# Volumetric and Ultrasonic Studies of the Poly(ethylene glycol) Methacrylate 360 + Alcohol Systems at 298.15 K

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Speed of sound and density of poly(ethylene glycol) methacrylate 360 (PEGMA) + methanol, + ethanol, + 2-propanol, and + 1-butanol systems have been measured experimentally over the whole range of composition at $T = 298.15$ K and atmospheric pressure. From these experimental data, the excess molar volumes, isentropic compressibility, and changes in speed of sound and isentropic compressibility have been determined for each composition. The results have been interpreted in light of polymer−solvent interactions and packing effects. Also, the excess molar volumes and the changes of the speed of sound and the isentropic compressibility were fitted to two different variable-degree polynomial equations.

## Introduction

Knowledge of volumetric and acoustical properties of polymer solutions has been proven to be a very useful tool in evaluating the structural interactions occurring in these solutions.[1,2] In this respect, the isentropic compressibility and excess molar volume evaluated from sound velocity and density measurements have been used to study the structure and the nature of molecular interactions in aqueous and nonaqueous solutions of polymers.[3,4] With this consideration, in this work, we report the volumetric and acoustical properties of the poly(ethylene glycol)methacrylate (PEGMA) + methanol, + ethanol, + 2-propanol, and + 1-butanol systems over the whole range of composition at $T = 298.15$ K. This is a continuation of our studies on the polymer + alcohol systems.[5] The values of the excess molar volume and changes in isentropic compressibility were then calculated from the measured density and speed of sound data. Excess molar volume and changes for speed of sound and isentropic compressibility were fitted to the Redlich−Kister[6] and Ott et al.[7] equations. To our knowledge, no experimental density or speed of sound measurements have been reported in the literature for the PEGMA + alcohol systems.

## Experimental Section

All the chemicals were obtained from Merck; except PEGMA 360, which was obtained from Aldrich. PEGMA 360 was used without further purification. Previously, the number average molar mass $M_n$ of this polymer was determined to be 361 g·mol$^{-1}$.[8]

The solutions were prepared by mass using an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with an accuracy of $\pm 1 \cdot 10^{-4}$ g. The speed of sound and density of mixtures were measured at 298.15 K with a digital vibrating-tube analyzer (Anton paar DSA 5000, Austria) with a proportional temperature controller that kept the samples at working temperature with an accuracy of 0.001 K. The apparatus was calibrated at 298.15 K with distilled water and dry air. The apparatus was also tested with the density of a known molality of aqueous NaCl using the data given by Pitzer et al.[9] Uncertainty of the measurement is $\pm$ 0.003 kg·m$^{-3}$ for density and 0.1 m·s$^{-1}$ for ultrasonic velocity.

## Results and Discussion

The experimental data for the density $\rho$ and speed of sound $u$ of various PEGMA + alcohol solutions together with the isentropic compressibility determined by means of the Laplace equation ($\kappa_s = \rho^{-1}u^{-2}$) are given in Tables 1 to 4 at 298.15 K. The excess molar volumes $V^{\mathrm{E}}$, change in speed of sound $\Delta u$, and changes in isentropic compressibilities $\Delta\kappa_s$, which were determined by the following expressions:

$$V^{\mathrm{E}} = \frac{1}{\rho} - \left(\frac{x_2}{\rho_2} + \frac{1 - x_2}{\rho_1}\right) \tag{1}$$

$$\Delta u = u - (x_2 u_2 + (1 - x_2)u_1) \tag{2}$$

$$\Delta\kappa_s = \kappa_s - (x_2\kappa_{s,2} + (1 - x_2)\kappa_{s,1}) \tag{3}$$

are also listed in Tables 1 to 4. In the above equations, $x$ is the mole fraction, and subscripts 1 and 2 stand for solvent and polymer, respectively. The excess molar volumes and the changes in speed of sounds and isentropic compressibilities were correlated by means of the Redlich−Kister equation:[6]

$$\Delta Q = x_1(1 - x_1)\sum_{p=0}^{N} A_p(1 - 2x_1)^p \tag{4}$$

here $\Delta Q$ is the changes or excess molar volumes; $A_p$ represents the fitting coefficients; and $N$ is the degree of the polynomic expansion. These properties were also fitted to the Ott et al. equation, which has an exponential switching factor:[7]

$$\Delta Q = x_1(1 - x_1)[(\exp(-\alpha x_1)\sum_{i=0}^{1} B_i(1 - 2x_1)^i + (1 - \exp(-\alpha x_1)) + \sum_{i=0}^{2} C_i(1 - 2x_1)^i] \tag{5}$$

where $\alpha$, $B_i$, and $C_i$ represent the fitting coefficients. The standard deviations ($\sigma$) between the calculated ($\Delta Q_{\mathrm{calc}}$) and the

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**Table 1. Speed of Sound $u$, Density $\rho$, Isentropic Compressibility $\kappa_s$, Change in Speed of Sound $\Delta U$, Excess Molar Volume $V^E$, and Change in Isentropic Compressibility $\Delta\kappa_s$ for the System Methanol (1) + PEGMA 360 (2) at 298.15 K**

| $x_2$ | $u$<br>$m\cdot s^{-1}$ | $\Delta u$<br>$m\cdot s^{-1}$ | $\rho$<br>$g\cdot cm^{-3}$ | $V^E$<br>$cm^3\cdot mol^{-1}$ | $\kappa_s$<br>$TPa^{-1}$ | $\Delta\kappa_s$<br>$TPa^{-1}$ |
|---|---|---|---|---|---|---|
| 0 | 1102.53 | 0 | 0.78649 | 0 | 1045.99 | 0 |
| 0.0037 | 1112.55 | 8.61 | 0.79650 | −0.052 | 1014.32 | −29.33 |
| 0.0077 | 1122.64 | 17.21 | 0.80643 | −0.102 | 983.90 | −57.28 |
| 0.0119 | 1132.98 | 25.95 | 0.81649 | −0.153 | 954.12 | −84.40 |
| 0.0168 | 1144.35 | 35.49 | 0.82729 | −0.206 | 923.05 | −112.42 |
| 0.0216 | 1155.26 | 44.56 | 0.83744 | −0.258 | 894.72 | −137.71 |
| 0.0272 | 1167.11 | 54.31 | 0.84826 | −0.310 | 865.46 | −163.47 |
| 0.0335 | 1180.00 | 64.82 | 0.85967 | −0.367 | 835.42 | −189.55 |
| 0.0398 | 1192.04 | 74.49 | 0.87016 | −0.421 | 808.76 | −212.28 |
| 0.0468 | 1204.62 | 84.42 | 0.88090 | −0.466 | 782.30 | −234.32 |
| 0.0551 | 1218.59 | 95.27 | 0.89260 | −0.525 | 754.45 | −257.00 |
| 0.0631 | 1231.21 | 104.87 | 0.90298 | −0.576 | 730.56 | −275.85 |
| 0.0751 | 1248.61 | 117.73 | 0.91694 | −0.642 | 699.53 | −299.34 |
| 0.0876 | 1264.74 | 129.15 | 0.92969 | −0.696 | 672.45 | −318.60 |
| 0.1015 | 1281.08 | 140.23 | 0.94235 | −0.753 | 646.60 | −335.70 |
| 0.1157 | 1295.94 | 149.73 | 0.95367 | −0.800 | 624.36 | −349.04 |
| 0.1362 | 1315.07 | 161.10 | 0.96794 | −0.862 | 597.39 | −363.12 |
| 0.1582 | 1332.32 | 170.06 | 0.98083 | −0.910 | 574.37 | −372.33 |
| 0.1659 | 1337.83 | 172.67 | 0.98483 | −0.923 | 567.33 | −374.57 |
| 0.1748 | 1343.86 | 175.33 | 0.98930 | −0.939 | 559.71 | −376.56 |
| 0.2097 | 1364.41 | 182.71 | 1.00423 | −0.980 | 534.90 | −379.50 |
| 0.2543 | 1385.12 | 186.56 | 1.01930 | −1.012 | 511.36 | −375.03 |
| 0.3132 | 1405.75 | 184.95 | 1.03429 | −1.011 | 489.26 | −360.16 |
| 0.3677 | 1420.15 | 178.77 | 1.04481 | −0.979 | 474.56 | −340.66 |
| 0.4914 | 1442.83 | 154.71 | 1.06170 | −0.869 | 452.45 | −285.14 |
| 0.6830 | 1463.13 | 102.79 | 1.07731 | −0.593 | 433.61 | −183.74 |
| 0.7271 | 1466.20 | 89.04 | 1.07989 | −0.523 | 430.76 | −158.91 |
| 0.7282 | 1466.26 | 88.86 | 1.07992 | −0.513 | 430.71 | −158.26 |
| 0.7403 | 1467.33 | 85.29 | 1.08062 | −0.504 | 429.80 | −151.55 |
| 0.8297 | 1472.40 | 56.62 | 1.08501 | −0.367 | 425.12 | −100.12 |
| 0.8648 | 1474.21 | 45.19 | 1.08634 | −0.267 | 423.56 | −79.67 |
| 0.9073 | 1476.75 | 31.69 | 1.08803 | −0.199 | 421.45 | −55.08 |
| 0.9419 | 1480.01 | 21.66 | 1.08930 | −0.141 | 419.11 | −35.70 |
| 1.0000 | 1480.11 | 0 | 1.09111 | 0 | 418.36 | 0 |

experimental ($\Delta Q_{exp}$) values have been estimated by using

$$\sigma = \left( \frac{\sum_{i=1}^{n_{DAT}} (\Delta Q_{exp} - \Delta Q_{calc})^2}{n_{DAT}} \right)^{1/2} \tag{6}$$

where $n_{DAT}$ is the number of experimental points. For eqs 4 and 5, the obtained adjustable parameters $A_p$, α, $B_i$, and $C_i$ are summarized in Tables 5 and 6 together with the standard deviations $\sigma$. On the basis of the obtained standard deviations, we conclude that both eqs 4 and 5 are suitable equations in representing the changes and excess molar volume data for the investigated alcohol + PEGMA systems. Figures 1 and 2 show respectively the values of $V^E$ and $\Delta u$ obtained experimentally and those calculated using eq 4 plotted against the mole fraction of polymer for the four studied systems. The quality of fittig the $V^E$ and $\Delta u$ data to eq 4 or eq 5 is very similar; however, in the case of $\Delta\kappa_s$ a smotter curve is obtained with eq 5 as can be seen from the comparison of Figure 3, panels a and b. In fitting the physical properties to eq 4, we found that the three-degree polynomial is suitable in representing the experimental data for all the studied systems. Also, it was found that by increasing the degree of the polynomial in eq 4 the quality of fitting $V^E$ and $\Delta u$ is not changed very much; however, in the case of $\Delta\kappa_s$ when the four-degree polynomial equation is used, rather small standard deviations are obtained for all the investigated systems, as can be seen in Table 5.

**Table 2. Speed of Sound $u$, Density $\rho$, Isentropic Compressibility $\kappa_s$, Change in Speed of Sound $\Delta u$, Excess Molar Volume $V^E$, and Change in Isentropic Compressibility $\Delta\kappa_s$ for the System Ethanol (1) + PEGMA 360 (2) at 298.15 K**

| $x_2$ | $u$<br>$m\cdot s^{-1}$ | $\Delta u$<br>$m\cdot s^{-1}$ | $\rho$<br>$g\cdot cm^{-3}$ | $V^E$<br>$cm^3\cdot mol^{-1}$ | $\kappa_s$<br>$TPa^{-1}$ | $\Delta\kappa_s$<br>$TPa^{-1}$ |
|---|---|---|---|---|---|---|
| 0 | 1143.22 | 0 | 0.78507 | 0 | 974.62 | 0 |
| 0.0053 | 1152.39 | 7.39 | 0.79462 | −0.048 | 947.64 | −24.04 |
| 0.0116 | 1162.37 | 15.26 | 0.80518 | −0.091 | 919.22 | −48.97 |
| 0.0170 | 1170.74 | 21.78 | 0.81398 | −0.131 | 896.33 | −68.82 |
| 0.0236 | 1180.49 | 29.32 | 0.82412 | −0.184 | 870.74 | −90.75 |
| 0.0306 | 1190.30 | 36.78 | 0.83412 | −0.227 | 846.18 | −111.43 |
| 0.0387 | 1201.16 | 44.90 | 0.84489 | −0.262 | 820.34 | −132.74 |
| 0.0472 | 1211.96 | 52.84 | 0.85554 | −0.308 | 795.76 | −152.62 |
| 0.0559 | 1222.16 | 60.09 | 0.86569 | −0.341 | 773.36 | −170.15 |
| 0.0648 | 1232.21 | 67.15 | 0.87536 | −0.374 | 752.39 | −186.16 |
| 0.0821 | 1250.36 | 79.47 | 0.89255 | −0.441 | 716.63 | −212.30 |
| 0.0880 | 1256.03 | 83.17 | 0.89781 | −0.452 | 706.02 | −219.65 |
| 0.1049 | 1271.12 | 92.55 | 0.91208 | −0.501 | 678.57 | −237.69 |
| 0.1203 | 1284.44 | 100.67 | 0.92374 | −0.535 | 656.18 | −251.50 |
| 0.1393 | 1298.97 | 108.83 | 0.93663 | −0.572 | 632.75 | −264.39 |
| 0.1605 | 1313.50 | 116.21 | 0.94946 | −0.609 | 610.47 | −274.89 |
| 0.1839 | 1327.81 | 122.62 | 0.96197 | −0.636 | 589.62 | −282.69 |
| 0.2466 | 1359.24 | 132.94 | 0.98891 | −0.681 | 547.33 | −290.11 |
| 0.2768 | 1371.64 | 135.19 | 0.99937 | −0.695 | 531.86 | −288.81 |
| 0.3116 | 1383.82 | 135.66 | 1.00972 | −0.680 | 517.18 | −284.13 |
| 0.3389 | 1392.50 | 135.10 | 1.01705 | −0.685 | 507.07 | −279.04 |
| 0.4030 | 1409.63 | 130.65 | 1.03151 | −0.666 | 487.88 | −262.55 |
| 0.4807 | 1426.10 | 120.89 | 1.04533 | −0.622 | 470.38 | −236.83 |
| 0.5741 | 1441.39 | 104.78 | 1.05823 | −0.551 | 454.84 | −200.44 |
| 0.7423 | 1461.03 | 67.70 | 1.07470 | −0.327 | 435.91 | −125.80 |
| 0.7982 | 1466.09 | 54.04 | 1.07911 | −0.292 | 431.13 | −99.49 |
| 0.8390 | 1469.27 | 43.39 | 1.08195 | −0.244 | 428.14 | −79.79 |
| 0.9222 | 1475.36 | 21.34 | 1.08698 | −0.108 | 422.65 | −38.96 |
| 1.0000 | 1480.11 | 0 | 1.09111 | 0 | 418.36 | 0 |

**Table 3. Speed of Sound $u$, Density $\rho$, Isentropic Compressibility $\kappa_s$, Change in Speed of Sound $\Delta u$, Excess Molar Volume $V^E$, and Change in Isentropic Compressibility $\Delta\kappa_s$ for the System 2-Propanol (1) + PEGMA 360 (2) at 298.15 K**

| $x_2$ | $u$<br>$m\cdot s^{-1}$ | $\Delta u$<br>$m\cdot s^{-1}$ | $\rho$<br>$g\cdot cm^{-3}$ | $V^E$<br>$cm^3\cdot mol^{-1}$ | $\kappa_s$<br>$TPa^{-1}$ | $\Delta\kappa_s$<br>$TPa^{-1}$ |
|---|---|---|---|---|---|---|
| 0 | 1138.98 | 0 | 0.78086 | 0 | 987.18 | 0 |
| 0.0070 | 1148.23 | 6.85 | 0.79028 | −0.026 | 959.76 | −23.42 |
| 0.0144 | 1157.26 | 13.36 | 0.79973 | −0.051 | 933.67 | −45.31 |
| 0.0221 | 1166.24 | 19.73 | 0.80902 | −0.074 | 908.79 | −65.84 |
| 0.0310 | 1176.31 | 26.75 | 0.81938 | −0.103 | 882.00 | −87.54 |
| 0.0396 | 1185.56 | 33.05 | 0.82884 | −0.126 | 858.39 | −106.24 |
| 0.0501 | 1196.25 | 40.19 | 0.83966 | −0.155 | 832.24 | −126.44 |
| 0.0601 | 1206.03 | 46.53 | 0.84949 | −0.181 | 809.33 | −143.64 |
| 0.0715 | 1216.46 | 53.10 | 0.85984 | −0.200 | 785.94 | −160.59 |
| 0.0839 | 1227.35 | 59.76 | 0.87049 | −0.223 | 762.61 | −176.86 |
| 0.0986 | 1239.62 | 67.01 | 0.88228 | −0.252 | 737.60 | −193.52 |
| 0.1162 | 1253.40 | 74.79 | 0.89523 | −0.276 | 711.03 | −210.07 |
| 0.1322 | 1265.07 | 80.99 | 0.90614 | −0.298 | 689.57 | −222.40 |
| 0.1498 | 1277.02 | 86.94 | 0.91715 | −0.316 | 668.60 | −233.36 |
| 0.1744 | 1292.52 | 94.04 | 0.93113 | −0.336 | 642.86 | −245.12 |
| 0.1972 | 1305.68 | 99.42 | 0.94291 | −0.355 | 622.10 | −252.89 |
| 0.2281 | 1321.83 | 105.06 | 0.95713 | −0.372 | 597.97 | −259.47 |
| 0.2597 | 1336.69 | 109.11 | 0.97007 | −0.384 | 576.95 | −262.49 |
| 0.2999 | 1353.29 | 112.02 | 0.98442 | −0.385 | 554.68 | −261.94 |
| 0.3450 | 1369.89 | 113.19 | 0.99851 | −0.396 | 533.67 | −257.24 |
| 0.4003 | 1386.94 | 111.39 | 1.01317 | −0.389 | 513.10 | −246.36 |
| 0.4672 | 1404.49 | 106.14 | 1.02801 | −0.366 | 493.14 | −228.30 |
| 0.5440 | 1421.14 | 96.58 | 1.04208 | −0.325 | 475.14 | −202.60 |
| 0.6076 | 1432.89 | 86.61 | 1.05193 | −0.292 | 463.01 | −178.57 |
| 0.7432 | 1453.18 | 60.71 | 1.06886 | −0.206 | 443.04 | −121.39 |
| 0.8415 | 1464.84 | 38.82 | 1.07862 | −0.141 | 432.07 | −76.43 |
| 0.9427 | 1475.10 | 14.51 | 1.08695 | −0.049 | 422.81 | −28.16 |
| 1.0000 | 1480.11 | 0 | 1.09111 | 0 | 418.36 | 0 |

Figure 1 shows that the excess molar volume is negative. Mainly, the behavior of $V^E$ is related to the intermolecular interactions between the hydrogen atom of the alcohol and the oxygen atoms of the poly(ethylene glycol) methacrylate and the difference between the size of alcohol and polymer. Strong hydrogen bond interactions between PEGMA and alcohol are consistent with the obtained negative excess molar volumes. Recently from isopiestic studies on these systems,[8] the solvent

**Table 4. Speed of Sound $u$, Density $\rho$, Isentropic Compressibility $\kappa_S$, Change in Speed of Sound $\Delta u$, Excess Molar Volume $V^E$, and Change in Isentropic Compressibility $\Delta\kappa_S$ for the System 1-Butanol (1) + PEGMA 360 (2) at 298.15 K**

| | $u$ | $\Delta u$ | $\rho$ | $V^E$ | $\kappa_S$ | $\Delta\kappa_S$ |
|---|---|---|---|---|---|---|
| $x_2$ | $m\cdot s^{-1}$ | $m\cdot s^{-1}$ | $g\cdot cm^{-3}$ | $cm^3\cdot mol^{-1}$ | $TPa^{-1}$ | $TPa^{-1}$ |
| 0 | 1240.44 | 0 | 0.80589 | 0 | 806.44 | 0 |
| 0.0086 | 1246.22 | 3.73 | 0.81457 | −0.009 | 790.46 | −12.61 |
| 0.0167 | 1251.51 | 7.08 | 0.82243 | −0.019 | 776.30 | −23.64 |
| 0.0259 | 1257.32 | 10.67 | 0.83105 | −0.030 | 761.16 | −35.18 |
| 0.0378 | 1264.74 | 15.23 | 0.84160 | −0.044 | 742.84 | −48.89 |
| 0.0491 | 1271.35 | 19.15 | 0.85101 | −0.056 | 727.00 | −60.36 |
| 0.0603 | 1277.71 | 22.83 | 0.85990 | −0.067 | 712.34 | −70.67 |
| 0.0748 | 1285.72 | 27.35 | 0.87081 | −0.079 | 694.68 | −82.68 |
| 0.0855 | 1291.31 | 30.37 | 0.87837 | −0.087 | 682.75 | −90.46 |
| 0.1040 | 1300.62 | 35.26 | 0.89066 | −0.101 | 663.72 | −102.33 |
| 0.1199 | 1308.27 | 39.10 | 0.90051 | −0.110 | 648.81 | −111.07 |
| 0.1302 | 1312.92 | 41.28 | 0.90657 | −0.118 | 639.91 | −115.98 |
| 0.1593 | 1325.84 | 47.22 | 0.92244 | −0.134 | 616.71 | −127.89 |
| 0.1704 | 1330.49 | 49.21 | 0.92807 | −0.139 | 608.69 | −131.58 |
| 0.1987 | 1341.69 | 53.63 | 0.94138 | −0.151 | 590.10 | −139.20 |
| 0.2356 | 1354.94 | 58.03 | 0.95691 | −0.161 | 569.23 | −145.74 |
| 0.2564 | 1361.89 | 59.99 | 0.96487 | −0.168 | 558.79 | −148.12 |
| 0.3026 | 1376.14 | 63.17 | 0.98081 | −0.179 | 538.38 | −150.59 |
| 0.3415 | 1386.78 | 64.48 | 0.99262 | −0.181 | 523.85 | −150.04 |
| 0.3850 | 1397.48 | 64.74 | 1.00437 | −0.176 | 509.82 | −147.19 |
| 0.4493 | 1411.55 | 63.44 | 1.01950 | −0.170 | 492.29 | −139.77 |
| 0.5152 | 1423.92 | 59.99 | 1.03277 | −0.166 | 477.56 | −128.93 |
| 0.5844 | 1435.28 | 54.77 | 1.04471 | −0.150 | 464.66 | −114.99 |
| 0.6810 | 1448.73 | 45.05 | 1.05865 | −0.099 | 450.06 | −92.12 |
| 0.7242 | 1453.86 | 39.83 | 1.06433 | −0.131 | 444.51 | −80.89 |
| 0.8008 | 1462.46 | 30.10 | 1.07299 | −0.089 | 435.75 | −59.95 |
| 0.8325 | 1465.44 | 25.50 | 1.07631 | −0.085 | 432.64 | −50.75 |
| 0.9029 | 1472.05 | 15.21 | 1.08287 | −0.014 | 426.16 | −29.92 |
| 1.0000 | 1480.11 | 0 | 1.09111 | 0 | 418.36 | 0 |

activity data and the Flory−Huggins parameters were obtained, and it was concluded that, by increasing the methylene group, the interaction between the oxygen atom of the PEGMA and the OH of the alcohol is increased. However, considering the molar volumes or sizes of these alcohols, which are in the order 1-butanol > 2-propanol > ethanol > methanol, we expect the effect due to packing of the unlike molecules to be in the order methanol > ethanol > 2-propanol > 1-butanol. Our results are consistent with this viewpoint, and the obtained order methanol > ethanol > 2-propanol > 1-butanol for the $V^E$ values indicate that in comparison with the contributions due to the unlike interactions, the packing effect has the dominant effect in $V^E$ values of these systems. The difference between the size of alcohol and polymer is the main reason for the packing effect. Since PEGMA is bulkier than the different alcohols considered

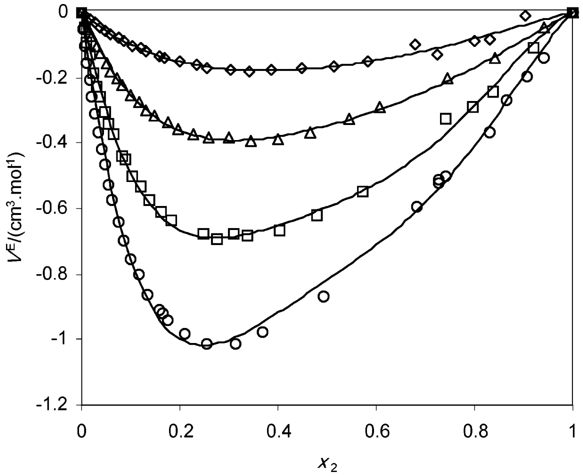

**Figure 1.** Excess molar volumes $V^E$/(cm$^3\cdot$mol$^{-1}$), plotted against mole fraction of polymer $x_2$, for alcohol + PEGMA systems: ◇, 1-butanol; △, 2-propanol; □, ethanol; ○, methanol. Lines were generated from fitting of the experimental data to the Redlich−Kister equation (eq 4).

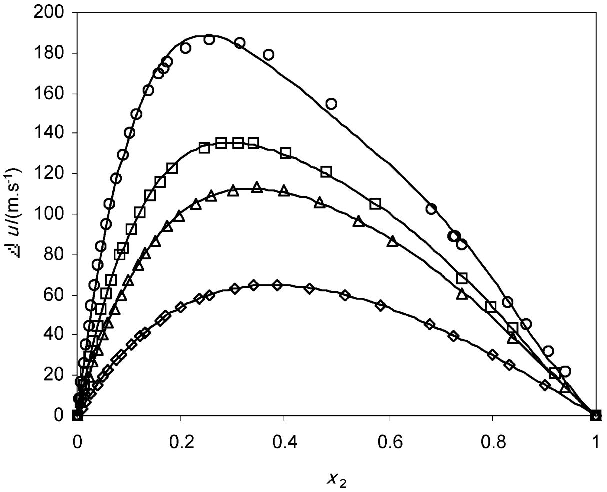

**Figure 2.** Changes in speed of sound $\Delta u$/(m$\cdot$s$^{-1}$), plotted against mole fraction of polymer $x_2$, for alcohol + PEGMA systems: ◇, 1-butanol; △, 2-propanol; □, ethanol; ○, methanol. Lines were generated from fitting of the experimental data to the Redlich−Kister equation (eq 4).

**Table 5. Correlation Parameters of Equation 4 and Standard Deviations, $\sigma$, for Alcohol (1) + PEGMA 360 (2) at 298.15 K**

| | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|
| | | | PEGMA + Methanol | | | |
| $\Delta u$/(m$\cdot$s$^{-1}$) | 587.680 | 430.442 | 561.728 | 497.434 | | 2.92 |
| $V^E$/(cm$^3\cdot$mol$^{-1}$) | −3.268 | −2.036 | −3.121 | −2.890 | | 0.02 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −1010.438 | −638.195 | −1741.573 | −2229.025 | | 19.12 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −1202.307 | −711.358 | 137.685 | −1935.690 | −2812.369 | 9.32 |
| | | | PEGMA + Ethanol | | | |
| $\Delta u$/(m$\cdot$s$^{-1}$) | 468.354 | 294.200 | 275.413 | 244.897 | | 1.03 |
| $V^E$/(cm$^3\cdot$mol$^{-1}$) | −2.382 | −1.241 | −1.646 | −2.057 | | 0.02 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −899.537 | −539.316 | −965.524 | −1309.625 | | 8.00 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −938.807 | −665.086 | −275.922 | −942.124 | −1226.721 | 4.16 |
| | | | PEGMA + 2-Propanol | | | |
| $\Delta u$/(m$\cdot$s$^{-1}$) | 408.341 | 229.290 | 160.714 | 115.020 | | 0.55 |
| $V^E$/(cm$^3\cdot$mol$^{-1}$) | −1.385 | −0.799 | −0.750 | −0.577 | | 0.01 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −857.965 | −540.737 | −718.382 | −822.195 | | 4.64 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −879.659 | −618.979 | −315.755 | −619.097 | −711.310 | 2.15 |
| | | | PEGMA + 1-Butanol | | | |
| $\Delta u$/(m$\cdot$s$^{-1}$) | 243.725 | 115.595 | 51.622 | 22.459 | | 0.11 |
| $V^E$/(cm$^3\cdot$mol$^{-1}$) | −0.667 | −0.308 | −0.156 | −0.171 | | 0.01 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −522.026 | −323.743 | −298.737 | −266.630 | | 1.26 |
| $\Delta\kappa_S$/(TPa$^{-1}$) | −528.878 | −339.977 | −188.196 | −214.015 | −202.125 | 0.49 |

**Table 6. Correlation Parameters of Equation 5 and Standard Deviations, $\sigma$, for Alcohol (1) + PEGMA 360 (2) at 298.15 K**

| | $\alpha$ | $B_0$ | $B_1$ | $C_0$ | $C_1$ | $C_2$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| | | | PEGMA + Methanol | | | | |
| $\Delta u/(\mathrm{m \cdot s^{-1}})$ | −7.347 | 284.196 | −4.799 | 68.952 | −5.926 | −74.878 | 0.52 |
| $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ | −4.393 | −2.404 | −0.010 | −0.572 | −0.004 | 0.569 | 0.03 |
| $\Delta\kappa_s/(\mathrm{TPa^{-1}})$ | −6.134 | −0.082 | 54.258 | 14.060 | 47.764 | 33.720 | 3.34 |
| | | | PEGMA + Ethanol | | | | |
| $\Delta u/(\mathrm{m \cdot s^{-1}})$ | −4.076 | 224.736 | −0.015 | 47.130 | −9.046 | −56.203 | 0.71 |
| $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ | −3.990 | −1.677 | −0.006 | −0.393 | −0.001 | 0.392 | 0.02 |
| $\Delta\kappa_s/(\mathrm{TPa^{-1}})$ | −5.410 | 0.080 | 48.578 | 16.660 | 48.174 | 31.530 | 1.54 |
| | | | PEGMA + 2-Propanol | | | | |
| $\Delta u/(\mathrm{m \cdot s^{-1}})$ | −2.535 | 0.076 | −0.038 | −40.351 | −44.678 | −4.576 | 1.40 |
| $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ | −3.036 | −1.078 | −0.009 | −0.236 | −0.001 | 0.236 | 0.01 |
| $\Delta\kappa_s/(\mathrm{TPa^{-1}})$ | −3.356 | −0.028 | 0.002 | 49.705 | 54.537 | 5.486 | 8.51 |
| | | | PEGMA + 1-Butanol | | | | |
| $\Delta u/(\mathrm{m \cdot s^{-1}})$ | −2.320 | 73.205 | −0.002 | −1.170 | −19.463 | −18.316 | 0.09 |
| $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ | −3.788 | −0.164 | 0.014 | −0.019 | 0.038 | 0.057 | 0.01 |
| $\Delta\kappa_s/(\mathrm{TPa^{-1}})$ | −4.209 | −0.005 | 29.139 | 18.309 | 40.150 | 21.848 | 0.22 |

in this study, it may accommodate alcohol molecules in the voids. Considering the smaller size of the methanol as compared with the other alcohols, we expect this packing effect has a greater effect on the obtained excess volume of the PEGMA + methanol system. This is indeed what we observe in Figure 1.

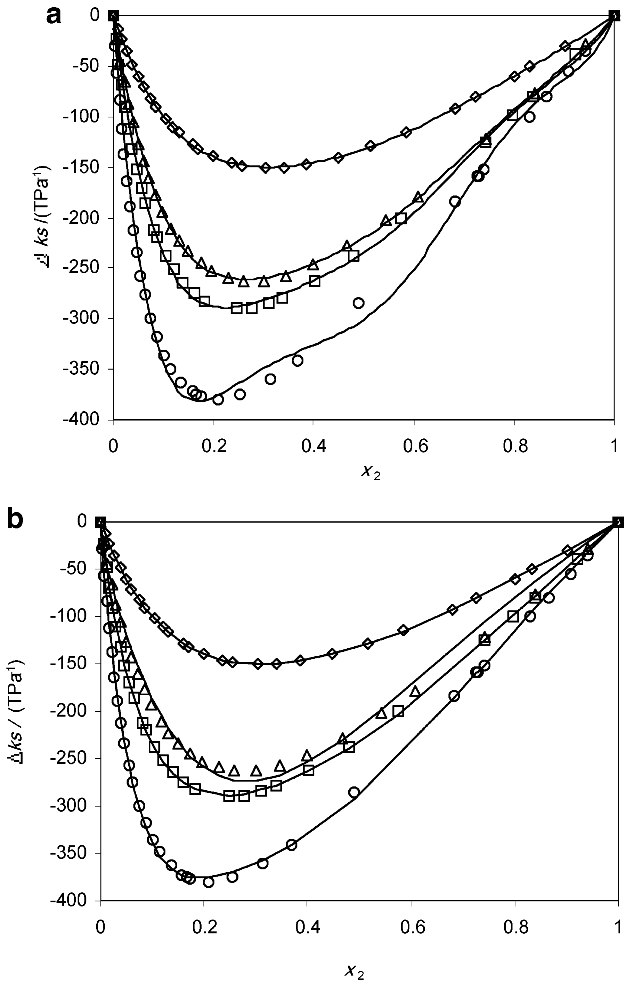

**Figure 3.** Changes in isentropic compressibility $\Delta\kappa_s/(\mathrm{TPa^{-1}})$, plotted against mole fraction of polymer $x_2$, for alcohol + PEGMA systems: ◇, 1-butanol; △, 2-propanol; □, ethanol; ○, methanol. Panels a and b show respectively the lines generated from fitting of experimental $\Delta\kappa_s$ data to the Redlich−Kister equation (eq 4) and Ott et al. equation (eq 5).

## Conclusions

Accurate experimental density and sound velocity data were obtained for the systems PEGMA + methanol, + ethanol, +2-propanol, and + 1-butanol at $T = 298.15$ K. From the experimental density data, values of the excess molar volumes were calculated. The excess molar volumes for all these systems were found to be negative and whose magnitude has the order of $V^E$ (PEGMA + methanol) > $V^E$ (PEGMA + ethanol) > $V^E$ (PEGMA + 2-propanol) > $V^E$ (PEGMA + 1-butanol). The Redlich−Kister and Ott et al. equations have been used for the correlation of the experimental excess molar volumes as well as changes in speed of sound and isentropic compressibility. Good agreement was obtained with the experimental data with both equations, especially using the Ott et al. equation.

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