Apparent Molar Volumes of Alkaline Earth Hexacyanocobaltates (III) in Aqueous Solution at 25°C

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The apparent molar volumes of Mg, Ca, Sr, and Ba hexacyanocobaltates (III) have been determined from 1×10⁻⁴ to 0.2M (mol·dm⁻³), using both vibrating tube densimeter and dilatometric methods. The semiempirical Pitzer equation has been used to reproduce the experimental data. Positive deviations from the Debye-Hückel limiting law (DHLL) have been observed at C < 0.01M and are compared with the predictions of two other electrostatic approaches, the DHLL+B₂ approximation of the Mayer theory and the numerical integration of the exponential Poisson-Boltzmann equation. A least squares procedure has been used to obtain the best fit parameters, including the apparent molar volume at infinite dilution.

KEY WORDS: Apparent molar volume; densities; electrolyte; aqueous solution; Mg₃[Co(CN)₆]₂; Ca₃[Co(CN)₆]₂; Sr₃[Co(CN)₆]₂; Ba₃[Co(CN)₆]₂.

1. INTRODUCTION

As a continuation of our previous work on high charge electrolytes we report here the volumetric behavior of aqueous solutions of four 2-3 salts: magnesium, calcium, strontium, and barium hexacyanocobaltates (III) and apply the relevant theory. The choice of hexacyanocobaltate salts was made because (i) the anion Co(CN)₆³⁻ is quite stable and does not hydrolyze, (ii) the cations Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ constitute a homologous series and the effect on \( V_\phi \) due to increasing ionic radius can be investigated.

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As far as we know, $V_6$ measurements for 2-3 and 3-2 salts have never been reported, with the exception of lanthanum sulphate which shows an anomalous volumetric behavior attributed to ion pair formation.$^{(9)}$ Other thermodynamic properties for this type of electrolyte in water which have been reported in the literature are the following: relative apparent molar enthalpies of calcium, strontium, and barium hexacyanoferrates (III)$^{(10)}$ and of lanthanum sulphate;$^{(11)}$ activity data for lanthanum, aluminum, indium, and tris-(ethylene diamine)cobalt(III) sulphates.$^{(12-15)}$ As already noticed,$^{(2,16)}$ none of these latter data extend to low enough concentrations to yield reliable extrapolations to infinite dilution, and hence reliable activity coefficients.

2. EXPERIMENTAL

2.1. Materials

The salts $\text{Mg}_3[\text{Co(CN)}_6]_2$, $\text{Ca}_3[\text{Co(CN)}_6]_2$, $\text{Sr}_3[\text{Co(CN)}_6]_2$, and $\text{Ba}_3[\text{Co(CN)}_6]_2$, were prepared from $\text{K}_3\text{Co(CN)}_6$ by ion exchange on a Dowex 50 wX8 resin in the hydrogen form, and by extracting the eluted $\text{H}_3\text{Co(CN)}_6$ on $\text{MgO}$, $\text{CaCO}_3$, $\text{SrCO}_3$, and $\text{BaCO}_3$, respectively. The salts were recrystallized three times from conductivity grade water and allowed to dry to constant weight. They contained appreciable amounts of water, 28 to 34% for the various salts. Heating is not successful in desiccating the salts even at reduced pressure, since partial decomposition to blue colored compounds occurs before water is completely lost. For this reason, an indirect determination of the water content was carried out using ion exchange columns (Dowex 50 in hydrogen form), then collecting $\text{H}_3\text{Co(CN)}_6$ on weighed $\text{Na}_2\text{CO}_3$, and titrating the excess carbonate with standardized $\text{HCl}$. The apparent molecular weights we obtained by this method were 763.3, 797.3, 1008.7, and 1181.0 for the series from magnesium to barium hexacyanocobaltate, with a maximum uncertainty of 0.2%. The actual accuracy is probably better than 0.5%, as suggested by a comparison of the above results with those obtained from different methods of analysis; EDTA titrations of Mg and Ca gave apparent molecular weights 0.5% and 0.2% lower for the corresponding salts, while gravimetric determinations of Sr and Ba as sulphates furnished apparent weights 0.5% higher and 0.3% lower, respectively.

Water employed either in densimetric or dilatometric measurements was first deionized and then distilled from KMnO$_4$ solution. It was degassed prior to use by boiling, and stored under vacuum.