# Temperature Dependence of the Densities and Speeds of Sound of the Binary Solutions of $LiClO_4$ with Diethyl Ether, Tetrahydrofuran, Acetone, and Ethyl Acetate

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Densities, $\rho$, and speeds of sound, $u$, of the solutions of $LiClO_4$ with diethyl ether, tetrahydrofuran, acetone, and ethyl acetate are reported from 288.15 K to 338.15 K. At 298.15 K, measurements have been made up to $\approx$ 5.37, 1.12, 4.78, and 3.61 mol kg$^{-1}$ of $LiClO_4$ in diethyl ether, tetrahydrofuran, acetone, and ethyl acetate, respectively. At other temperatures, densities and sound velocities are measured to $m$ < 0.2 mol kg$^{-1}$ in order to calculate the infinite dilution apparent molal volumes, $\phi_V{}^o$, and compressibilities, $\phi_K{}^o$, in different solvents. The $\rho$ and $u$ data for these solutions can be analyzed by Pitzer equations with average standard deviations, $\sigma$, as 0.08 kg m$^{-3}$ and 0.5 m s$^{-1}$, respectively.

## Introduction

The aqueous and nonaqueous solutions of salt are proving to be valuable agents in enhancing the reaction rates of Diels−Alder reactions, benzoin condensation, Claissen rearrangement, etc.[1] In the process of examining the possible origin of forces responsible for such impressive rate enhancement, we recently attempted to study the applications of energy and volume parameters derived from experimental volumetric data of these systems in developing significant correlations involved in the reaction kinetics of the Diels−Alder reactions.[2] Solutions of $LiClO_4$ with diethyl ether, tetrahydrofuran, acetone, and ethyl acetate have been effectively used in the recent synthetic work.[3,4]

In this article, we present experimental density, $\rho$, and speeds of sound, $u$, data of $LiClO_4$ + diethyl ether, + tetrahydrofuran, + acetone, and + ethyl acetate at 298.15 K and analyze them using the specific ion-interaction theory. We have also measured these properties in low concentration ($m$ < 0.2 mol kg$^{-1}$ of $LiClO_4$) at 288.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K for determining the infinite dilution apparent molal volume, $\phi_V{}^o$, and compressibility, $\phi_K{}^o$, of $LiClO_4$ in different solvents. A thorough literature search reveals that the experimental data on these systems are not available. There are a few papers with only abstracts in the earlier Russian journals, which are not accessible to readers.

## Experimental Section

All the solvents employed in the present investigation procured from Aldrich were high-purity AR grade. Solvents were dried before use.[5] $LiClO_4$ (Aldrich) was used as such after heating it to 150 °C for about 5 h and then cooling to room temperature. Due care was taken to keep $LiClO_4$ moisture free.

Densities were measured by a pycnometer with a volume of $50 \times 10^{-6}$ m$^3$ with a precision of ±0.005%. The pycnometer was calibrated against the densities of aqueous NaCl solutions with an agreement of 0.01%.[6] An ultrasonic interferometer (Mittal Enterprises) was used to measure the sound velocities in solutions at 2 MHz. The interferometer was calibrated against the literature data on NaCl solutions with an accuracy of ±0.05%.[7] The sound velocities were precise to within 0.01%. The temperature for all the measurements was kept constant to within 0.05 K. The solutions were prepared by mass on a single-pan Mettler balance within the accuracy of 0.01 mg. The molalities were accurate to within $2 \times 10^{-4}$ mol kg$^{-1}$.

## Results and Discussion

The experimental density, $\rho$, and speed of sound, $u$, data as a function of concentration, $m$, for $LiClO_4$ + diethyl ether, + tetrahydrofuran, + acetone, and + ethyl acetate systems at 298.15 K are listed in Table 1. The experimental data on the $LiClO_4$ + tetrahydrofuran system were collected up to $m \approx 1.75$ mol kg$^{-1}$ owing to limited solubility of $LiClO_4$ in tetrahydrofuran. As pointed out above, there are limited compilations to compare our data. However, there exists good agreement between our and reported density values (with an average error of 0.011%) for $LiClO_4$ + diethyl ether solutions.[8] The density or speeds of sound ($y$) for these systems are fitted by a nonlinear least-squares method using commercially available ORIGIN v 5.0 supplied by Microcal Inc. USA to the equation of the form

$$y = y_0 + am^{1/2} + bm + cm^{3/2} + dm^2 + em^{5/2} \qquad (1)$$

where $a$−$e$ are the adjustable parameters and $y_0$ is density or speed of sound ($y_0 = \rho^0$ or $y_0 = u^0$) of the pure solvent. Adjustable parameters (with their errors) obtained from the regression of both the $\rho$ and $u$ up to high concentrations for all the four systems at 298.15 K are listed in Table 2 together with average standard deviation of fits, $\sigma$. For clarity, parameters $a$−$e$ are used for the density correlation while $a^o$−$e^o$ indicate the parameters for the speed of sound. These density and sound velocity data can be employed to calculate the adiabatic compressibility, $\beta$ (by the Laplace equation), apparent molal volume, $\phi_V$, and compressibility, $\phi_K$, using the standard definitions.[6,7] At temperatures other than 298.15 K, we measured both the $\rho$ and $u$ in dilute concentrations of $LiClO_4$ ($m$ < 0.2 mol kg$^{-1}$) only in order to calculate the $\phi_V{}^o$ and $\phi_K{}^o$ in different solvents. The $\rho$ and

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**Table 1. Experimental Densities, $\rho$, and Speeds of Sound, $u$, of the $LiClO_4$ in Diethyl Ether, Tetrahydrofuran, Acetone, and Ethyl Acetate Solutions at 298.15 K**

| $m$ (mol kg$^{-1}$) | $\rho$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $m$ (mol kg$^{-1}$) | $\rho$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) |
|---|---|---|---|---|---|
| $LiClO_4$ + diethyl ether | | | | | |
| 0 | 707.6 | 990.9 | 1.1121 | 798.6 | 1172.3 |
| 0.0459 | 711.2 | 1001.3 | 1.3959 | 822.7 | 1214.1 |
| 0.0989 | 715.2 | 1008.9 | 2.6805 | 958.8 | 1446.5 |
| 0.1352 | 718.9 | 1016.7 | 3.6997 | 1129.9 | 1704.5 |
| 0.1798 | 721.7 | 1023.2 | 4.5023 | 1313.8 | 1980.1 |
| 0.1958 | 723.4 | 1025.7 | 5.0459 | 1522.6 | 2259.6 |
| 0.2823 | 729.8 | 1045.7 | 5.3699 | 1755.5 | 2577.8 |
| 0.8432 | 775.4 | 1128.7 | | | |
| $LiClO_4$ + Tetrahydrofuran | | | | | |
| 0 | 878.8 | 1189.9 | 0.8639 | 1011.1 | 1411.2 |
| 0.0317 | 881.1 | 1195.0 | 1.0612 | 1048.7 | 1450.6 |
| 0.0848 | 895.0 | 1206.8 | 1.2483 | 1088.9 | 1495.6 |
| 0.1223 | 900.7 | 1214.9 | 1.4194 | 1135.2 | 1536.4 |
| 0.1662 | 906.4 | 1225.9 | 1.5110 | 1152.2 | 1554.1 |
| 0.1913 | 910.4 | 1230.3 | 1.5797 | 1183.0 | 1571.3 |
| 0.2241 | 913.8 | 1235.6 | 1.7563 | 1121.6 | 1605.7 |
| 0.6583 | 975.2 | 1344.9 | | | |
| $LiClO_4$ + Acetone | | | | | |
| 0 | 784.4 | 1007.9 | 1.2168 | 914.7 | 1245.7 |
| 0.0435 | 788.7 | 1014.1 | 2.3174 | 1075.7 | 1491.8 |
| 0.0891 | 794.4 | 1024.9 | 3.1774 | 1263.2 | 1721.8 |
| 0.1346 | 799.7 | 1034.1 | 3.9264 | 1444.1 | 1922.2 |
| 0.2528 | 809.0 | 1057.3 | 4.3941 | 1669.6 | 2080.8 |
| 0.7466 | 860.2 | 1151.6 | 4.7829 | 1892.3 | 2215.3 |
| 0.9839 | 886.9 | 1196.9 | | | |
| $LiClO_4$ + Ethyl Acetate | | | | | |
| 0 | 894.3 | 1031.9 | 0.8689 | 1010.2 | 1240.7 |
| 0.0317 | 898.7 | 1037.2 | 1.0672 | 1043.4 | 1293.4 |
| 0.0785 | 905.0 | 1048.7 | 2.0279 | 1235.4 | 1564.6 |
| 0.1255 | 910.2 | 1061.2 | 2.7037 | 1428.6 | 1795.4 |
| 0.1662 | 916.6 | 1069.8 | 3.2317 | 1663.1 | 1959.7 |
| 0.2219 | 921.9 | 1079.9 | 3.6101 | 1916.7 | 2041.1 |
| 0.6560 | 979.9 | 1193.0 | | | |

**Table 2. Parameters of Eq 1 for Correlating $\rho$ and $u$ with $m$ up to High Concentrations of the $LiClO_4$ in Diethyl Ether, Tetrahydrofuran, Acetone, and Ethyl Acetate Solutions at 298.15 K**

| params | $LiClO_4$ + diethyl ether | $LiClO_4$ + tetrahydrofuran | $LiClO_4$ + acetone | $LiClO_4$ + ethyl acetate |
|---|---|---|---|---|
| $\rho$ Values | | | | |
| $\rho^0$ (kg m$^{-3}$) | 707.6 | 878.8 | 784.4 | 894.3 |
| $a$ (kg$^{1.5}$ m$^{-3}$ mol$^{-0.5}$) | 218.5 ± 1.2 | 24.66 ± 0.55 | 178.9 ± 2.20 | 145.3 ± 1.91 |
| $b$ (kg$^2$ m$^{-3}$ mol$^{-1}$) | −959 ± 8 | 106.58 ± 2.11 | −806 ± 7 | −684 ± 6 |
| $c$ (kg$^{2.5}$ m$^{-3}$ mol$^{-1.5}$) | 1542 ± 18 | −48.4 ± 1.1 | 1412 ± 19 | 1448 ± 20 |
| $d$ (kg$^3$ m$^{-3}$ mol$^{-2}$) | −911 ± 6 | 76.58 ± 0.59 | −872 ± 9 | −1047 ± 25 |
| $e$ (kg$^{3.5}$ m$^{-3}$ mol$^{-2.5}$) | 190.8 ± 12 | 0 | 194.9 ± 6.4 | 279 ± 9 |
| $\sigma$ (kg m$^{-3}$) | 0.03 | 0.02 | 0.01 | 0.02 |
| $u$ Values | | | | |
| $u^0$ (ms$^{-1}$) | 990.9 | 1189.9 | 1007.9 | 1031.9 |
| $a°$ (m kg$^{0.5}$ s$^{-1}$ mol$^{-0.5}$) | 286.0 ± 1.7 | 5.54 ± 0.11 | 16.64 ± 0.94 | −150.09 ± 2.6 |
| $b°$ (m kg s$^{-1}$ mol$^{-1}$) | −1135± 13 | 109.3 ± 6.4 | 110.47 ± 0.65 | 1026 ± 17 |
| $c°$ (m kg$^{1.5}$ s$^{-1}$ mol$^{-1.5}$) | 1909 ± 28 | 255.4 ± 7 | 111.31 ± 2.5 | −1355 ± 16 |
| $d°$ (m kg$^2$ s$^{-1}$ mol$^{-2}$) | −1136 ± 15 | −122.72 ± 5.9 | −62.80 ± 1.72 | 929 ± 12 |
| $e°$ (m kg$^{2.5}$ s$^{-1}$ mol$^{-2.5}$) | 239.2 ± 3.6 | 0 | 18.26 ± 1.98 | −211.16 ± 7.3 |
| $\sigma$ (m s$^{-1}$) | 0.6 | 0.8 | 0.2 | 0.3 |

$u$ data of the solutions of $LiClO_4$ in four solvents in low concentration range at 288.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K are listed in Table 3. We describe these data using eq 1 with only 2 parameters i.e., $a$, $b$ and $a^o$, $b^o$. The parameters $a$, $b$ are used for $\rho$, while the $a^o$, $b^o$ parameters are for $u$. These temperature-dependent adjustable parameters as calculated from the data in the dilute solutions (below $m = 0.2$ mol kg$^{-1}$) of $LiClO_4$ in all the four solutions at 288.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K are listed in Table 4. These adjustable parameters at 298.15 K were obtained from the experimental density and speeds of sound data below $m = 0.2$ mol kg$^{-1}$ reported in Table 1. It should be noted that eq 1 with five adjustable parameters was used to fit the density and speeds of sound data up to high concentrations at 298.15 K. On the other hand, only two adjustable parameters were required to fit these data at low concentrations for all the temperatures, including at 298.15 K. These dilute range data when converted to $\phi_V$ and $\phi_K$ were used to estimate $\phi_V{}^o$ and $\phi_K{}^o$ at different temperatures as described earlier.[9,10] These values can be represented by a temperature-dependent polynomial expression as

$$\phi^o = q_1 + q_2(T - T_{ref}) + q_3(T - T_{ref})^2 \qquad (2)$$

with $T_{ref} = 298.15$ K. The values of $q_1$, $q_2$, and $q_3$ together with uncertainties for all the systems are recorded in Table 5. Figure 1a, and b shows the temperature dependence of $\phi_V{}^o$ and $\phi_K{}^o$, respectively, in the $LiClO_4$ + diethyl ether, + tetrahydrofuran, + acetone, and + ethyl acetate solutions.

**Table 3. Experimental Density, $\rho$, and Speeds of Sounds, $u$, of the $LiClO_4$ + Diethyl Ether, + Tetrahydrofran, + Acetone, and + Ethyl Acetate Solutions up to $m$ < 0.2 mol kg$^{-1}$ at 288.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K**

| $m$ (mol kg$^{-1}$) | $\rho$ (kg m$^{-3}$) | $u$ (ms$^{-1}$) | $m$ (mol kg$^{-1}$) | $\rho$ (kg m$^{-3}$) | $u$ (ms$^{-1}$) |
|---|---|---|---|---|---|
| $LiClO_4$ + Diethyl Ether | | | | | |
| $T$ = 288.15 K | | | | | |
| 0 | 724.8 | 1130.4 | 0.0994 | 737.4 | 1309.4 |
| 0.0378 | 728.1 | 1190.4 | 0.1221 | 740.5 | 1370.3 |
| 0.0652 | 733.3 | 1250.4 | 0.1495 | 744.6 | 1420.2 |
| $T$ = 308.15 K | | | | | |
| 0 | 667.5 | 970.9 | 0.0882 | 678.3 | 987.2 |
| 0.0251 | 672.3 | 975.4 | 0.1198 | 680.1 | 992.5 |
| 0.0555 | 676.4 | 980.6 | 0.1523 | 683.3 | 1001.0 |
| $T$ = 318.15 K | | | | | |
| 0 | 656.3 | 950.9 | 0.1017 | 660.1 | 969.3 |
| 0.0252 | 657.5 | 956.2 | 0.1335 | 664.3 | 975.4 |
| 0.0592 | 658.7 | 961.1 | 0.1614 | 668.6 | 978.5 |
| $T$ = 328.15 K | | | | | |
| 0 | 644.3 | 930.4 | 0.0792 | 650.5 | 944.1 |
| 0.0229 | 646.1 | 934.1 | 0.1017 | 652.1 | 946.8 |
| 0.0484 | 648.5 | 938.6 | 0.1492 | 654.3 | 955.2 |
| $T$ = 338.15 K | | | | | |
| 0 | 632.4 | 912.1 | 0.0594 | 635.1 | 920.7 |
| 0.0352 | 634.7 | 915.8 | 0.1295 | 640.0 | 930.0 |
| 0.1023 | 635.8 | 925.1 | 0.1520 | 644.3 | 933.1 |
| $LiClO_4$ + Tetrahydrofuran | | | | | |
| $T$ = 288.15 K | | | | | |
| 0 | 898.9 | 1210.1 | 0.0812 | 912.4 | 1225.5 |
| 0.0174 | 902.3 | 1213.1 | 0.1140 | 918.3 | 1227.3 |
| 0.0421 | 905.1 | 1218.4 | | | |
| $T$ = 308.15 K | | | | | |
| 0 | 848.8 | 1170.0 | 0.0944 | 855.1 | 1190.2 |
| 0.0199 | 850.3 | 1174.1 | 0.1231 | 860.8 | 1197.3 |
| 0.0512 | 852.4 | 1181.3 | | | |
| $T$ = 318.15 K | | | | | |
| 0 | 838.7 | 1149.1 | 0.0895 | 843.1 | 1167.8 |
| 0.0113 | 840.1 | 1152.2 | 0.1189 | 846.0 | 1175.1 |
| 0.0615 | 841.3 | 1161.3 | | | |
| $T$ = 328.15 K | | | | | |
| 0 | 828.6 | 1128.8 | 0.0644 | 832.1 | 1143.2 |
| 0.0195 | 830.1 | 1133.7 | 0.0922 | 835.0 | 1147.9 |
| 0.0390 | 831.2 | 1138.3 | 0.1221 | 840.3 | 1154.2 |
| $T$ = 338.15 K | | | | | |
| 0 | 817.9 | 1109.0 | 0.0705 | 822.3 | 1123.9 |
| 0.0291 | 819.3 | 1112.7 | 0.1015 | 825.4 | 1130.7 |
| 0.0400 | 821.3 | 1117.0 | | | |
| $LiClO_4$ + Acetone | | | | | |
| $T$ = 288.15 K | | | | | |
| 0 | 801.1 | 1024.9 | 0.0895 | 807.9 | 1048.1 |
| 0.0245 | 802.0 | 1033.2 | 0.1304 | 814.3 | 1056.8 |
| 0.0552 | 804.5 | 1040.4 | | | |
| $T$ = 308.15 K | | | | | |
| 0 | 745.1 | 979.0 | 0.1130 | 751.8 | 1006.5 |
| 0.0344 | 746.2 | 987.8 | 0.1298 | 758.2 | 1010.1 |
| 0.754 | 750.3 | 997.2 | | | |
| $T$ = 318.15 K | | | | | |
| 0 | 734.0 | 957.9 | 0.0951 | 735.9 | 978.8 |
| 0.0114 | 734.1 | 958.5 | 0.1122 | 738.0 | 983.2 |
| 0.0424 | 734.7 | 965.1 | | | |
| $T$ = 328.15 K | | | | | |
| 0 | 723.2 | 933.4 | 0.0954 | 727.2 | 953.0 |
| 0.0254 | 724.5 | 937.1 | 0.1134 | 730.2 | 966.8 |
| 0.0666 | 725.4 | 946.8 | | | |
| $T$ = 338.15 K | | | | | |
| 0 | 711.9 | 905.2 | 0.0758 | 715.8 | 924.1 |
| 0.0135 | 712.5 | 910.4 | 0.1007 | 718.0 | 930.6 |
| 0.0420 | 714.2 | 916.8 | | | |
| $LiClO_4$+ Ethyl Acetate | | | | | |
| $T$ = 288.15 K | | | | | |
| 0 | 912.6 | 1060.7 | 0.0856 | 917.9 | 1080.5 |
| 0.0179 | 913.2 | 1065.2 | 0.1152 | 920.5 | 1090.1 |
| 0.0422 | 915.4 | 1070.2 | 0.1357 | 922.4 | 1095.3 |
| $T$ = 308.15 K | | | | | |
| 0 | 840.6 | 1001.2 | 0.0994 | 867.2 | 1023.8 |
| 0.0343 | 856.8 | 1010.4 | 0.1212 | 868.9 | 1028.8 |
| 0.0751 | 863.4 | 1019.3 | | | |
| $T$ = 318.15 K | | | | | |
| 0 | 841.1 | 969.9 | 0.0811 | 852.1 | 986.8 |
| 0.0314 | 854.7 | 977.0 | 0.0954 | 854.3 | 992.8 |
| 0.0452 | 847.0 | 979.9 | 0.1120 | 856.2 | 997.3 |
| $T$ = 328.15 K | | | | | |
| 0 | 828.6 | 940.1 | 0.0894 | 841.7 | 960.4 |
| 0.0224 | 831.8 | 945.2 | 0.1134 | 843.2 | 967.9 |
| 0.0651 | 837.3 | 950.2 | | | |
| $T$ = 338.15 K | | | | | |
| 0 | 816.6 | 909.9 | 0.0644 | 824.7 | 925.1 |
| 0.0139 | 818.9 | 912.6 | 0.0921 | 827.1 | 930.7 |
| 0.0342 | 821.8 | 918.2 | 0.1125 | 829.0 | 934.8 |

**Table 4. Coefficients of Eq 1 for Correlating the Isothermal $\rho$ and $u$ Data with Concentration (<0.2 M) for $LiClO_4$ in Diethyl Ether, Tetrahydrofuran, Acetone, and Ethyl Acetate Solutions from 288.15 K to 338.15 K**

| | $\rho$ (kg m$^{-3}$) | | | $u$ (m s$^{-1}$) | | |
|---|---|---|---|---|---|---|
| | $\rho^0$ | $a$ | $b$ | $u°$ | $a°$ | $b°$ |
| $T$/K | kg m$^{-3}$ | kg$^{1.5}$ m$^{-3}$ mol$^{-1.5}$ | kg$^2$ m$^{-3}$ mol$^{-1}$ | m s$^{-1}$ | m kg$^{0.5}$ s$^{-1}$ mol$^{-0.5}$ | m kg s$^{-1}$ mol$^{-1}$ |
| | | | $LiClO_4$ + Diethyl Ether | | | |
| 288.15 | 724.9 | −0.868 | 82.801 | 1092.5 | 98.07 | −70.32 |
| 298.15 | 707.6 | −1.65 | 81.91 | 990.9 | 59.21 | −93.59 |
| 308.15 | 667.5 | −0.983 | 75.564 | 965.3 | 55.81 | −67.50 |
| 318.15 | 655.6 | 0.397 | 65.269 | 940.1 | 33.40 | −55.90 |
| 328.15 | 643.4 | 3.343 | 65.173 | 931.0 | 10.63 | −22.59 |
| 338.15 | 632.3 | 5.234 | 69.091 | 900.4 | 6.33 | −8.07 |
| | | | $LiClO_4$ + Tetrahydrofuran | | | |
| 288.15 | 897.8 | 10.51 | 122.58 | 1198.6 | 115.78 | 112.2 |
| 298.15 | 878.8 | 4.22 | 130.10 | 1189.9 | 73.2 | 105.43 |
| 308.15 | 849.4 | −5.75 | 131.15 | 1165.3 | 50.41 | −10.58 |
| 318.15 | 839.5 | −5.96 | 125.53 | 1145.8 | 43.72 | −25.89 |
| 328.15 | 829.5 | −7.98 | 122.17 | 1127.7 | 17.66 | 15.14 |
| 338.15 | 815.5 | −10.62 | 112.21 | 1114.5 | −45.33 | 21.07 |
| | | | $LiClO_4$ + Acetone | | | |
| 288.15 | 802.0 | −9.76 | 118.43 | 1014.1 | 109.36 | −78.55 |
| 298.15 | 784.4 | −2.83 | 113.99 | 1007.9 | 62.11 | −43.55 |
| 308.15 | 747.8 | −4.28 | 114.51 | 976.5 | 38.34 | −67.39 |
| 318.15 | 734.5 | −6.81 | 107.59 | 956.9 | 21.15 | −48.61 |
| 328.15 | 724.2 | −11.37 | 105.09 | 922.1 | 22.15 | −54.15 |
| 338.15 | 712.3 | −14.24 | 96.24 | 902.7 | 36.93 | −133.29 |
| | | | $LiClO_4$ + Ethyl Acetate | | | |
| 288.15 | 899.5 | −4.416 | 144.20 | 1198.0 | 134.55 | 43.53 |
| 298.15 | 894.3 | −2.39 | 137.50 | 1031.9 | 31.62 | 68.01 |
| 308.15 | 872.3 | −1.514 | 109.51 | 970.1 | 84.95 | −154.33 |
| 318.15 | 841.0 | −1.138 | 119.73 | 966.7 | 42.07 | −101.54 |
| 328.15 | 828.9 | −5.181 | 117.52 | 938.4 | 32.61 | −111.22 |
| 338.15 | 816.1 | −1.322 | 111.31 | 908.1 | 29.92 | −134.91 |

**Table 5. Adjustable Parameters of Eq 2 for Correlating $\phi_V°$ and $\phi_K°$ with $T - T_{ref}$ of $LiClO_4$ in Diethyl Ether, Tetrahydrofuran, Acetone, and Ethyl Acetate Solutions**

| | $\phi_V°$ (m$^3$ mol$^{-1}$) | | | | $\phi_K°$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | $10^6 q_1$ | $10^7 q_2$ | $10^9 q_3$ | $10^6\sigma$ ($\phi_V°$) | $10^{13} q_1$ | $10^{14} q_2$ | $10^{13}\sigma$ ($\phi_K°$) |
| system | m$^3$ mol$^{-1}$ | m$^3$ mol$^{-1}$ K$^{-1}$ | m$^3$ mol$^{-1}$ K$^{-2}$ | m$^3$ mol$^{-1}$ | m$^3$ mol$^{-1}$ Pa$^{-1}$ | m$^3$ mol$^{-1}$ Pa$^{-1}$ K$^{-1}$ | m$^3$ mol$^{-1}$ Pa$^{-1}$ |
| $LiClO_4$ + diethyl ether | −5.5 ± 0.1 | 1.87 ± 0.09 | −0.95 ± 0.11 | 0.2 | −11.6 ± 0.3 | 5.82 ± 0.11 | 0.1 |
| $LiClO_4$ + tetrahydrofuran | −39.1 ± 0.5 | 10.31 ± 0.50 | −8.20 ± 0.73 | 0.2 | −47.8 ± 0.7 | 5.12 ± 0.17 | 0.2 |
| $LiClO_4$ + acetone | −19.9 ± 0.4 | 7.00 ± 0.62 | −6.24 ± 0.77 | 0.1 | −86.1 ± 1.3 | 5.77 ± 0.67 | 0.1 |
| $LiClO_4$ + ethyl acetate | −38.7 ± 0.7 | 3.73 ± 0.34 | −0.148 ± 0.030 | 0.1 | −66.2 ± 1.3 | 5.27 ± 0.44 | 0.2 |
| av $\sigma$ | | | | 0.2 | | | 0.2 |

The $\phi_V$ and $\phi_K$ data for these solutions can be analyzed by the specific interaction theory of Pitzer.[11] Though the details of the Pitzer equations are given elsewhere,[12] they are summarized below for a prompt use. The Pitzer equations for $\phi_V$ or $\phi_K$ of a 1:1 electrolyte can be written as

$$\phi = \phi^o + (A/b)\ln(1 + bm^{0.5}) + 2RT[B_{MX}m + C_{MX}m^2] \tag{3}$$

where

$$B_{MX} = \beta^{(0)} + \beta^{(1)}(2/\alpha^2 m)[1 - (1 - \alpha m^{0.5})]\exp(\alpha m^{0.5}) \tag{4}$$

and

$$C_{MX} = 0.5C^{\phi} \tag{5}$$

In eq 3 the second and third terms on the right-hand side of the equation indicate the Debye−Huckel and virial coefficient expressions, respectively. The Pitzer−Debye−Huckel limiting slope values, $A$ for $\phi_V$ and $\phi_K$, were calculated as described by Ananthaswamy and Atkinson.[13] The dielectric constants of the solvents were taken from Marcus.[14] The terms, $\partial D/\partial P$ and $\partial\beta/\partial P$ for each solvent were computed from the experimental data listed elsewhere.[5,8,14] The input values for $\partial D/\partial P$ for diethyl ether, tetrahydrofuran, acetone, and ethyl acetate were $1.1 \times 10^{-3}$, $2.2 \times 10^{-3}$, $2.8 \times 10^{-3}$, and $1.8 \times 10^{-3}$, respectively. Similarly, the values of $\partial\beta/\partial P$ for diethyl ether, tetrahydrofuran, acetone, and ethyl acetate were $0.29 \times 10^{-13}$, $0.81 \times 10^{-13}$, $0.22 \times 10^{-13}$ and $0.61 \times 10^{-13}$ Pa$^{-2}$, respectively. The values of $\partial^2 \ln D/\partial P^2$ for all the solvents were assigned as zero due to their negligible magnitudes. Thus, the values of $A$ used in the case of volumes are $0.181 \times 10^{-6}$ m$^3$ kg$^{1/2}$ mol$^{-3/2}$, $0.468 \times 10^{-6}$ m$^3$ kg$^{1/2}$ mol$^{-3/2}$, $1.991 \times 10^{-6}$ m$^3$ kg$^{1/2}$ mol$^{-3/2}$, and $0.334 \times 10^{-6}$ m$^3$ kg$^{1/2}$ mol$^{-3/2}$ for diethyl ether, tetrahydrofuran, acetone, and ethyl acetate, respectively. Similarly, for compressibilities the values of $A$ as calculated for diethyl ether, tetrahydrofuran, acetone, and ethyl acetate are $-0.391 \times 10^{-17}$ m$^3$ kg $^{1/2}$ mol$^{-3/2}$ Pa$^{-1}$, $-1.011 \times 10^{-17}$ m$^3$ kg $^{1/2}$ mol$^{-3/2}$ Pa$^{-1}$, $-4.29 \times 10^{-17}$ m$^3$ kg $^{1/2}$ mol$^{-3/2}$ Pa$^{-1}$, and $-0.721 \times 10^{-17}$ m$^3$ kg $^{1/2}$ mol$^{-3/2}$ Pa$^{-1}$, respectively. In the case of $\phi_V$, the parameters $B_{MX}$ and $C_{MX}$ are comprised of $(\partial\beta^{(0)}/\partial P)_T$, $(\partial\beta^{(1)}/\partial P)_T$, and $(\partial C^{\phi}/\partial P)_T$. The second pressure derivatives, $(\partial^2\beta^{(0)}/\partial P^2)_T$, $(\partial\,^2\beta^{(1)}/\partial P^2)_T$, and $(\partial^2 C^{\phi}/\partial P^2)$, are used for correlating $\phi_K$ with concentration. $\alpha$ and $b$ are set to 2.0 and 1.2, respectively.

We applied eqs 3−5 for analyzing $\phi_V$ and $\phi_K$ data. Since $\phi_V$ and $\phi_K$ can be converted into $\rho$ and $u$, respectively, of

**Table 6. Pitzer Coefficients Obtained from the Analysis of $\rho$ and $u$ Data (for $\phi_V$ and $\phi_K$) of the $LiClO_4$ in Diethyl Ether, Tetrahydrofuran, Acetone, and Ethyl Acetate Solutions at 298.15 K**

for $\phi_V$

| | $-10^6\phi_V^\circ$ | $10^9(\partial\beta^{(0)}/\partial P)_T$ | $10^9(\partial\beta^{(1)}/\partial P)_T$ | $10^9(\partial C^\phi/\partial P)_T$ | $10^6\sigma$ |
|---|---|---|---|---|---|
| systems | $m^3\ mol^{-1}$ | $m^3\ mol^{-1}\ Pa^{-1}$ | $m^3\ mol^{-1}\ Pa^{-1}$ | $m^3\ mol^{-1}\ Pa^{-1}$ | $m^3\ mol^{-1}$ |
| $LiClO_4$ + diethyl ether | 5.8 | −1.05 | −5.31 | 1.04 | $0.2_5$ |
| $LiClO_4$ + tetrahydrofuran | 39.4 | 16.69 | 14.69 | 4.33 | 0.9 |
| $LiClO_4$ + acetone | 20.0 | −2.91 | −14.14 | −0.69 | 0.4 |
| $LiClO_4$ + ethyl acetate | 38.0 | −0.68 | −0.62 | −2.52 | 0.7 |

for $\phi_K$

| | $10^{13}-\phi_K^\circ$ | $10^{17}(\partial^2\beta^{(0)}/\partial P^2)_T$ | $10^{17}(\partial^2\beta^{(1)}/\partial P^2)_T$ | $10^{17}(\partial^2 C^\varphi/\partial P^2)_T$ | $10^{13}\sigma$ |
|---|---|---|---|---|---|
| systems | $m^3\ mol^{-1}\ Pa^{-1}$ | $m^3\ mol^{-1}\ Pa^{-2}$ | $m^3\ mol^{-1}\ Pa^{-2}$ | $m^3\ mol^{-1}\ Pa^{-2}$ | $m^3\ mol^{-1}\ Pa^{-1}$ |
| $LiClO_4$ + diethyl ether | 11.5 | 18.87 | 58.31 | −3.32 | $0.2_5$ |
| $LiClO_4$ + tetrahydrofuran | 48.0 | −0.59 | −9.94 | 0.29 | 0.4 |
| $LiClO_4$ + acetone | 85.3 | 4.58 | 2.71 | −0.83 | 0.6 |
| $LiClO_4$ + ethyl acetate | 65.9 | 2.69 | −2.85 | −0.59 | $0.4_5$ |

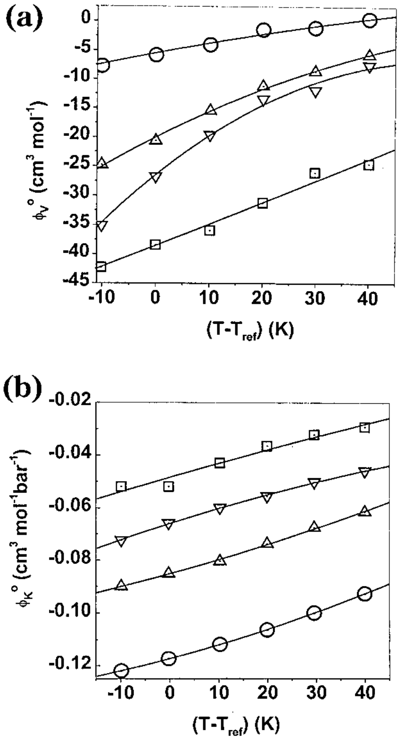

**Figure 1.** (a) Plots of $\phi_V^\circ$ as a function of $T - T_{ref}$ for $LiClO_4$–diethyl ether (○), –tetrahydrofuran (□), –acetone (△), and –ethyl acetate (▽) solutions. (b) Plots of $\phi_K^\circ$ as a function of $T - T_{ref}$ for $LiClO_4$–diethyl ether, –tetrahydrofuran, –acetone, and –ethyl acetate solutions; symbols are the same as in (a).

the solutions, we fitted the experimental $\rho$ and $u$ data with weighted regression analysis procedure for all the four systems at 298.15 K. Fittings of $\rho$ and $u$ through the Pitzer equations can be more accurate in obtaining reliable predictions for $\phi_V$ and $\phi_K$, respectively, as the errors in the $\phi_V$ and $\phi_K$ data are magnified in the dilute salt solutions.[15]

The results of this fitting exercise are summarized in Table 6 in the form of the Pitzer parameters for all the solutions at 298.15 K. It is noted that the $\phi_V$ and $\phi_K$ data for all the solutions can be accurately fitted by the Pitzer equations. The Pitzer parameters are adjustable parameters resulting from the nonlinear least-squares fitting of the experimental data. In Figure 2 a are plotted the calculated values of $\phi_V$ (shown by solid lines) in contrast to those of experimental (points) as a function of m for the $LiClO_4$ + diethyl ether, + tetrahydrofuran, + acetone, and + ethyl acetate solutions. Analogous plots are shown for $\phi_K$ in Figure 2b. An examination of these plots suggests that both the $\phi_V$ and $\phi_K$ for the $LiClO_4$ + diethyl ether, + tetrahydrofuran, + acetone, and + ethyl acetate solutions can be correlated with an average $\sigma$ of $0.45 \times 10^{-6}$ $m^3\ mol^{-1}$ and $0.39 \times 10^{-13}$ $m^3\ mol^{-1}\ Pa^{-1}$ for $\phi_V$ and $\phi_K$, respectively. To seek better appreciation of the effectiveness of the Pitzer equations, we have also plotted the deviations, $\delta$ ($\delta = \rho_{expt} - \rho_{calc}$ or $u_{exp} - u_{cal}$), as a function of the salt concentration, $m$, in Figure 3 a,b for $\rho$ and $u$, respectively. The deviations are larger in the low concentration range for both $\rho$ and $u$ in all the systems studied. At higher concentrations, these deviations are small and random. In the low concentrations of $LiClO_4$ ($m < 1$ mol kg$^{-1}$) the instrument precision becomes important. The uncertainties in molalities and

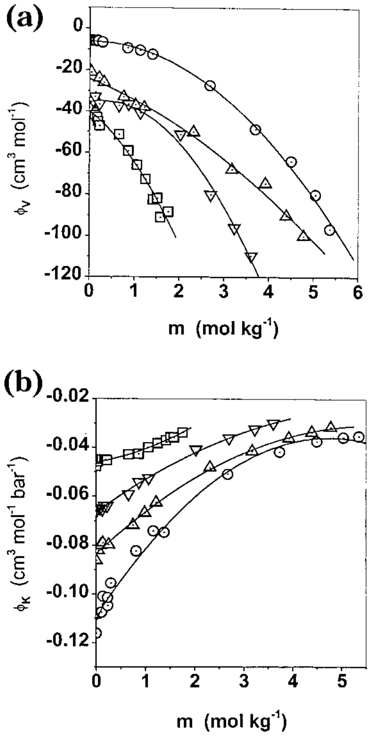

**Figure 2.** 2. (a) $\phi_V$ as a function of concentration of $LiClO_4$, $m$, for $LiClO_4$–diethyl ether, –tetrahydrofuran, –acetone, and – ethyl acetate solutions at 298.15 K. Symbols are for the experimental data, and lines are calculated by the Pitzer equations. Symbols are the same as in Figure 1a. (b) $\phi_k$ as a function of concentration of $LiClO_4$, $m$, for $LiClO_4$–diethyl ether, –tetrahydrofuran, –acetone, and –ethyl acetate solutions at 298.15 K. Symbols are the same as in Figure 1a. Symbols are for the experimental data; lines are calculated by the Pitzer equations.

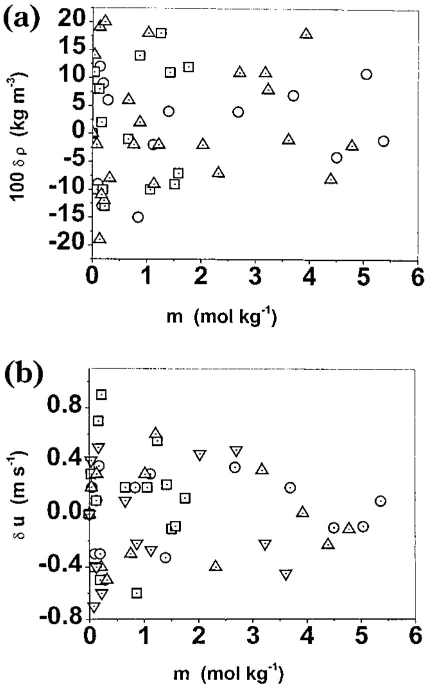

**Figure 3.** (a) Plot of $\triangle\rho$ (experimental $\rho$ − calculated $\rho$) as a function of concentration of $LiClO_4$, $m$, in $LiClO_4$−diethyl ether, −tetrahydrofuran, −acetone, and −ethyl acetate solutions at 298.15 K. Symbols are the same as in Figure 1a. (b) Plot of $\triangle u$ (experimental $u$ − calculated $u$) as a function of concentration of $LiClO_4$, $m$, in $LiClO_4$−diethyl ether, −tetrahydrofuran, −acetone, and −ethyl acetate solutions at 298.15 K. Symbols are the same as in Figure 1a.

densities of solvent and solutions determine the errors in $\phi_V$, denoted by $\sigma_{\phi V}$. The error propagation calculations show an uncertainty of $\pm 0.4 \times 10^{-6}$ m$^3$ mol$^{-1}$ in $\phi_V$ at $m = 0.015$. In the Pitzer fits, the weighting was proportional to $1/\sigma_{\phi V}$, where $\sigma_{\phi V} \approx (M_2/\rho^2 + 1/m\rho^2)(\sigma\rho)^2$. The molecular weight of $LiClO_4$ is denoted by $M_2$. The errors in density, $\sigma\rho$, decrease from low to high salt concentrations. In other words, the Pitzer equations can correlate concentration dependence of $\rho$ and $u$ with average standard deviations for all the four systems as 0.08 kg m$^{-3}$ and 0.51 m s$^{-1}$, respectively.

No efforts were made to fit the volume and compressibility data of dilute solutions at other temperatures, as the purpose of these measurements was to compute $\phi_V{}^o$ and $\phi_K{}^o$ values of $LiClO_4$ in different solvents.

In summary, we have presented experimental density and speeds of sound data of the $LiClO_4$ in diethyl ether, tetrahydrofuran, acetone, and ethyl acetate from 288.15 to 338.15 K with an interval of 10 K. We have not considered the ion-pair formation in our calculations, though the evidence from NMR data shows the formation of contact ion pairs.

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