# Solution Thermodynamics of First-Row Transition Elements. 2. Apparent Molal Volumes of Aqueous $MnCl_2$, $Mn(ClO_4)_2$, $CoCl_2$, $Co(ClO_4)_2$, $FeCl_2$, and $Fe(ClO_4)_2$, from 15 to 55 °C

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**The densities of aqueous $MnCl_2$, $Mn(ClO_4)_2$, $CoCl_2$, $Co(ClO_4)_2$, $FeCl_2$, and $Fe(ClO_4)_2$ solutions have been measured from 15 to 55 °C over the concentration range 0–3.5 *m*. The derived apparent molal volumes have been fitted to a Redlich–Meyer equation to obtain $\phi_v^0$ and to the Pitzer formalism for the whole concentration range. The conventional ionic values for $Mn^{2+}$, $Co^{2+}$, and $Fe^{2+}$ are calculated and their temperature dependence is examined.**

## Introduction

As part of our continuing program on the volumetric properties of aqueous transition-metal ions, we have made density measurements on solutions of six electrolytes; $MnCl_2$, $Mn(ClO_4)_2$, $FeCl_2$, $Fe(ClO_4)_2$, $CoCl_2$, and $Co(ClO_4)_2$. The measurements were made over the temperature range 15–55 °C at 10 °C intervals and cover the concentration range 0–3.5 *m*.

The results of the measurements were used to calculate the apparent molal volumes for the various electrolytes. The apparent molal volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution. The volume data have been fitted to the Pitzer formalism over the entire temperature and concentration range. Finally, the infinite dilution partial molal volumes for the $M^{2+}$ ions were calculated and the values compared to the literature.

## Experimental Section

Solution densities have been measured with a vibrating tube densimeter (Mettler/Paar, Model DMA 602). The experimental details were given in an earlier paper (*1*). The relative densities are precise to within 2 ppm. Experimental temperatures were controlled to ±0.005 °C with a Neslab EX-100 bath in conjunction with a NBS platinum resistance thermometer.

The chloride and perchlorate salts were Fisher Scientific ACS certified and Sargent Welch certified reagent grade, respectively. All stock solutions were prepared with distilled water that was passed through a NANOpure (Barnstead 18.5 Mohm) ion-exchange apparatus and subsequently filtered with a 10-μm fritted-glass filter.

The chloride stock solution concentrations were determined to within ±0.05% by gravimetric analysis of chloride. The $Mn(ClO_4)_2$ and $Co(ClO_4)_2$ stock solution $M^{2+}$ concentrations were determined by EDTA titration as described by Schwarzenbach and Flaschka (*2*). The $Fe(ClO_4)_2$ stock solution concentration was determined by redox titration as described by Skoog and West (*3*). All concentrations determined by titration were within ±0.07%. Solutions utilized in subsequent measurements were prepared by weight dilution of these stock solutions. To prevent hydrolysis of the $M^{2+}$ cation, the pH of each solution was maintained between 4 and 5 by appropriate addition of HCl or $HClO_4$.

Removal of dissolved oxygen and careful control of the pH of the $Fe^{2+}$ solutions were necessary to prevent the oxidation of the ferrous ion. The ferric ion makes a negligible contribution to the solution properties at temperatures 15–45 °C. Measurements were not made at 55 °C because the oxidation reaction becomes fast enough that the ferric ion contributions can no longer be neglected.

## Results and Discussion

The experimental results have been used to obtain the apparent molal volumes listed in Table I. The apparent molal volume, $\phi_v$, can be directly related to the solution densities, *d*, by the equation

$$\phi_v = \frac{M_2}{d} - \frac{1000(d - d_0)}{mdd_0} \quad (1)$$

where $d_0$ is the density of water, $M_2$ is the solute molecular weight, and *m* is the solute molality.

The dilute apparent molal volume data were fitted to the Redlich–Meyer equation (*4*)

$$\phi_v = \phi_v^0 + S_v m^{1/2} + b_v m \quad (2)$$

where $\phi_v^0$ is the value of $\phi_v$ at infinite dilution, $S_v$ is the Debye–Hückel limiting slope, and $b_v$ is a solute-dependent adjustable parameter. The $\phi_v^0$ values have been determined by fitting the dilute data ($m < 0.2$) to eq 2 using a weighted least-squares fit. Weighting was proportional to $1/(\sigma_{\phi_v})$, where $\sigma_{\phi_v}$ is the estimated error in the experimental $\phi_v$. The values of $\phi_v^0$ and $b_v$ at each temperature are reported in Table II. The estimated uncertainties in $\phi_v^0$ are equal to one standard deviation, and the $\sigma$'s are the root mean square of the deviations between the experimental and calculated $\phi_v$ for each data point.

Results of our present measurements at 25 °C can be compared with results of earlier investigators. The values of $\phi_v^0(M^{2+})$ were determined independently from values of $\phi_v^0(Cl^-)$ and $\phi_v^0(ClO_4^-)$ (*5*) by use of the additivity principle. These two values were then averaged, yielding $\phi_v^0(M^{2+})$ values with deviations less than ±0.12 $cm^3\ mol^{-1}$ at 25 °C, an error within experimental uncertainty. The conventional values of $\phi_v^0(M^{2+})$ at each temperature are listed in Table III. Our present 25 °C value of $\phi_v^0(Mn^{2+}) = -17.4\ cm^3\ mol^{-1}$ is in good agreement with the $-17.4\ cm^3\ mol^{-1}$ value reported by Hepler et al. (*6*) from $Mn(ClO_4)_2$ and the $-17.6\ cm^3\ mol^{-1}$ reported by Millero and Lo Surdo (*7*) from $MnCl_2$. We have reported $\phi_v^0(Co^{2+}) = -25.8\ cm^3\ mol^{-1}$ at 25 °C, which is in satisfactory agreement with the $-25.4\ cm^3\ mol^{-1}$ reported by Hepler et al. (*6*) from $CoCl_2$ data but differs from the $-24.6\ cm^3\ mol^{-1}$ reported by Hepler et al. (*8*) from their $Co(NO_3)_2$ data. Finally, our 25 °C value of $\phi_v^0(Fe^{2+}) = -22.7\ cm^3\ mol^{-1}$ is more negative than the $-22.1\ cm^3\ mol^{-1}$ and the $-21.7\ cm^3\ mol^{-1}$ reported by Swaddle and Mak (*9*) and Sanaev et al. (*10*), respectively. In both cases

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**Table I. Relative Densities and Apparent Molal Volumes of Aqueous $MnCl_2$, $Mn(ClO_4)_2$, $CoCl_2$, $Co(ClO_4)_2$, $FeCl_2$, and $Fe(ClO_4)_2$ Solutions**

| molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ | molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ | molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $MnCl_2$ | | | | |
| | | | | 15 °C | | | | |
| 0.00971 | 1.04 | 17.92 | 0.2028 | 21.29 | 20.33 | 1.4979 | 146.65 | 24.30 |
| 0.01972 | 2.11 | 18.30 | 0.4018 | 41.66 | 21.17 | 1.9854 | 190.12 | 25.22 |
| 0.02927 | 3.13 | 18.48 | 0.5992 | 61.43 | 21.88 | 2.4993 | 234.11 | 26.01 |
| 0.04979 | 5.30 | 19.04 | 0.7945 | 80.59 | 22.52 | 3.0071 | 275.93 | 26.66 |
| 0.07421 | 7.89 | 19.30 | 0.9978 | 100.13 | 23.10 | 3.4336 | 309.83 | 27.14 |
| 0.1005 | 10.65 | 19.60 | | | | | | |
| | | | | 25 °C | | | | |
| 0.00971 | 1.03 | 19.02 | 0.2028 | 21.11 | 21.03 | 1.4979 | 145.56 | 24.83 |
| 0.01972 | 2.09 | 19.36 | 0.4018 | 41.32 | 21.85 | 1.9854 | 188.78 | 25.70 |
| 0.02927 | 3.10 | 19.52 | 0.5992 | 60.92 | 22.55 | 2.4993 | 232.53 | 26.45 |
| 0.04979 | 5.25 | 19.85 | 0.7945 | 79.94 | 23.14 | 3.0071 | 274.14 | 27.06 |
| 0.07421 | 7.82 | 20.00 | 0.9978 | 99.33 | 23.70 | 3.4336 | 307.81 | 27.53 |
| 0.1005 | 10.56 | 20.29 | | | | | | |
| | | | | 35 °C | | | | |
| 0.00971 | 1.02 | 19.40 | 0.2028 | 21.02 | 21.23 | 1.4979 | 144.82 | 25.09 |
| 0.01972 | 2.08 | 19.58 | 0.4018 | 41.11 | 22.11 | 1.9854 | 187.82 | 25.95 |
| 0.02927 | 3.09 | 19.67 | 0.5992 | 60.60 | 22.84 | 2.4993 | 231.37 | 26.69 |
| 0.04979 | 5.24 | 19.93 | 0.7945 | 79.56 | 23.38 | 3.0071 | 272.71 | 27.32 |
| 0.07421 | 7.78 | 20.27 | 0.9978 | 98.84 | 23.96 | 3.4336 | 306.18 | 27.79 |
| 0.1005 | 10.51 | 20.49 | | | | | | |
| | | | | 45 °C | | | | |
| 0.00971 | 1.01 | 18.29 | 0.2028 | 20.92 | 21.44 | 1.4979 | 144.08 | 25.30 |
| 0.01972 | 2.09 | 19.04 | 0.4018 | 40.92 | 22.30 | 1.9854 | 186.79 | 26.19 |
| 0.02927 | 3.08 | 19.58 | 0.5992 | 60.29 | 23.07 | 2.4993 | 230.24 | 26.88 |
| 0.04979 | 5.22 | 19.97 | 0.7945 | 79.11 | 23.65 | 3.0071 | 271.33 | 27.52 |
| 0.07421 | 7.76 | 20.35 | 0.9978 | 98.39 | 24.13 | 3.4336 | 304.21 | 28.10 |
| 0.1005 | 10.47 | 20.67 | | | | | | |
| | | | | 55 °C | | | | |
| 0.00971 | 1.02 | 18.46 | 0.2028 | 20.90 | 21.18 | 1.4979 | 143.69 | 25.26 |
| 0.01972 | 2.07 | 19.05 | 0.4018 | 40.86 | 22.08 | 1.9854 | 186.34 | 26.13 |
| 0.02927 | 3.08 | 19.50 | 0.5992 | 60.20 | 22.86 | 2.4993 | 229.57 | 26.87 |
| 0.04979 | 5.21 | 19.95 | 0.7945 | 79.09 | 23.34 | 3.0071 | 270.37 | 27.57 |
| 0.07421 | 7.74 | 20.20 | 0.9978 | 98.10 | 24.08 | 3.4336 | 303.38 | 28.09 |
| 0.1005 | 10.46 | 20.37 | | | | | | |
| | | | | $Mn(ClO_4)_2$ | | | | |
| | | | | 15 °C | | | | |
| 0.01005 | 1.85 | 68.72 | 0.1970 | 35.63 | 70.37 | 1.4776 | 238.04 | 74.84 |
| 0.02020 | 3.69 | 68.59 | 0.3976 | 70.53 | 71.31 | 1.9539 | 302.08 | 76.16 |
| 0.05028 | 9.21 | 69.04 | 0.5848 | 101.97 | 72.03 | 2.4321 | 361.45 | 77.24 |
| 0.06570 | 12.06 | 69.36 | 0.8076 | 137.98 | 72.85 | 2.7536 | 398.75 | 77.90 |
| 0.09846 | 17.99 | 69.73 | 0.9813 | 165.09 | 73.39 | | | |
| | | | | 25 °C | | | | |
| 0.01005 | 1.82 | 71.95 | 0.1970 | 34.96 | 73.50 | 1.4476 | 234.26 | 77.01 |
| 0.02020 | 3.65 | 72.35 | 0.3976 | 69.26 | 74.20 | 1.9539 | 297.68 | 78.04 |
| 0.05028 | 9.06 | 72.56 | 0.5848 | 100.18 | 74.75 | 2.4321 | 356.58 | 78.89 |
| 0.06570 | 11.82 | 72.76 | 0.8076 | 135.65 | 75.36 | 2.7536 | 393.58 | 79.45 |
| 0.09846 | 17.64 | 73.05 | 0.9813 | 162.31 | 75.85 | | | |
| | | | | 35 °C | | | | |
| 0.01005 | 1.80 | 73.89 | 0.1970 | 34.41 | 75.98 | 1.4776 | 230.86 | 78.91 |
| 0.02020 | 3.62 | 73.77 | 0.3976 | 68.11 | 76.74 | 1.9539 | 293.64 | 79.72 |
| 0.05028 | 8.94 | 74.75 | 0.5848 | 98.53 | 77.19 | 2.4321 | 352.04 | 80.40 |
| 0.06570 | 11.66 | 74.92 | 0.8076 | 133.47 | 77.67 | 2.7536 | 388.74 | 80.86 |
| 0.09846 | 17.39 | 75.32 | 0.9813 | 159.82 | 77.99 | | | |
| | | | | 45 °C | | | | |
| 0.01005 | 1.76 | 77.26 | 0.1970 | 33.81 | 78.66 | 1.4776 | 227.53 | 80.75 |
| 0.02020 | 3.54 | 77.23 | 0.3976 | 66.92 | 79.33 | 1.9539 | 289.38 | 81.49 |
| 0.05028 | 8.76 | 77.64 | 0.5848 | 96.96 | 79.47 | 2.4321 | 347.09 | 82.04 |
| 0.06570 | 11.44 | 77.90 | 0.8076 | 131.28 | 79.96 | 2.7536 | 383.55 | 82.38 |
| 0.09846 | 17.07 | 78.21 | 0.9813 | 157.24 | 80.19 | | | |
| | | | | 55 °C | | | | |
| 0.01005 | 1.75 | 78.44 | 0.1970 | 33.32 | 80.24 | 1.4776 | 225.04 | 82.04 |
| 0.02020 | 3.50 | 78.77 | 0.3976 | 66.08 | 81.03 | 1.9539 | 286.21 | 82.74 |
| 0.05028 | 8.67 | 79.37 | 0.5848 | 95.71 | 81.18 | 2.4321 | 343.59 | 83.14 |
| 0.06570 | 11.30 | 79.53 | 0.8076 | 129.71 | 81.49 | 2.7536 | 379.58 | 83.49 |
| 0.09846 | 16.86 | 79.86 | 0.9813 | 155.34 | 81.71 | | | |

**Table I** (Continued)

| molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ | molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ | molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $CoCl_2$ | | | | |
| | | | | 15 °C | | | | |
| 0.01009 | 1.20 | 10.12 | 0.2044 | 23.94 | 12.31 | 1.5012 | 165.37 | 16.81 |
| 0.01993 | 2.37 | 10.49 | 0.4014 | 46.63 | 12.95 | 2.0051 | 216.18 | 18.03 |
| 0.02966 | 3.53 | 10.50 | 0.5822 | 66.98 | 13.76 | 2.4983 | 264.04 | 19.04 |
| 0.04971 | 5.90 | 10.90 | 0.7980 | 90.84 | 14.58 | 2.9898 | 310.07 | 19.88 |
| 0.07440 | 8.81 | 11.22 | 1.0045 | 113.18 | 15.33 | 3.3516 | 342.97 | 20.42 |
| 0.1000 | 11.81 | 11.47 | | | | | | |
| | | | | 25 °C | | | | |
| 0.01009 | 1.19 | 10.85 | 0.2044 | 23.72 | 13.15 | 1.5012 | 164.08 | 17.40 |
| 0.01993 | 2.35 | 11.14 | 0.4014 | 46.20 | 13.77 | 2.0051 | 214.60 | 18.56 |
| 0.02966 | 3.50 | 11.22 | 0.5822 | 66.38 | 14.55 | 2.4983 | 262.20 | 19.51 |
| 0.04971 | 5.85 | 11.67 | 0.7980 | 90.05 | 15.32 | 2.9898 | 308.03 | 20.30 |
| 0.07440 | 8.73 | 11.98 | 1.0045 | 112.22 | 16.03 | 3.3516 | 340.70 | 20.84 |
| 0.1000 | 11.70 | 12.34 | | | | | | |
| | | | | 35 °C | | | | |
| 0.01009 | 1.18 | 11.52 | 0.2044 | 23.57 | 13.57 | 1.5012 | 163.10 | 17.74 |
| 0.01993 | 2.34 | 11.77 | 0.4014 | 45.90 | 14.20 | 2.0051 | 213.41 | 18.85 |
| 0.02966 | 3.48 | 11.74 | 0.5822 | 65.95 | 14.97 | 2.4983 | 260.79 | 19.78 |
| 0.04971 | 5.81 | 12.11 | 0.7980 | 89.48 | 15.71 | 2.9898 | 306.31 | 20.58 |
| 0.07440 | 8.67 | 12.45 | 1.0045 | 111.54 | 16.39 | 3.3516 | 338.82 | 21.11 |
| 0.1000 | 11.64 | 12.67 | | | | | | |
| | | | | 45 °C | | | | |
| 0.01009 | 1.19 | 11.21 | 0.2044 | 22.31 | 13.59 | 1.5012 | 162.09 | 18.05 |
| 0.01993 | 2.33 | 11.91 | 0.4014 | 45.63 | 14.51 | 2.0051 | 212.20 | 19.09 |
| 0.02966 | 3.46 | 12.25 | 0.5822 | 65.53 | 15.32 | 2.4983 | 259.25 | 20.04 |
| 0.04971 | 5.78 | 12.44 | 0.7980 | 88.91 | 16.05 | 2.9898 | 304.57 | 20.82 |
| 0.07440 | 8.62 | 12.79 | 1.0045 | 110.85 | 16.70 | 3.3516 | 336.55 | 21.43 |
| 0.1000 | 11.56 | 13.08 | | | | | | |
| | | | | 55 °C | | | | |
| 0.01009 | 1.17 | 11.77 | 0.2044 | 23.37 | 13.70 | 1.5012 | 161.65 | 17.94 |
| 0.01993 | 2.32 | 11.71 | 0.4014 | 45.49 | 14.38 | 2.0051 | 211.63 | 19.01 |
| 0.02966 | 3.45 | 11.96 | 0.5822 | 65.36 | 15.16 | 2.4983 | 259.36 | 19.69 |
| 0.04971 | 5.76 | 12.29 | 0.7980 | 88.68 | 15.91 | 2.9898 | 306.43 | 20.01 |
| 0.07440 | 8.62 | 12.49 | 1.0045 | 110.61 | 16.52 | 3.3516 | 338.76 | 20.60 |
| 0.1000 | 11.53 | 12.84 | | | | | | |
| | | | | $Co(ClO_4)_2$ | | | | |
| | | | | 15 °C | | | | |
| 0.01004 | 1.98 | 60.04 | 0.09870 | 19.28 | 61.16 | 0.8009 | 147.11 | 64.54 |
| 0.02002 | 3.94 | 60.17 | 0.2059 | 39.83 | 61.77 | 0.9964 | 180.02 | 65.29 |
| 0.03013 | 5.93 | 60.45 | 0.3540 | 67.57 | 62.56 | 1.4987 | 259.74 | 67.01 |
| 0.04986 | 9.79 | 60.66 | 0.6013 | 112.35 | 63.72 | 1.9217 | 321.74 | 68.33 |
| 0.07546 | 14.77 | 60.97 | | | | | | |
| | | | | 25 °C | | | | |
| 0.01004 | 1.94 | 63.52 | 0.09870 | 18.91 | 64.56 | 0.8009 | 144.54 | 67.29 |
| 0.02002 | 3.87 | 63.77 | 0.2059 | 39.08 | 65.06 | 0.9964 | 176.95 | 67.88 |
| 0.03013 | 5.82 | 63.83 | 0.3540 | 66.32 | 65.73 | 1.4987 | 255.64 | 69.25 |
| 0.04985 | 9.60 | 64.06 | 0.6013 | 110.32 | 66.66 | 1.9217 | 316.97 | 70.32 |
| 0.07546 | 14.49 | 64.37 | | | | | | |
| | | | | 35 °C | | | | |
| 0.01004 | 1.91 | 66.01 | 0.09870 | 18.61 | 67.27 | 0.8009 | 142.29 | 69.60 |
| 0.02002 | 3.81 | 66.27 | 0.2059 | 38.46 | 67.70 | 0.9964 | 174.29 | 70.06 |
| 0.03013 | 5.73 | 66.48 | 0.3540 | 65.26 | 68.29 | 1.4987 | 252.00 | 71.16 |
| 0.04986 | 9.45 | 66.75 | 0.6013 | 108.58 | 69.09 | 1.9217 | 312.70 | 72.03 |
| 0.07546 | 14.26 | 67.09 | | | | | | |
| | | | | 45 °C | | | | |
| 0.01004 | 1.88 | 68.95 | 0.09870 | 18.30 | 69.98 | 0.8009 | 140.02 | 71.90 |
| 0.02002 | 3.75 | 68.94 | 0.2059 | 37.82 | 70.33 | 0.9964 | 171.57 | 72.24 |
| 0.03013 | 5.63 | 69.22 | 0.3540 | 64.22 | 70.73 | 1.4987 | 248.21 | 73.13 |
| 0.04986 | 9.30 | 69.42 | 0.6013 | 106.82 | 71.50 | 1.9217 | 308.17 | 73.84 |
| 0.07546 | 14.02 | 69.82 | | | | | | |
| | | | | 55 °C | | | | |
| 0.01004 | 1.86 | 70.48 | 0.09870 | 18.08 | 71.64 | 0.8009 | 138.35 | 73.45 |
| 0.02002 | 3.71 | 70.55 | 0.2059 | 37.35 | 72.12 | 0.9964 | 169.59 | 73.70 |
| 0.03013 | 5.56 | 71.02 | 0.3540 | 63.44 | 72.42 | 1.4987 | 245.39 | 74.50 |
| 0.04986 | 9.19 | 71.15 | 0.6013 | 105.48 | 73.20 | 1.9217 | 304.76 | 75.12 |
| 0.07546 | 13.86 | 71.42 | | | | | | |

Table I (Continued)

| molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ | molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ | molality, mol kg$^{-1}$ | 1000(RD), g cm$^{-3}$ | $\phi_v$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $FeCl_2$ | | | | |
| | | | | 15 °C | | | | |
| 0.02510 | 2.83 | 13.68 | 0.2501 | 27.60 | 15.88 | 1.0450 | 110.10 | 19.20 |
| 0.05136 | 5.77 | 14.20 | 0.5322 | 57.72 | 17.22 | 1.5322 | 157.77 | 20.48 |
| 0.07416 | 8.33 | 14.23 | 0.8246 | 88.00 | 18.34 | 2.0932 | 210.35 | 21.64 |
| 0.1009 | 11.27 | 14.77 | | | | | | |
| | | | | 25 °C | | | | |
| 0.02610 | 2.92 | 14.42 | 0.2501 | 27.34 | 16.72 | 1.0861 | 113.52 | 19.74 |
| 0.05190 | 5.78 | 15.06 | 0.5435 | 58.33 | 18.10 | 1.4891 | 152.68 | 20.80 |
| 0.07846 | 8.72 | 15.26 | 0.8401 | 88.84 | 19.05 | 2.0932 | 208.93 | 22.09 |
| 0.09903 | 10.98 | 15.43 | | | | | | |
| | | | | 35 °C | | | | |
| 0.02526 | 2.81 | 14.70 | 0.2501 | 27.18 | 17.07 | 1.0730 | 111.53 | 20.07 |
| 0.05153 | 5.71 | 15.37 | 0.5291 | 56.53 | 18.34 | 1.6069 | 163.03 | 21.34 |
| 0.07635 | 8.43 | 15.62 | 0.7871 | 82.99 | 19.21 | 2.0932 | 207.94 | 22.31 |
| 0.1015 | 11.18 | 15.85 | | | | | | |
| | | | | 45 °C | | | | |
| 0.02555 | 2.83 | 14.93 | 0.09856 | 10.80 | 16.09 | 0.8438 | 88.13 | 19.73 |
| 0.05239 | 5.77 | 15.60 | 0.2501 | 27.02 | 17.35 | 1.0560 | 109.25 | 20.26 |
| 0.07629 | 8.38 | 15.83 | 0.4931 | 52.43 | 18.53 | 2.0932 | 206.62 | 22.62 |
| | | | | $Fe(ClO_4)_2$ | | | | |
| | | | | 15 °C | | | | |
| 0.02650 | 5.05 | 63.72 | 0.2095 | 39.14 | 65.23 | 1.1801 | 202.38 | 69.17 |
| 0.05245 | 9.97 | 63.94 | 0.5658 | 102.23 | 67.08 | 1.7043 | 279.51 | 70.85 |
| 0.07956 | 15.06 | 64.37 | 0.8714 | 153.50 | 68.05 | 2.4491 | 379.17 | 72.40 |
| 0.1036 | 19.57 | 64.35 | | | | | | |
| | | | | 25 °C | | | | |
| 0.02776 | 5.18 | 67.36 | 0.2095 | 38.42 | 68.37 | 1.1736 | 197.91 | 71.65 |
| 0.05237 | 9.75 | 67.56 | 0.5580 | 99.08 | 69.93 | 1.7431 | 280.81 | 72.92 |
| 0.07823 | 14.53 | 67.69 | 0.8487 | 147.11 | 70.71 | 2.4491 | 374.01 | 74.09 |
| 0.1069 | 19.78 | 67.97 | | | | | | |
| | | | | 35 °C | | | | |
| 0.02603 | 4.78 | 69.99 | 0.2095 | 37.85 | 70.73 | 1.1424 | 190.26 | 73.63 |
| 0.05221 | 9.57 | 70.19 | 0.5812 | 101.57 | 72.05 | 1.6610 | 265.97 | 74.72 |
| 0.08002 | 14.62 | 70.31 | 0.8835 | 150.39 | 72.97 | 2.4491 | 369.03 | 75.68 |
| 0.1046 | 19.08 | 70.34 | | | | | | |
| | | | | 45 °C | | | | |
| 0.02557 | 4.62 | 72.85 | 0.2095 | 37.19 | 73.49 | 1.1207 | 184.20 | 75.58 |
| 0.05216 | 9.39 | 73.02 | 0.5851 | 100.74 | 74.91 | 1.7589 | 274.82 | 76.65 |
| 0.07863 | 14.11 | 73.05 | 0.8177 | 137.54 | 75.27 | 2.4491 | 364.57 | 77.07 |
| 0.1040 | 18.50 | 73.13 | | | | | | |

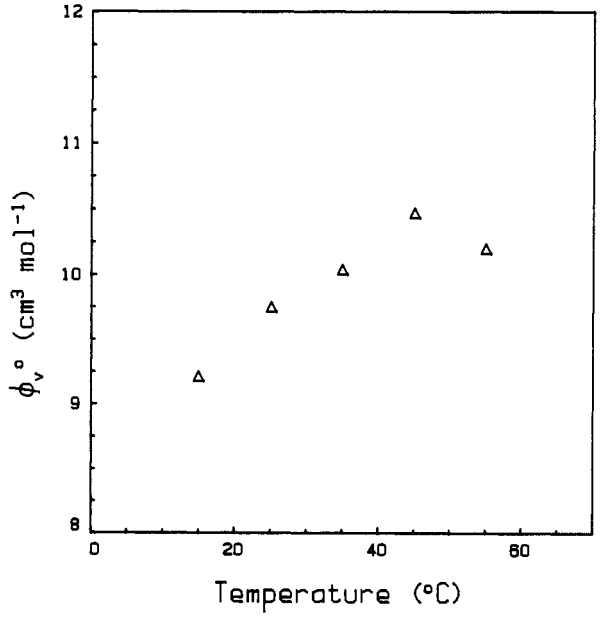


Figure 1. Temperature dependence of $\phi_v^0$ for $CoCl_2$.

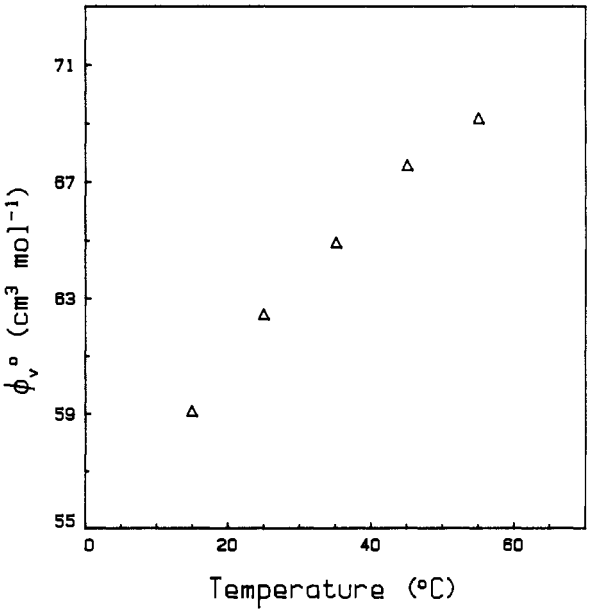


Figure 2. Temperature dependence of $\phi_v^0$ for $Co(ClO_4)_2$.

**Table II. Parameters for Eq 2 for Temperatures 15–55 °C**

| salt | t, °C | $\phi_v^0$, cm³ mol⁻¹ | $b_v$, cm³ kg mol⁻² | $\sigma$, cm³ mol⁻¹ |
|---|---|---|---|---|
| $MnCl_2$ | 15 | 17.19 ● 0.07 | −3.75 | 0.07 |
| | 25 | 18.11 ± 0.07 | −9.08 | 0.05 |
| | 35 | 18.13 ± 0.07 | −10.08 | 0.14 |
| | 45 | 17.70 ± 0.10 | −6.80 | 0.22 |
| | 55 | 17.69 ± 0.10 | −12.91 | 0.16 |
| $Mn(ClO_4)_2$ | 15 | 67.42 ± 0.08 | −4.91 | 0.20 |
| | 25 | 70.89 ± 0.08 | −8.77 | 0.13 |
| | 35 | 72.65 ± 0.08 | −6.98 | 0.15 |
| | 45 | 75.69 ± 0.09 | −11.22 | 0.22 |
| | 55 | 77.19 ± 0.03 | −13.05 | 0.05 |
| $CoCl_2$ | 15 | 9.21 ± 0.05 | −5.26 | 0.07 |
| | 25 | 9.75 ± 0.07 | −4.95 | 0.09 |
| | 35 | 10.27 ± 0.08 | −9.70 | 0.14 |
| | 45 | 10.47 ± 0.08 | −10.94 | 0.14 |
| | 55 | 10.20 ● 0.12 | −14.28 | 0.19 |
| $Co(ClO_4)_2$ | 15 | 59.09 ± 0.04 | −7.08 | 0.06 |
| | 25 | 62.44 ± 0.07 | −9.56 | 0.11 |
| | 35 | 64.93 ± 0.04 | −10.10 | 0.05 |
| | 45 | 67.57 ± 0.10 | −12.64 | 0.15 |
| | 55 | 69.18 ± 0.09 | −15.67 | 0.11 |
| $FeCl_2$ | 15 | 12.25 ± 0.10 | −3.11 | 0.12 |
| | 25 | 12.88 ± 0.09 | −4.10 | 0.11 |
| | 35 | 13.09 ± 0.07 | −5.40 | 0.09 |
| | 45 | 13.15 ± 0.07 | −6.44 | 0.09 |
| $Fe(ClO_4)_2$ | 15 | 62.19 ± 0.14 | −4.89 | 0.15 |
| | 25 | 65.77 ± 0.09 | −8.89 | 0.12 |
| | 35 | 68.28 ± 0.15 | −11.75 | 0.18 |
| | 45 | 70.95 ± 0.18 | −13.47 | 0.22 |

**Table III. Values of $\phi_v^0$ for $Mn^{2+}$, $Co^{2+}$, and $Fe^{2+}$ from 15 to 55 °C**

| t, °C | $\phi_v^0(Mn^{2+})$, cm³ mol⁻¹ | $\phi_v^0(Co^{2+})$, cm³ mol⁻¹ | $\phi_v^0(Fe^{2+})$, cm³ mol⁻¹ |
|---|---|---|---|
| 15 | −17.0 ± 0.1 | −25.2 ± 0.1 | −21.6 ± 0.3 |
| 25 | −17.4 ± 0.1 | −25.8 ± 0.1 | −22.7 ± 0.1 |
| 35 | −18.1 ± 0.3 | −25.6 ± 0.5 | −22.5 ± 0.3 |
| 45 | −17.9 ± 0.4 | −25.6 ± 0.1 | −22.4 ± 0.4 |
| 55 | −17.9 ± 0.1 | −25.6 ± 0.3 | |

our value was within the experimental uncertainty reported by the investigators.

The agreement of the 25 °C data reported here with the existing literature values is within experimental uncertainty for each cation. This comparison indicates that the measurements made at temperatures other than 25 °C have yielded good results.

The Pitzer formalism was used to fit the apparent molal volume data over the entire experimental concentration range. The Pitzer equation for the apparent molal volume of a single salt $M_{\nu_M}X_{\nu_X}$ is

$$\phi_v = \phi_v^0 + \nu|Z_M Z_X|\frac{A_v}{2b}\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RT[mB'_{MX} + m^2(\nu_M\nu_X)^{1/2}C'_{MX}] \quad (3)$$

where

$$B'_{MX} = \left(\frac{\delta\beta^{(0)}}{\delta P}\right)_T + \left(\frac{\delta\beta^{(1)}}{\delta P}\right)_T\left(\frac{2}{\alpha^2 I}\right)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (4)$$

$$C'_{MX} = \frac{1}{2}\left(\frac{\delta C^\phi}{\delta P}\right)_T \quad (5)$$

$$\nu = \nu_M + \nu_X \quad (6)$$

$$\alpha = 2.0\ \text{kg}^{1/2}\ \text{mol}^{-1/2} \quad (7)$$

$$b = 1.2\ \text{kg}^{1/2}\ \text{mol}^{-1/2} \quad (8)$$

$$R = 8.314\,41\ \text{cm}^3\ \text{bar}\ \text{mol}^{-1}\ \text{K}^{-1} \quad (9)$$

The values of $A_v$ have been reported as 1.715, 1.874, 2.055, 2.260, and 2.495 at 15, 25, 35, 45, and 55 °C, respectively

**Table IV. Pitzer Parameters for Eq 3**

| salt | t, °C | $\phi_v^0$, cm³ mol⁻¹ | $10^5\beta_v^0$, kg mol⁻¹ bar⁻¹ | $10^5\beta_v^{(1)}$, kg² mol⁻² bar⁻¹ | $10^6C^\phi$, kg² mol⁻² bar⁻¹ | $\sigma$, cm³ mol⁻¹ |
|---|---|---|---|---|---|---|
| $MnCl_2$ | 15 | 17.43 ± 0.06 | 1.73 ± 0.09 | −4.59 ± 0.90 | −2.55 ± 0.28 | 0.07 |
| | 25 | 18.15 ± 0.04 | 1.47 ± 0.06 | −7.23 ± 0.59 | −2.26 ± 0.18 | 0.04 |
| | 35 | 18.20 ± 0.04 | 1.26 ± 0.06 | −8.00 ± 0.56 | −1.89 ± 0.18 | 0.04 |
| | 45 | 18.00 ± 0.08 | 0.81 ± 0.12 | −6.35 ± 1.19 | −0.81 ± 0.38 | 0.05 |
| | 55 | 17.77 ± 0.08 | 1.04 ± 0.12 | −11.33 ± 1.15 | −1.57 ± 0.37 | 0.03 |
| $Mn(ClO_4)_2$ | 15 | 67.72 ± 0.07 | 2.37 ± 0.14 | −8.69 ± 1.14 | −2.14 ± 0.51 | 0.05 |
| | 25 | 71.25 ± 0.04 | 1.69 ± 0.08 | −15.39 ± 0.65 | −1.73 ± 0.29 | 0.03 |
| | 35 | 73.00 ± 0.10 | 0.07 ± 0.19 | −6.11 ± 1.55 | 1.89 ± 0.69 | 0.08 |
| | 45 | 76.06 ± 0.12 | −0.42 ± 0.23 | −12.68 ± 1.90 | 2.36 ± 0.85 | 0.10 |
| | 55 | 77.40 ± 0.14 | −1.24 ± 0.26 | −10.62 ± 2.12 | 4.13 ± 0.95 | 0.11 |
| $FeCl_2$ | 15 | 12.50 ± 0.15 | 2.93 ± 0.44 | −5.06 ± 3.01 | −6.42 ± 1.94 | 0.07 |
| | 25 | 13.00 ± 0.09 | 1.11 ± 0.26 | 0.97 ± 1.81 | 0.49 ± 1.14 | 0.04 |
| | 35 | 13.32 ± 0.06 | 1.24 ± 0.17 | −2.99 ± 1.15 | −1.00 ± 0.76 | 0.03 |
| | 45 | 13.28 ± 0.07 | 0.49 ± 0.22 | −0.98 ± 1.39 | 1.76 ± 0.95 | 0.03 |
| $Fe(ClO_4)_2$ | 15 | 62.49 ± 0.23 | 3.34 ± 0.55 | −10.86 ± 4.28 | −5.97 ± 2.15 | 0.11 |
| | 25 | 65.97 ± 0.14 | 2.25 ± 0.32 | −13.88 ± 2.48 | −4.54 ± 1.26 | 0.07 |
| | 35 | 68.71 ± 0.08 | 2.88 ± 0.18 | −24.21 ± 1.39 | −8.49 ± 0.70 | 0.04 |
| | 45 | 71.07 ± 0.32 | 0.76 ± 0.72 | −16.05 ± 5.42 | −3.05 ± 2.81 | 0.16 |
| $CoCl_2$ | 15 | 9.52 ± 0.09 | 2.78 ± 0.16 | −10.50 ± 1.50 | −4.09 ± 0.49 | 0.10 |
| | 25 | 10.18 ± 0.10 | 2.21 ± 0.17 | −10.06 ± 1.58 | −3.05 ± 0.52 | 0.11 |
| | 35 | 10.08 ± 0.10 | 2.05 ± 0.15 | −11.93 ± 1.49 | −2.86 ± 0.49 | 0.10 |
| | 45 | 10.62 ± 0.08 | 1.65 ± 0.12 | −12.93 ± 1.21 | −2.09 ± 0.40 | 0.09 |
| | 55 | 10.39 ± 0.16 | 1.93 ± 0.24 | −16.65 ± 2.28 | −4.35 ± 0.75 | 0.17 |
| $Co(ClO_4)_2$ | 15 | 59.27 ± 0.04 | 3.47 ± 0.17 | −13.16 ± 0.98 | −4.60 ± 0.82 | 0.04 |
| | 25 | 62.64 ± 0.04 | 2.11 ± 0.18 | −13.81 ± 1.05 | −2.00 ± 0.88 | 0.04 |
| | 35 | 65.20 ± 0.06 | 1.08 ± 0.23 | −13.59 ± 1.32 | −0.24 ± 1.10 | 0.05 |
| | 45 | 67.89 ± 0.09 | 0.59 ± 0.35 | −17.03 ± 2.05 | −0.20 ± 1.71 | 0.08 |
| | 55 | 69.33 ± 0.11 | −0.38 ± 0.40 | −15.19 ± 2.31 | 2.62 ± 1.93 | 0.09 |

**Table V. $\phi_v^0$ Temperature Parameters for Eq 10**

| electrolyte | $A$, $cm^3\ mol^{-1}$ | $B$, $cm^3\ mol^{-1}\ °C^{-1}$ | $10^3C$, $cm^3\ mol^{-1}\ °C^{-2}$ | $\sigma$, $cm^3\ mol^{-1}$ | $t_{max}$, °C |
|---|---|---|---|---|---|
| $MnCl_2$ | 15.16 | 0.159 | −2.04 | 0.28 | 39.0 |
| $FeCl_2$ | 10.87 | 0.115 | −1.42 | 0.06 | 40.3 |
| $CoCl_2$ | 6.69 | 0.183 | −2.21 | 0.46 | 41.4 |
| $Mn(ClO_4)_2$ | 61.30 | 0.442 | −2.83 | 0.18 | 78.1 |
| $Fe(ClO_4)_2$ | 56.40 | 0.424 | −2.28 | 0.26 | 93.0 |
| $Co(ClO_4)_2$ | 53.01 | 0.447 | −2.83 | 0.22 | 79.0 |

(*11*). The parameters for eq 3 for each salt at all temperatures are listed in Table IV. The $\phi_v^0$ values reported in Table IV are fitting parameters and may not be the same as the values determined from extrapolation by using eq 1.

The temperature dependence of $\phi_v^0$ for $CoCl_2$ and $Co(ClO_4)_2$ is illustrated in Figures 1 and 2. The temperature dependence is typical of each electrolyte system studied. The $\phi_v^0$ data were fitted to the equation

$$\phi_v^0 = A + Bt + Ct^2 \qquad (10)$$

where $A$, $B$, and $C$ are empirical parameters and $t$ is the Celsius temperature. The resulting parameters are listed in Table V. It is useful to examine the temperature dependence of the chloride and perchlorate salts separately. In each case the $\phi_v^0$ values increase with temperature. The chloride salts reach a maximum volume at a temperature less than 50 °C while the perchlorate systems indicate the existence of maximums at temperatures above 80 °C. The temperature difference at which the apparent molal volume maximum occurs for the chloride and perchlorate salts must be attributed to the anion, in particular, their hydration properties.

The $\phi_v^0$ values of the $M^{2+}$ cations show only a slight temperature effect, which is not significant enough to establish a trend. The $\phi_v^0$ values for each cation fluctuate approximately 1 $cm^3\ mol^{-1}$ over the experimental temperature range, but no systematic trend is observed. The absence of any discernible temperature dependence in the cation $\phi_v^0$ values occurs due to the assumption made by the convention that the proton volume is zero at all temperatures. Ignoring the temperature dependence of the proton volume obscures the temperature dependence of the transition-metal-cation volumes calculated with the convention. It is evident that another method of determining ionic volumes is needed when studying ionic volume temperature dependence.

## Conclusions

It has been shown that the Redlich–Meyer equation provides a consistent method of extrapolation for dilute apparent molal volume data to determine the desired $\phi_v^0$ values. Additionally, the Pitzer formalism successfully fit the apparent molal volume data at each temperature over the entire experimental concentration range for each electrolyte. The performance of both fitting equations was considered quite satisfactory.

The temperature dependence of the $\phi_v^0$ values for each electrolyte was found to resemble the temperature dependence of the previously reported $Ni^{2+}$ and $Cu^{2+}$ electrolytes (*5*). The temperature dependence was adequately described by a second-order polynomial. Furthermore, anion hydration properties were found to be important in determining the temperature at which the maximum electrolyte volume occurred.

The conventional cation $\phi_v^0$ values were found to have no significant temperature dependence. The absence of a temperature–volume correlation is an indication that some other method must be used to calculate the ionic apparent molal volumes when their temperature dependence is to be examined.

**Registry No.** $MnCl_2$, 7773-01-5; $Mn(ClO_4)_2$, 13770-16-6; $CoCl_2$, 7646-79-9; $Co(ClO_4)_2$, 13455-31-7; $FeCl_2$, 7758-94-3; $Fe(ClO_4)_2$, 13933-23-8.

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