.0107 | −0.1082 |
| 0.3088 | 1.1435 | 0.9258 | 1293.6 | −0.1597 | −1.1940 | 1.0000 | 1.0041 | 1.6021 | 1512.9 | 0.0000 | 0.0000 |
| 0.4073 | 1.1194 | 1.0169 | 1330.8 | −0.1653 | −1.2775 | | | | | | |
| $T = 313.15$ K | | | | | | | | | | | |
| 0.0000 | 1.2237 | 0.6419 | 1153.5 | 0.0000 | 0.0000 | 0.5122 | 1.0876 | 1.0479 | 1355.9 | −0.2091 | −1.0551 |
| 0.0165 | 1.2187 | 0.6456 | 1161.0 | −0.0307 | −0.1351 | 0.6480 | 1.0588 | 1.1649 | 1399.9 | −0.1734 | −0.7460 |
| 0.1059 | 1.1915 | 0.7080 | 1200.5 | −0.1041 | −0.6695 | 0.8003 | 1.0295 | 1.2986 | 1447.6 | −0.1318 | −0.4338 |
| 0.2041 | 1.1635 | 0.7877 | 1243.7 | −0.1549 | −1.2053 | 0.9705 | 0.9999 | 1.4556 | 1499.1 | −0.0489 | −0.1167 |
| 0.3088 | 1.1361 | 0.8746 | 1285.3 | −0.2074 | −1.3927 | 1.0000 | 0.9995 | 1.4893 | 1503.4 | 0.0000 | 0.0000 |
| 0.4073 | 1.1118 | 0.9576 | 1320.8 | −0.2221 | −1.3006 | | | | | | |
| $T = 303.15$ K | | | | | | | | | | | |
| 0.0000 | 1.4250 | 1.0192 | 1129.2 | 0.0000 | 0.0000 | 0.5545 | 1.1734 | 1.5447 | 1342.8 | −0.0867 | −0.4351 |
| 0.0185 | 1.4156 | 1.0463 | 1137.0 | −0.0085 | −0.1167 | 0.6861 | 1.1217 | 1.6310 | 1393.4 | −0.0704 | −0.2884 |
| 0.1212 | 1.3649 | 1.1580 | 1176.7 | −0.0492 | −0.3562 | 0.8245 | 1.0703 | 1.7063 | 1446.6 | −0.0489 | −0.0695 |
| 0.2319 | 1.3126 | 1.2635 | 1219.7 | −0.0741 | −0.5311 | 0.9720 | 1.0184 | 1.7576 | 1505.3 | −0.0096 | 0.1132 |
| 0.3463 | 1.2611 | 1.3652 | 1263.4 | −0.0911 | −0.5641 | 1.0000 | 1.0088 | 1.7613 | 1519.2 | 0.0000 | 0.0000 |
| 0.4450 | 1.2186 | 1.4537 | 1301.0 | −0.0954 | −0.5262 | | | | | | |
| $T = 308.15$ K | | | | | | | | | | | |
| 0.0000 | 1.4161 | 0.9483 | 1115.9 | 0.0000 | 0.0000 | 0.5545 | 1.1689 | 1.4114 | 1343.3 | −0.2483 | −1.2946 |
| 0.0185 | 1.4072 | 0.9728 | 1125.0 | −0.0282 | −0.2566 | 0.6861 | 1.1173 | 1.4907 | 1392.9 | −0.2014 | −0.9404 |
| 0.1212 | 1.3586 | 1.0637 | 1168.2 | −0.1837 | −0.8472 | 0.8245 | 1.0657 | 1.5615 | 1445.1 | −0.1219 | −0.5125 |
| 0.2319 | 1.3073 | 1.1628 | 1214.2 | −0.2512 | −1.2310 | 0.9720 | 1.0137 | 1.5945 | 1498.7 | −0.0280 | 0.1081 |
| 0.3463 | 1.2562 | 1.2587 | 1261.9 | −0.2698 | −1.4896 | 1.0000 | 1.0041 | 1.6021 | 1512.9 | 0.0000 | 0.0000 |
| 0.4450 | 1.2140 | 1.3358 | 1301.5 | −0.2682 | −1.5023 | | | | | | |
| $T = 313.15$ K | | | | | | | | | | | |
| 0.0000 | 1.4096 | 0.8888 | 1096.1 | 0.0000 | 0.0000 | 0.5545 | 1.1636 | 1.3069 | 1332.8 | −0.2573 | −1.7041 |
| 0.0185 | 1.4005 | 0.9045 | 1105.9 | −0.0193 | −0.3290 | 0.6861 | 1.1121 | 1.3811 | 1383.2 | −0.2016 | −1.2572 |
| 0.1212 | 1.3512 | 0.9825 | 1150.9 | −0.1051 | −1.0190 | 0.8245 | 1.0607 | 1.4357 | 1431.8 | −0.1107 | −0.4451 |
| 0.2319 | 1.3006 | 1.0735 | 1199.9 | −0.1988 | −1.6208 | 0.9720 | 1.0090 | 1.4772 | 1488.9 | −0.0229 | 0.1046 |
| 0.3463 | 1.2502 | 1.1688 | 1248.1 | −0.2562 | −1.8460 | 1.0000 | 0.9995 | 1.4893 | 1503.4 | 0.0000 | 0.0000 |
| 0.4450 | 1.2084 | 1.2416 | 1288.9 | −0.2771 | −1.8713 | | | | | | |
| $T = 303.15$ K | | | | | | | | | | | |
| 0.0000 | 1.5796 | 1.4562 | 1134.7 | 0.0000 | 0.0000 | 0.5852 | 1.2364 | 2.0169 | 1343.4 | −0.2724 | −0.5801 |
| 0.0221 | 1.5665 | 1.4892 | 1142.0 | −0.0426 | −0.0698 | 0.7131 | 1.1642 | 1.9660 | 1393.9 | −0.1731 | −0.4136 |
| 0.1374 | 1.4972 | 1.6612 | 1179.7 | −0.1587 | −0.2533 | 0.8414 | 1.0939 | 1.8939 | 1446.4 | −0.1154 | −0.1675 |
| 0.2564 | 1.4269 | 1.8384 | 1220.9 | −0.2630 | −0.4484 | 0.9748 | 1.0225 | 1.7719 | 1504.3 | −0.0487 | 0.1278 |
| 0.3743 | 1.3588 | 1.9540 | 1263.5 | −0.3892 | −0.6101 | 1.0000 | 1.0088 | 1.7613 | 1519.2 | 0.0000 | 0.0000 |
| 0.4799 | 1.2972 | 2.0114 | 1303.1 | −0.3563 | −0.6476 | | | | | | |
| $T = 308.15$ K | | | | | | | | | | | |
| 0.0000 | 1.5706 | 1.3544 | 1115.5 | 0.0000 | 0.0000 | 0.5852 | 1.2317 | 1.8316 | 1329.5 | −0.4215 | −0.5941 |
| 0.0221 | 1.5585 | 1.3757 | 1125.0 | −0.1092 | −0.2872 | 0.7131 | 1.1602 | 1.7956 | 1381.0 | −0.3492 | −0.3796 |
| 0.1374 | 1.4901 | 1.5285 | 1166.3 | −0.2512 | −0.6988 | 0.8414 | 1.0899 | 1.7246 | 1436.5 | −0.2530 | −0.1755 |
| 0.2564 | 1.4200 | 1.6778 | 1209.3 | −0.3360 | −0.9197 | 0.9748 | 1.0182 | 1.6171 | 1497.2 | −0.1139 | 0.1249 |
| 0.3743 | 1.3517 | 1.7750 | 1251.5 | −0.4025 | −0.9092 | 1.0000 | 1.0041 | 1.6021 | 1512.9 | 0.0000 | 0.0000 |
| 0.4799 | 1.2915 | 1.8374 | 1289.9 | −0.4463 | −0.7884 | | | | | | |
| $T = 313.15$ K | | | | | | | | | | | |
| 0.0000 | 1.5637 | 1.2613 | 1095.5 | 0.0000 | 0.0000 | 0.5852 | 1.2262 | 1.6818 | 1323.9 | −0.4281 | −1.2882 |
| 0.0221 | 1.5517 | 1.2768 | 1107.4 | −0.1121 | −0.5196 | 0.7131 | 1.1549 | 1.6451 | 1373.2 | −0.3478 | −0.7771 |
| 0.1374 | 1.4835 | 1.4127 | 1154.6 | −0.2528 | −1.3876 | 0.8414 | 1.0850 | 1.5974 | 1426.2 | −0.2604 | −0.2823 |
| 0.2564 | 1.4138 | 1.5439 | 1201.6 | −0.3442 | −1.8315 | 0.9748 | 1.0135 | 1.5031 | 1487.4 | −0.1121 | 0.1232 |
| 0.3743 | 1.3459 | 1.6299 | 1245.6 | −0.4247 | −1.8352 | 1.0000 | 0.9995 | 1.4893 | 1503.4 | 0.0000 | 0.0000 |
| 0.4799 | 1.2859 | 1.6744 | 1283.9 | −0.4691 | −1.5834 | | | | | | |
| Phenylacetonitrile (1) + Trichloroethene (2) | | | | | | | | | | | |
| $T = 303.15$ K | | | | | | | | | | | |
| 0.0000 | 1.4475 | 0.5172 | 1014.7 | 0.0000 | 0.0000 | 0.5443 | 1.1845 | 1.0655 | 1293.3 | −0.1924 | −2.0286 |
| 0.0195 | 1.4370 | 0.5201 | 1024.6 | −0.0212 | −0.2081 | 0.6782 | 1.1288 | 1.2478 | 1364.1 | −0.1233 | −1.8731 |

**Table 2. Continued**

| $x_1$ | $10^{-3}\cdot\rho$ / (kg·m$^{-3}$) | $10^{3}\cdot\eta$ / (mPa·s) | $u$ / (m·s$^{-1}$) | $10^{6}\cdot V^{E}$ / (m$^3$·mol$^{-1}$) | $10^{11}\cdot\Delta\kappa_s$ / (m$^2$·N$^{-1}$) | $x_1$ | $10^{-3}\cdot\rho$ / (kg·m$^{-3}$) | $10^{3}\cdot\eta$ / (mPa·s) | $u$ / (m·s$^{-1}$) | $10^{6}\cdot V^{E}$ / (m$^3$·mol$^{-1}$) | $10^{11}\cdot\Delta\kappa_s$ / (m$^2$·N$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.1190 | 1.3838 | 0.5905 | 1073.5 | −0.0633 | −0.8314 | 0.8190 | 1.0741 | 1.4555 | 1435.8 | −0.0678 | −1.3446 |
| 0.2263 | 1.3295 | 0.6901 | 1128.2 | −0.1052 | −1.4284 | 0.9692 | 1.0197 | 1.6982 | 1504.1 | −0.0269 | −0.1857 |
| 0.3478 | 1.2719 | 0.8200 | 1191.0 | −0.1803 | −1.8767 | 1.0000 | 1.0088 | 1.7613 | 1519.2 | 0.0000 | 0.0000 |
| 0.4396 | 1.2302 | 0.9316 | 1238.9 | −0.2008 | −2.0413 | | | | | | |
| | | | | | $T = 308.15$ K | | | | | | |
| 0.0000 | 1.4378 | 0.4992 | 993.7 | 0.0000 | 0.0000 | 0.5443 | 1.1796 | 0.9721 | 1284.6 | −0.3339 | −2.8024 |
| 0.0195 | 1.4285 | 0.4860 | 1004.9 | −0.0907 | −0.4448 | 0.6782 | 1.1247 | 1.1471 | 1356.5 | −0.2976 | −2.4863 |
| 0.1190 | 1.3772 | 0.5530 | 1057.5 | −0.2185 | −1.5454 | 0.8190 | 1.0703 | 1.3395 | 1428.4 | −0.2306 | −1.6914 |
| 0.2263 | 1.3239 | 0.6417 | 1114.1 | −0.2899 | −2.2564 | 0.9692 | 1.0153 | 1.5460 | 1502.7 | −0.0761 | −0.5477 |
| 0.3478 | 1.2663 | 0.7558 | 1179.2 | −0.3291 | −2.7364 | 1.0000 | 1.0041 | 1.6021 | 1512.9 | 0.0000 | 0.0000 |
| 0.4396 | 1.2250 | 0.8529 | 1228.9 | −0.3516 | −2.9080 | | | | | | |
| | | | | | $T = 313.15$ K | | | | | | |
| 0.0000 | 1.4304 | 0.4833 | 982.0 | 0.0000 | 0.0000 | 0.5443 | 1.1742 | 0.9137 | 1279.3 | −0.3593 | −3.4133 |
| 0.0195 | 1.4200 | 0.4908 | 992.5 | −0.0134 | −0.3044 | 0.6782 | 1.1195 | 1.0750 | 1351.0 | −0.3129 | −2.9782 |
| 0.1190 | 1.3695 | 0.5292 | 1045.8 | −0.1688 | −1.5819 | 0.8190 | 1.0649 | 1.2478 | 1425.0 | −0.1917 | −2.1898 |
| 0.2263 | 1.3169 | 0.6092 | 1102.9 | −0.2672 | −2.3961 | 0.9692 | 1.0102 | 1.4388 | 1499.2 | −0.0287 | −0.9100 |
| 0.3478 | 1.2601 | 0.7150 | 1169.9 | −0.3341 | −3.0825 | 1.0000 | 0.9995 | 1.4893 | 1503.4 | 0.0000 | 0.0000 |
| 0.4396 | 1.2192 | 0.7976 | 1221.9 | −0.3680 | −3.4388 | | | | | | |
| | | | | | $T = 303.15$ K | | | | | | |
| 0.0000 | 1.6072 | 0.7971 | 1028.0 | 0.0000 | 0.0000 | 0.5767 | 1.2457 | 1.2686 | 1288.5 | −0.0566 | −0.8826 |
| 0.0231 | 1.5919 | 0.8124 | 1037.5 | −0.0118 | −0.1037 | 0.7051 | 1.1714 | 1.4134 | 1355.0 | −0.0432 | −0.7681 |
| 0.1322 | 1.5201 | 0.8840 | 1082.9 | −0.0330 | −0.4471 | 0.8386 | 1.0965 | 1.5715 | 1428.0 | −0.0329 | −0.5527 |
| 0.2490 | 1.4452 | 0.9577 | 1133.9 | −0.0442 | −0.7307 | 0.9720 | 1.0239 | 1.7262 | 1504.1 | −0.0132 | −0.1749 |
| 0.3700 | 1.3698 | 1.0605 | 1188.9 | −0.0564 | −0.8902 | 1.0000 | 1.0088 | 1.7613 | 1519.2 | 0.0000 | 0.0000 |
| 0.4713 | 1.3083 | 1.1593 | 1236.8 | −0.0635 | −0.9311 | | | | | | |
| | | | | | $T = 308.15$ K | | | | | | |
| 0.0000 | 1.5979 | 0.7657 | 1014.0 | 0.0000 | 0.0000 | 0.5767 | 1.2398 | 1.1718 | 1278.5 | −0.1045 | −1.0216 |
| 0.0231 | 1.5830 | 0.7752 | 1024.4 | −0.0295 | −0.2178 | 0.7051 | 1.1661 | 1.2945 | 1345.0 | −0.0922 | −0.8109 |
| 0.1322 | 1.5121 | 0.8382 | 1070.9 | −0.0714 | −0.6620 | 0.8386 | 1.0916 | 1.4299 | 1419.2 | −0.0702 | −0.5636 |
| 0.2490 | 1.4380 | 0.9171 | 1123.3 | −0.0945 | −1.0385 | 0.9720 | 1.0192 | 1.5697 | 1497.9 | −0.0244 | −0.2132 |
| 0.3700 | 1.3631 | 0.9982 | 1178.8 | −0.1046 | −1.1681 | 1.0000 | 1.0041 | 1.6021 | 1512.9 | 0.0000 | 0.0000 |
| 0.4713 | 1.3020 | 1.0769 | 1226.7 | −0.1101 | −1.1383 | | | | | | |
| | | | | | $T = 313.15$ K | | | | | | |
| 0.0000 | 1.5906 | 0.7395 | 996.6 | 0.0000 | 0.0000 | 0.5767 | 1.2343 | 1.0957 | 1268.9 | −0.1184 | −1.4653 |
| 0.0231 | 1.5757 | 0.7460 | 1010.5 | −0.0264 | −0.6540 | 0.7051 | 1.1608 | 1.2069 | 1335.7 | −0.1025 | −1.1411 |
| 0.1322 | 1.5053 | 0.8001 | 1060.1 | −0.0794 | −1.4027 | 0.8386 | 1.0866 | 1.3295 | 1409.3 | −0.0790 | −0.7133 |
| 0.2490 | 1.4316 | 0.8680 | 1113.4 | −0.1130 | −1.7831 | 0.9720 | 1.0145 | 1.4583 | 1486.1 | −0.0290 | −0.1096 |
| 0.3700 | 1.3571 | 0.9342 | 1168.9 | −0.1268 | −1.7994 | 1.0000 | 0.9995 | 1.4893 | 1503.4 | 0.0000 | 0.0000 |
| 0.4713 | 1.2962 | 1.0030 | 1216.8 | −0.1278 | −1.6668 | | | | | | |

the mixtures. The uncertainty in mole fraction was estimated to be less than $\pm\ 1\cdot10^{-4}$.

Densities of pure liquids and their mixtures were determined by using a double arm pycnometer of volume $1\cdot10^{-5}$ m$^3$.[10] The uncertainty in density and excess molar volume values was found to be $\pm$ 0.04 kg·m$^{-3}$ and $\pm$ 0.01 m$^3$·mol$^{-1}$, respectively.

A suspended level viscometer[11,15] was used to measure the flow times of pure liquids and liquid mixtures, and it was calibrated with benzene and doubly distilled water (water conductivity less than $1\cdot10^{-6}$ $\Omega^{-1}$·cm$^{-1}$ with (0.9970 and 0.9940) g·cm$^{-3}$ as its density at (298.15 and 308.15) K, respectively, and the density of benzene of (0.87381 and 0.87341) g·cm$^{-3}$ at (298.15 and 308.15) K, respectively). Viscosity values $\eta$ of pure liquids and mixtures were calculated using the flow times by relation

$$\eta = (at - b/t)\rho \tag{1}$$

where $a$ and $b$ are the characteristic constants of the viscometer; $\rho$ is the density; and $t$ represents the flow time. The flow times of pure liquids and liquid mixtures were determined by the average of five measurements. The uncertainty of viscosity was found to be $\pm$ 0.005 mPa·s.

Speeds of sound were determined by using an ultrasonic interferometer [model M-82, Mittal Enterprises, India], working at a frequency of 2 MHz. The working principle used in the measurement of speed of sound through medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by a quartz crystal in the measuring cell.[7,9] The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of the double-walled cell. The speed of sound was measured with relative uncertainty of $\pm$ 0.3 %.

In all the property measurements, the temperature was controlled within $\pm$ 0.01 K using a constant-temperature bath [INSREF model IRI-016 C, India], and the temperature was monitored with a platinum resistance thermometer with an accuracy of $\pm$ 0.001 K and an uncertainty of $\pm$ 0.004 K.

## 3. Results and Discussion

Table 2 lists the measured density, viscosity, sound speed $u$, excess molar volume $V^E$, and deviation in isentropic compressibility $\Delta\kappa_s$ for (phenylacetonitrile + 1,2-dichloroethane), (phenylacetonitrile + 1,1,2-trichloroethane), (phenylacetonitrile + 1,1,2,2-tetrachloroethane), (phenylacetonitrile + trichloroethene), and (phenylacetonitrile + tetrachloroethene) at $T$ = (303.15, 308.15, and 313.15) K along with the mole fraction.

The excess molar volumes ($V^E$) have been evaluated from density using

$$V^E = (x_1M_1 + x_2M_2)/\rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{2}$$

where $\rho_m$ is the density of the mixture; $x_1$, $M_1$, $\rho_1$, and $x_2$, $M_2$, and $\rho_2$ are the mole fraction, molar mass, and density of pure components, respectively. The deviations in isentropic compressibility ($\Delta\kappa_s$) have been evaluated using the equation

$$\Delta\kappa_s/(m^2 \cdot N^{-1}) = \kappa_s - (\Phi_1\kappa_{s1} + \Phi_2\kappa_{s2}) \quad (3)$$

where $\Phi_i$ is the volume fraction of pure components and is calculated from the individual pure molar volumes, $V_i$, using the relation

$$\Phi_i = x_iV_i/(\sum x_iV_i) \quad (4)$$

and $\kappa_{s1}$, $\kappa_{s2}$, and $\kappa_s$ are the isentropic compressibility of the pure components and observed isentropic compressibility of the liquid mixture, respectively.

The excess or deviation properties $\Delta Y$ are fitted by the method of nonlinear least-squares to the fourth-order Redlich−Kister-type polynomial equation.[16]

$$\Delta Y = x_1x_2\sum A_i(x_1 - x_2)^i \quad (5)$$

where $A_0$, $A_1$, $A_2$, $A_3$, and $A_4$ are adjustable binary coefficients. The coefficients $A_i$ were estimated using multiparametric regression analysis based on a nonlinear least-squares method. The number of $A_i$ parameters was optimized using the $F$-test and is found to be five ($m = 5$). In each case, the optimum number of coefficients $A_i$ is determined from an examination of the variation of standard deviation ($\sigma$) as calculated by

$$\sigma(Y^E) = \left[\sum(\Delta Y_{obs} - \Delta Y_{cal})^2/(n - m)\right]^{1/2} \quad (6)$$

where $n$ represents the number of experimental points and $m$ is the number of coefficients used in fitting the data. The coefficients $A_i$ and standard deviations $(\sigma)V^E$ and $(\sigma)\Delta\kappa_s$ of the fit are summarized in Table 3.

***3.1. Excess Molar Volume ($V^E$).*** The excess molar volume ($V^E$) curves are negative for (phenylacetonitrile + 1,2-dichloroethane), (phenylacetonitrile + 1,1,2-trichloroethane), (phenylacetonitrile + 1,1,2,2-tetrachloroethane), (phenylacetonitrile + trichloroethene), and (phenylacetonitrile + tetrachloroethene).

The observed $V^E$ values in the chloroethane system over the entire range of compositions can be attributed to the following volume reduction factors: (i) specific interactions between the unlike molecules, dipole−induced dipole interactions; (ii) complex formation between unlike molecules; (iii) formation of new hydrogen bonds between unlike molecules of the type of C−H···$\pi$ electrons.

The isothermal curves at $T = 303.15$ K shown in Figure 1 suggest that in the binary mixtures the volume reduction factors are preponderant. The algebraic values of $V^E$ of phenylacetonitrile with chloroethanes fall in the order: 0 > 1,2-dichloroethane > 1,1,2-trichloroethane > 1,1,2,2-tetrachloroethane.

The above-mentioned order indicates that an increase in the number of chlorine atoms in the molecule entails a reduction in the volume of the system.

$V^E$ values for the systems of phenylacetonitrile with chloroethenes are explained by taking the following factors into consideration: (i) double bond character of chloroethenes, (ii) shielding of the ethylenic double bond by chlorine atoms, and (iii) partial saturation of the electron accepting nature of chlorine atoms by $\pi$-electrons of the ethylenic double bond. The algebraic values of $V^E$ of phenylacetonitrile with chloroethenes fall in the order: 0 > tetrachloroethene > trichloroethene.

The more negative deviation in excess volumes of the system phenylacetonitrile with trichloroethene than 1,2-dichloroethane

**Table 3. Binary Coefficients ($A_i$) and Standard Errors ($\sigma$) of Phenylacetonitrile (1) + Chloroethanes and Ethenes (2)**

| function | $T$/K | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| | | Phenylacetonitrile (1) + 1,2-Dichloroethane (2) | | | | | |
| $10^6 \cdot V^E/(m^3 \cdot mol^{-1})$ | 303.15 | −0.321 | 0.138 | 0.25 | −0.03 | −0.5 | 0.0037 |
| | 308.15 | −0.643 | 0.119 | −0.28 | 0.44 | 0.03 | 0.0043 |
| | 313.15 | −0.863 | 0.370 | 0.33 | −0.65 | −1.24 | 0.0048 |
| $10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$ | 303.15 | −4.939 | 1.59 | 2.40 | −2.15 | −5.1 | 0.027 |
| | 308.15 | −5.032 | 0.29 | 0.09 | −0.63 | −0.7 | 0.024 |
| | 313.15 | −5.223 | 3.46 | 2.2 | −4.16 | −1.8 | 0.022 |
| | | Phenylacetonitrile (1) + 1,1,2-Trichloroethane (2) | | | | | |
| $10^6 \cdot V^E/(m^3 \cdot mol^{-1})$ | 303.15 | −0.3679 | 0.117 | 0.011 | −0.08 | −0.116 | 0.0013 |
| | 308.15 | −1.040 | 0.400 | −0.33 | 0.27 | −0.12 | 0.0052 |
| | 313.15 | −1.0902 | 0.321 | 0.483 | −0.26 | −0.20 | 0.0031 |
| $10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$ | 303.15 | −2.1 | 0.83 | −0.6 | 2.19 | 2.9 | 0.037 |
| | 308.15 | −5.92 | 0.95 | 1.6 | 2.99 | −0.4 | 0.076 |
| | 313.15 | −7.51 | 0.58 | 1 | 6.28 | 3.9 | 0.063 |
| | | Phenylacetonitrile (1) + 1,1,2,2-Tetrachloroethane (2) | | | | | |
| $10^6 \cdot V^E/(m^3 \cdot mol^{-1})$ | 303.15 | −1.411 | 1.14 | 1.91 | −1.70 | −2.68 | 0.015 |
| | 308.15 | −1.806 | 0.04 | 1.66 | 0.03 | −4.61 | 0.015 |
| | 313.15 | −1.88 | 0.17 | 1.94 | −0.26 | −4.97 | 0.014 |
| $10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$ | 303.15 | −2.54 | −0.31 | 0.8 | 2.22 | 2.5 | 0.046 |
| | 308.15 | −3.1 | 2.38 | −0.8 | 2.34 | 0.3 | 0.071 |
| | 313.15 | −6.48 | 4.60 | −0.1 | 4.70 | −1.0 | 0.086 |
| | | Phenylacetonitrile (1) + Trichloroethene (2) | | | | | |
| $10^6 \cdot V^E/(m^3 \cdot mol^{-1})$ | 303.15 | −0.812 | 0.292 | 1.46 | −0.4 | −1.80 | 0.0039 |
| | 308.15 | −1.395 | 0.14 | 0.21 | 0.16 | −2.23 | 0.013 |
| | 313.15 | −1.461 | 0.069 | −0.10 | 0.29 | 0.47 | 0.0076 |
| $10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$ | 303.15 | −8.09 | −2.4 | −1.5 | −0.26 | 0.9 | 0.049 |
| | 308.15 | −11.65 | −1.10 | 1.7 | 0.09 | −9.9 | 0.06 |
| | 313.15 | −13.76 | −2.3 | 5.6 | −4.17 | −17.8 | 0.12 |
| | | Phenylacetonitrile (1) + Tetrachloroethene (2) | | | | | |
| $10^6 \cdot V^E/(m^3 \cdot mol^{-1})$ | 303.15 | −0.2486 | 0.0459 | 0.266 | −0.06 | −0.60 | 0.0007 |
| | 308.15 | −0.4407 | 0.032 | 0.1 | 0.05 | −0.71 | 0.0033 |
| | 313.15 | −0.5085 | 0.134 | −0.002 | −0.17 | −0.60 | 0.0026 |
| $10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$ | 303.15 | −3.731 | 0.14 | 0.42 | −1.57 | −2.25 | 0.012 |
| | 308.15 | −4.629 | 1.62 | 1.40 | −2.02 | −4.8 | 0.031 |
| | 313.15 | −6.79 | 2.49 | −0.4 | 4.27 | −7.5 | 0.094 |

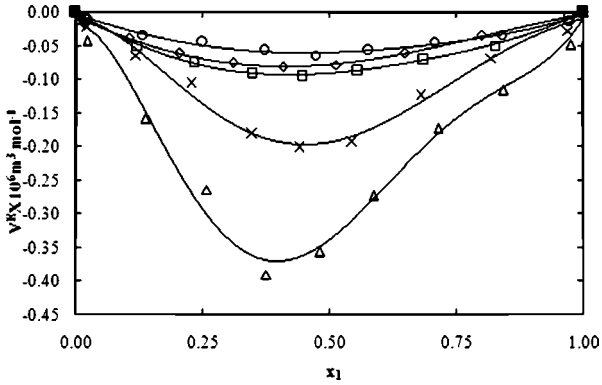


**Figure 1.** Plots of excess molar volumes $V^E$ against mole fraction $x_1$ of phenylacetonitrile (1) with ◇, 1,2-dichloroethane (2); □, 1,1,2-trichloroethane (2); Δ, 1,1,2,2-tetrachloroethane (2); ×, trichloroethene (2); and ○, tetrachloroethylene (2) at $T = 303.15$ K.

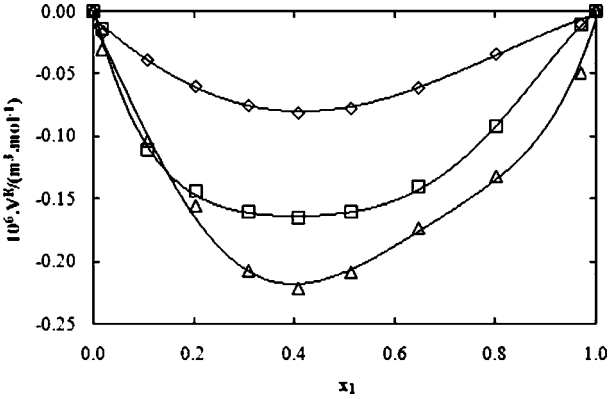


**Figure 2.** Plots of excess molar volumes $V^E$ against mole fraction $x_1$ of phenylacetonitrile (1) with 1,2-dichloroethane (2) at ◇, 303.15 K; □, 308.15 K; and ○, 313.15 K.

and 1,1,2-trichloroethane may be attributed to the $\pi-\pi$ interactions between the unlike molecules.

The $V^E$ values for equimolar mixtures were found to vary in the order

$$0 > \text{TECEE} > \text{DCE} > \text{TCE} > \text{TCEE} > \text{TECE}$$

It is interesting to observe that the $V^E$ of mixtures containing tetrachloroethene is less negative than the mixtures containing 1,1,2,2-tetrachloroethane but more negative than the mixtures containing 1,2-dichloroethane and 1,1,2-trichloroethane. This observation lends support to the contention that the $\pi$-electrons in tetrachloroethene are shielded by four chlorine atoms,[17] and also the electron-accepting ability of these chlorine atoms is partially saturated by the $\pi$-electrons.[18]

A comparison of algebraic values of $V^E$ at (303.15, 308.15, and 313.15) K shows that $V^E$ becomes more negative with an increase in temperature, shown in Figure 2, and it is observed that this does not affect the order of chloroethanes and chloroethenes.

***3.2. Deviation in Isentropic Compressibility ($\Delta\kappa_s$).*** The data presented in Table 2 show that the deviations in isentropic compressibility are negative in the mixtures of phenylacetonitrile with chloroethanes and chloroethenes over the entire range of composition at $T = 303.15$ K shown in Figure 3. All are showing maxima at the mole fraction around $x_1 = 0.5$, indicating maximum interactions at that mole fraction range in every system.

The observed negative values of $\Delta\kappa_s$ over the entire range of compositions for phenylacetonitrile with chloroethane binary mixtures at (303.15, 308.15, and 313.15) K may be explained in terms of

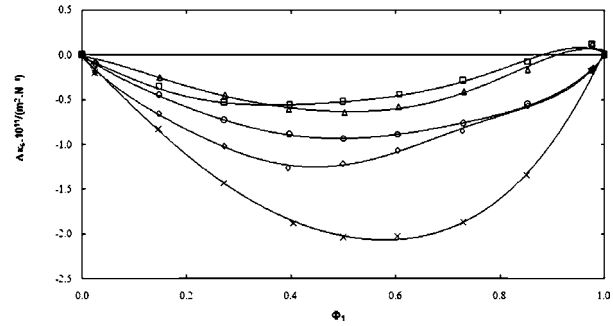


**Figure 3.** Variation of deviation in isentropic compressibility, ($\Delta\kappa_s$), versus volume fraction ($\Phi_1$) of binary mixtures of phenylacetonitrile (1) with ◇, 1,2-dichloroethane (2); □, 1,1,2-trichloroethane (2); Δ, 1,1,2,2-tetrachloroethane (2); ×, trichloroethene (2); and ○, tetrachloroethene (2) at 303.15 K.

(i) Contraction of volume due to dipole−dipole and dipole−induced dipole interactions.

(ii) Complex formation between phenylacetonitrile with chloroethanes.

From Figure 3 it is observed that the isotherm of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane shows a little positive lobe in the rich region of phenylacetonitrile. A small hump in the isotherms of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane may be due to addition of a small amount of phenylacetonitrile to 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane where many molecules of these two solvents are liberated. Thus, these molecules may form weaker molecular complexes leading to negative deviation in the lower range of phenylacetonitrile, whereas a small positive in the rich region of phenylacetonitrile may be attributed to the poor availability of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane molecules for interactions. The same trend is observed at temperatures of (308.15 and 313.15) K.

The negative $\Delta\kappa_s$ values of chloroethanes decrease in the following order

$$\text{1,1,2-trichloroethane} > \text{1,1,2,2-tetrachloroethane} > \text{1,2-dichloroethane}$$

The $\Delta\kappa_s$ values for the systems of phenylacetonitrile with chloroethenes are explained by taking three factors into consideration, that is:

(i) Double bond character of chloroethenes;

(ii) Deshielding of ethylenic double bond by chlorine atoms; and

(iii) Partial saturation of the electron-accepting nature of chlorine atoms by $\pi$-electrons of the ethylenic double bond.

The negative $\Delta\kappa_s$ values of chloroethenes are in the following order:

$$\text{tetrachloroethene} > \text{trichloroethene}$$

However, it is found that in all the binary systems negative $\Delta\kappa_s$ values decreased with an increase in temperature.

## 4. Conclusion

Experimental data of density, viscosity, and speed of sound for the system of phenylacetonitrile with chloroethanes and chloroethenes were measured over the whole range of composition from the temperature range of (303.15 to 313.15) K. The excess isentropic compressibilities of these systems are correlated using the Redlich−Kister-type polynomial equation. Estimated coefficients and standard deviation values are also presented. Thus, it can be concluded that the evaluated

experimental results are interpreted in terms of specific interactions through complex formation and dipole−dipole and $\pi-\pi$ interactions.

**Acknowledgment**

One of the authors (A.B.S.) thanks Dr. K. Sampath Kumar, Assistant Professor, Department of Applied Statistics, Telangana University, Nizamabad (Andhra Pradesh, India), for his assistance in calculating the coefficients of polynomial equation of various degrees through nonlinear regression analysis.

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Received for review July 6, 2009. Accepted August 5, 2009.

JE900570E