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The Partial Molar Volumes of $FeCl_2$ and $FeCl_3$ in Ternary Solutions H_20-HCl-$FeCl_x$ from Density Measurements

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Abstract

The partial molar volumes of iron (III) and iron (II) in water at infinite dilution were extrapolated from high precision density measurements giving a value of -33.89 [cm^3 $mole^{-1}$] for iron (III) and a value of -2.45 [cm^3 $mole^{-1}$] for iron (II) in the conventional scale where $\overline{V^0_{H+}}$ = 0[$cm^3 mole^{-1}$]. Density measurements were carried on in ternary solutions of $FeCl_x$-H_2O-HCl to suppress potential hydrolysis and oxidation processes. A brief comparison of this work with previously published data is provided supporting our determination for the partial molar volume of iron (III). The value for the partial molar volume of iron (II) should still be object of study since poor agreement was found with the very few fragmented literature data.

Introduction

Partial molar volumes are thermodynamic quantities useful in deriving the activity coefficient of the electrolytes in solution. The most important application of the partial molar volumes is in calculating the effect of temperature and pressure on the activity[1]:

$$(\partial(\ln\gamma_i)/\partial P)_T = (V_i - V°_i)/RT \tag{1}$$

Equation (1) describes the relationship between the change in the activity coefficients γ_i for the i-component in a water solution and the pressure at constant temperature. The dependency between the changes in γ_i and the pressure P, has a logarithmic fashion and it's limited by the difference of the partial molar volume of the i-component in the solution and its partial molar volume at infinite dilution. A clear understanding of this change is relevant for interpreting reaction's rates in geothermal processes[2], chemical oceanography[3], hydrometallurgy, and seawater desalinization. We focused our attention on the partial molar volumes of iron because its importance in environmental processes. In the late nineties it has been hypothesized that iron is a limiting nutrient in the waters of the Southern Ocean[4]. Several field[5] and lab experiments[6] identified the quick conversion of iron (II) into iron (III) as the main cause for the lack of bioavailable iron. Iron III is not a form of iron readily available to the biomass because at the pH of seawater it precipitates solid as iron hydroxide.

The goal of this study is to provide accurate values for the molar partial volumes of iron II and iron III as a strong basis for more complex theoretical calculation leading to the determination of the proper activity coefficients for both species. To our knowledge the most reliable measurements for the partial molar volumes of iron II and iron III were the ones reported by Swaddle and Mak, in 1982 from density measurements in perchloric solutions.

Experimental

The density measurements were performed with a vibrating tube flow densimeter Sodev model 02-D. The instrument was calibrated with Standard Seawater using known densities of pure water and sea water. The densities of the solutions were measured to a precision of ± 3x 10^{-6} [g cm^{-3}] while the accuracy was ± 6x 10^{-6} [g cm^{-3}]. The accuracy of the instrument was checked several times comparing the results for $\Delta\rho$ and V_i for NaCl weighed solution with the corresponding literature values. Each experimental value was checked three times and then averaged. The temperature baths controlling the densimeter was set to ± 0,002 °C with a quartz thermometer.

The vibrating tube densimeter applies the principle of the vibrating tube[8], whose resonant frequency is sustained and monitored by appropriate electronic devices. The solutions are circulated into the vibrating tube during the period of measurement. Absent any interference the relationship between the density of the solutions and the natural vibration of the tube is given by:

$$\rho=A+B\tau \qquad (2)$$

where ρ is the density of the liquid, τ is the oscillation period, and A and B are constant characteristics of the specific mechanical system. Periodic checks were made on the density measurements with calibrated pycnometers to ensure proper calibration of the instrumental parameters. The solutions were circulated in alternated cycles with bi-distilled water trough the vibrating tube. Relative densities $\Delta\rho$ were measured as a function of the difference of the two vibration time periods:

$$\Delta\rho= (\rho-\rho_0)=B(\tau -\tau_0) \qquad (3)$$

where ρ_0 is the density of pure water and ρ is the density of the solutions. HCl stock solutions were prepared by dilution of concentrated HCl with bi-distilled water. The concentration of HCl solutions was double checked by chemical titration with NaOH and by comparing the densities at 25°C of the solutions with the densities calculated from equation (4):

$$\rho=\rho_o+18.54168\ m-1.325942\ m^{1.5}-0.006989\ m^{2}-0.058992\ m^{2.5}+0{,}007638\ m^{3} \qquad (4)$$

adapted from Hershey et al.[9] In equation (4) m is the number of moles of HCL per Kilogram of solvent, ρ_o is the density of pure water at 25°C: ρ_o=997.045 [Kg m^{-3}] taken from Kell[10]. The correlation of our experimental measurements with the values for the density of HCl solutions produced with equation (3) gave a χ^2 =0.998 indicating a substantial agreement between our experiments and the literature values.

Weighed amounts of $FeCl_2$ ad $FeCl_3$ (Fisher Chemicals analytical grade) were dissolved in the stock solutions of HCl. Most of the densities measurements were made at constant HCl concentration, varying only the molality of the metal salts. The partial molar volume of hydrochloric acid is affected by the ionic strength I [$I = 0.5 \times (\Sigma_i m_i z_i^2)$] but in the limited range of ionic strength of our experiments we could safely assume that $(\partial\phi_{HCl}/\partial I)=0$.

Iron (III) is a relatively strong Lewis acid reacting with the hydroxyl ion at pH higher than 6 to form iron (III) hydroxide. In the iron (III) density measurements an acidic environment was needed to prevent possible precipitation pheomena. Iron (II) is thermodynamically stable for in the range of pE between -10 and 10 for pH lower than 6[11].

Hence in the iron (II) density measurements the low pH environment was needed to prevent potential oxidation processes. Looking at the published data we noticed that in two works[7,12] the investigators just measured the density of solutions containing iron (II) salts without addressing or preventing possible oxidation of iron(II) to iron(III) due, for example, to the dissolved oxygen. In the measurements by Swaddle and Mak[3] $HClO_4$ was used to lower the pH, with the consequences of suppressing hydrolysis. In comparison with $Cl0_4^-$ the Cl^- ion has a smaller volume, and its volume is slightly dependent on the ionic strength. While $HClO_4$ may be efficient in preventing the hydrolysis of iron (III), its relatively high standard potential may create an interference in the measurements of the partial molar volumes of iron (II). In acidic environment $E°_{clo4/cl} > E°_{Fe+3/Fe+2}$, hence one would think that in the perchloric solutions of iron (II) used in the previous studies potential oxidation phenomena may have taken place transforming,

completely, or partially the ferrous salt into the ferric one. Because the low oxidation state of the Cl^- ion any oxidation process of the iron (II) in low HCl solutions is unlikely.
For binary solutions the formula:

$$\phi_2 = \{[(1+m_2 M_2)/\rho] - (1/\rho_0)\}/m_2 \tag{5}$$

can be used to calculate the apparent molar volume of component 2, at concentration m_2 [moles Kg^{-1}] But both our salts required acidic environment by HCl, to prevent either hydrolysis or oxidation processes. A third component HCl kept the pH at sufficiently low levels to prevent either problem. For ternary solutions the total volume is calculated with a different expression and, being an additive property, it is the result of the contribution of the three components. We calculated the mixing volume due to the addition of component 3 to the solution of components 1 and 2 as:

$$\phi(2,3) = \frac{M_T}{\rho} - \frac{1000(\rho - \rho_0)}{\rho_0 \rho m_T} \tag{6}$$

In equation (6) ρ and ρ_0 are the densities of the solution and of pure water respectively in [g cm^{-3}] , m_T is the total molality of the mixture in [moles Kg^{-1}] ($m_T=m_2+m_3$) and M_T is the weighted average molar mass of the mixture in [g $mole^{-1}$] calculated as $M_T=M_2X_2+M_3X_3$ where M is the molar mass of the *i*-component and X_i is its molar fraction in the solution. The apparent molal volume of the sole component 3 can be derived with the Young's rule[13]:

$$\phi(2,3) = \phi_2\left(\frac{m_2}{m_T}\right) + \phi_3\left(\frac{m_3}{m_T}\right) \tag{7}$$

According to equation (7) an independent estimate of the other component is needed to determine the value seek. In the range of temperature, concentration and ionic strength used in our experiments we estimated the partial molar volume of the HCl to be $\phi_3 \approx \overline{V_{HCl}}$ = 17.87 ± 0.5[$cm^3 mole^{-1}$] after Hershey et al[9]. In addition to that the partial molar volume at infinite dilution of hydrochloric acid was measured independently to minimize calibration errors and was in substantial agreement with the literature value[9] of 17.83 [$cm^3 mole^{-1}$]. The more immediate way to derive the value of the molar partial volume at infinite dilution is to use the simple Masson equation[14]:

$$\phi_2 = \phi^\circ_2 + S_v c^{0.5} \tag{8}$$

In the Masson equation S_V is an empirical parameter, and *c* is the concentration of the metal salt in moles per liter. While commonly used for binary solutions this equation does not take into account the total ionic strength of the solution. Millero[3,15] suggested using a rearrangement of the Redlich-Meyer equation to extrapolate the partial molar volumes at infinite dilution from apparent molal volumes:

$$\phi_2 = \phi^\circ_2 + kwxc^{0.5} + b_v c \qquad (9)$$

While the Masson equation is purely empirical, the Redlich-Mayer equation is based on Debye-Hückel equation. In equation (9) w is the valence factor ($w = 0.5\ x \sum_i v_i z_i^2$) where z_i and v_i are respectively the ionic charge and the molar number of ions formed by the electrolyte, k is the Debye-Huckel slope (k=1 .868 at 25 °C) and b is the only adjustable fitting parameter. We fitted the experimental data for the ferric chloride at room temperature with both formalisms obtaining values for ϕ_2 within the experimental error: $\phi_{2masson} = 19.62 \pm 0.6$ [cm^3 mole^{-1}] $\approx \phi_{2redlych\text{-}meyer} = 19.06 \pm 0.3$ [cm^3 mole^{-1}].

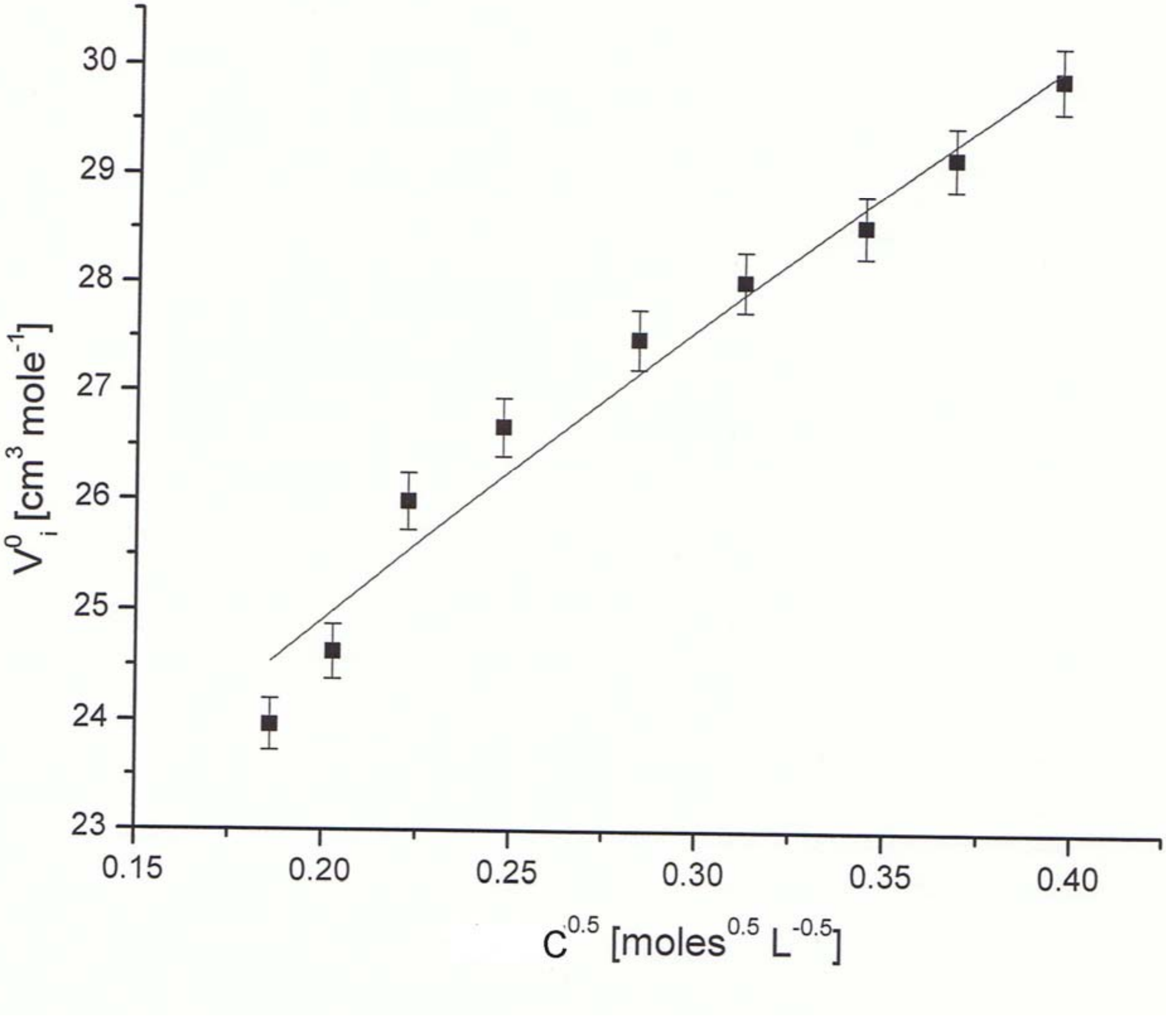

Fig. 1 - Linear fits of the apparent molal volumes for $FeCl_3$ at room temperature using the simple Masson equation.

The Redlich Mayer equation is derived by theoretical considerations ultimately related to the Debye-Hückel equation, while at a first look it seemed to slightly improve the fit of the iron (III) data its application was not conclusive for the iron (II) set of data. In addition to that the simple Masson equation is more intuitive and has less adjustable parameters, resulting in fits that adhere more to the experimental data rather than to the fitting procedure. In conclusion the latter was used for all subsequent fits.
The error associated with our calculated values could be estimated by propagating the errors on the density and molality measurements. Nevertheless due to the high accuracy of the density measurements ± 6x 10^{-6} [g cm^{-3}] and of the analytical balance used to measure the masses of salts, ±5x1 0^{-5} [g], the derived errors would be negligible if compared with the uncertainty introduced in the fitting procedure. Hence the errors associated with the volumes are mainly a result of the overall fits.

Results and Discussion

The world of ocean can be compared, to a limited extent, to a large chemical reactor where reactions take place in conditions of high ionic strength, low concentration of reagents, and in a relatively wide range of pressures and temperatures. Because of these conditions, far from the ideality, it is important to have as much basic information as possible on thermodynamic quantities like the molar partial volumes, equilibrium constants, and activity coefficient to get a better picture of the factors that affects chemical reactions in this environment. There are only four studies on the partial molar volume of ferric iron. Two of these studies are from the early seventies[3,12] and report a value for the conventional ionic volume of -43,7 [cm^3 $mole^{-1}$], while the third one, by Swaddle and Mak[7] was published in 1982 and reported a value of -36,5 [cm^3 $mole^{-1}$]. Both values are expressed in the conventional scale in which the proton has volume 0 [cm^3 $mole^{-1}$]. The most recent study was authored in India by Dey[16] and coworkers, and then published in 1997.
Our experimental value of -33.89 ± 0,6 [cm^3 $mole^{-1}$] is substantially closer to the value by Swaddle and Mak[7], rather than to the earlier measurements by Coutrer[2]. One issue in comparing partial molar volumes older measurements with modern data is that often older studies report the values the partial molar volumes at infinite dilution using the conventional scale ($\overline{V^0_{H+}}$ = *0*[cm^3 $mole^{-1}$]) while a more modern approach takes into consideration the experimental volume of the proton in aqueous solutions ($\overline{V^0_{H+}}$ = *-5.5*[cm^3 $mole^{-1}$]). Dey[16] and coworkers report a value of $\overline{V^0_{Fe+3}}$ = —47.6[cm^3 $mole^{-1}$] but do not explicitly address which scale they are using to calculate their data but from their wording it is possible to infer that they most likely reported their value in the ionic scale, and if that is the case their partial molar volume at infinite dilution in the conventional scale would be -31.1 [cm^3 $mole^{-1}$] reasonably close to Swaddle and Mak[7] and to this work.
The way to reconcile the two scales is by converting the conventional volume into the ionic partial molar volume at infinite dilution and vice versa by using the formula[15]:

$$\overline{V^0_{ionic}} = \overline{V^0}_{conventional} + z\overline{V^0_{H+}} \tag{10}$$

In equation (10) *z* is the charge of the electrolyte and $\overline{V^0_{H+}}$ = -5.5[cm^3 $mole^{-1}$]. For years there has been a general agreement on the partial molar volume of the proton in aqueous solution and it should be safe to assume that the conversion process does not introduce any major source of error[7,9,17]. On the other hand a recently published review of the single ionic volumes suggests a
$\overline{V^0_{H+}}$ = *-4.6*[cm^3 $mole^{-1}$][18]. While the difference between the two estimates is only one cm^3 per mole, since ferric iron has z=+3 the total correction to make on older values reported using $\overline{V^0_{H+}}$ = -5.5[cm^3 $mole^{-1}$] is 3 cm^3. If this new value is to be confirmed the partial molar volume at infinite dilution measured by Swaddle and Mak[7] would be in surprisingly excellent agreement with our values, while agreement with the value with Dey[16] and coworkers would be slightly worsened. It is beyond the scope of this article to analyze the assumptions behind the partial molar volume of proton in water solutions, but it is to point out that even a small change on the currently accepted value of*-5.5*[cm^3 $mole^{-1}$] would create the need to re-calculate most of the literature data.

Table. 1 - Apparent molal volumes for ferric and ferrous chlorides in hydrochloric acid solutions as calculated at room temperatures from density data.

m_{FeCl_3} [moles Kg^{-1}]	m_{HCl} [moles Kg^{-1}]	ρ [g cm^{-3}]	ϕ_{FeCl_3} [cm^3 mole^{-1}]
0.1539	0.1471	1.019929	29.94
0.0409	0.1452	1.005332	24.63
0.0345	0.1452	1.004481	23.96
0.1167	0.1452	1.015202	28.96
0.0963	0.1452	1.012557	28.04
0.0492	0.1452	1.006398	25.99
0.0798	0.1452	1.010409	27.50
0.0609	0.1452	1.007937	26.68
0.1330	0.1452	1.017267	29.20
m_{FeCl_3} [moles Kg^{-1}]	m_{HCl} [moles Kg^{-1}]	ρ [g cm^{-3}]	ϕ_{FeCl_2} [cm^3 mole^{-1}]
0.0490	0.1351	1.004857	18.11
0.2499	0.1351	1.030370	2.94
0.0087	0.1351	1.000422	26.71
0.1350	0.1351	1.015032	11.56
0.0063	0.1351	1.000168	29.05

The partial molar volume for Fe^{+2} we determined is substantially different from previous works. The early data from Millero[3] were estimates from critical parameters, while the more recent study by Pougue and Atkinson[19] seems to represent the best estimate according to the previous literature. While we plan to perform further experiments to verify this observation, our preliminary explanation lies on the fact that previous studies measured the densities of iron (II) salts either in a oxygen rich environment or in perchloric acid solutions: both to be considered a relatively strong oxidative environment, while our choice of using HCl as acid should have both kept the pH sufficiently low and avoid conversion of Fe^{+2} to Fe^{+3} due to oxidative processes.

Table. 2 - Conventional molar partial volumes for Fe(III) and Fe(II) at room temperature calculated using $\overline{V^0_{H+}}$ = -5.5[cm^3 mole^{-1}].

$\overline{V^0_{Fe+3}}$ [cm^3 mole^{-1}]		$\overline{V^0_{Fe+2}}$ [cm^3 mole^{-1}]	
This work	-33.89±0.6	This work	-2.45±0.9
Swaddle and Mak[7]	-36.5±1.2	Swaddle and Mak[7]	-22.1±1.2
Coutrer et al.[12]	-43.7	Coutrer et al.[12]	-17.7
Millero[3]	-43.7	Millero[3]	-24.7
Dey et al. [16]	-31.1	Pougue et al. [19]	-21.9

Conclusion

In this work we present values for the partial molar volumes of iron (III) and iron (II) in water at infinite dilution, extrapolated from high precision density measurements. We measured a value of – 33.89 [cm^3 mole^{-1}] for iron (III) and a value of -2,45 [cm^3 mole^{-1}] for iron (II). The analysis of our experimental results in the iron (III) experiments is supported by previous published studies that are consistent with our conclusions.

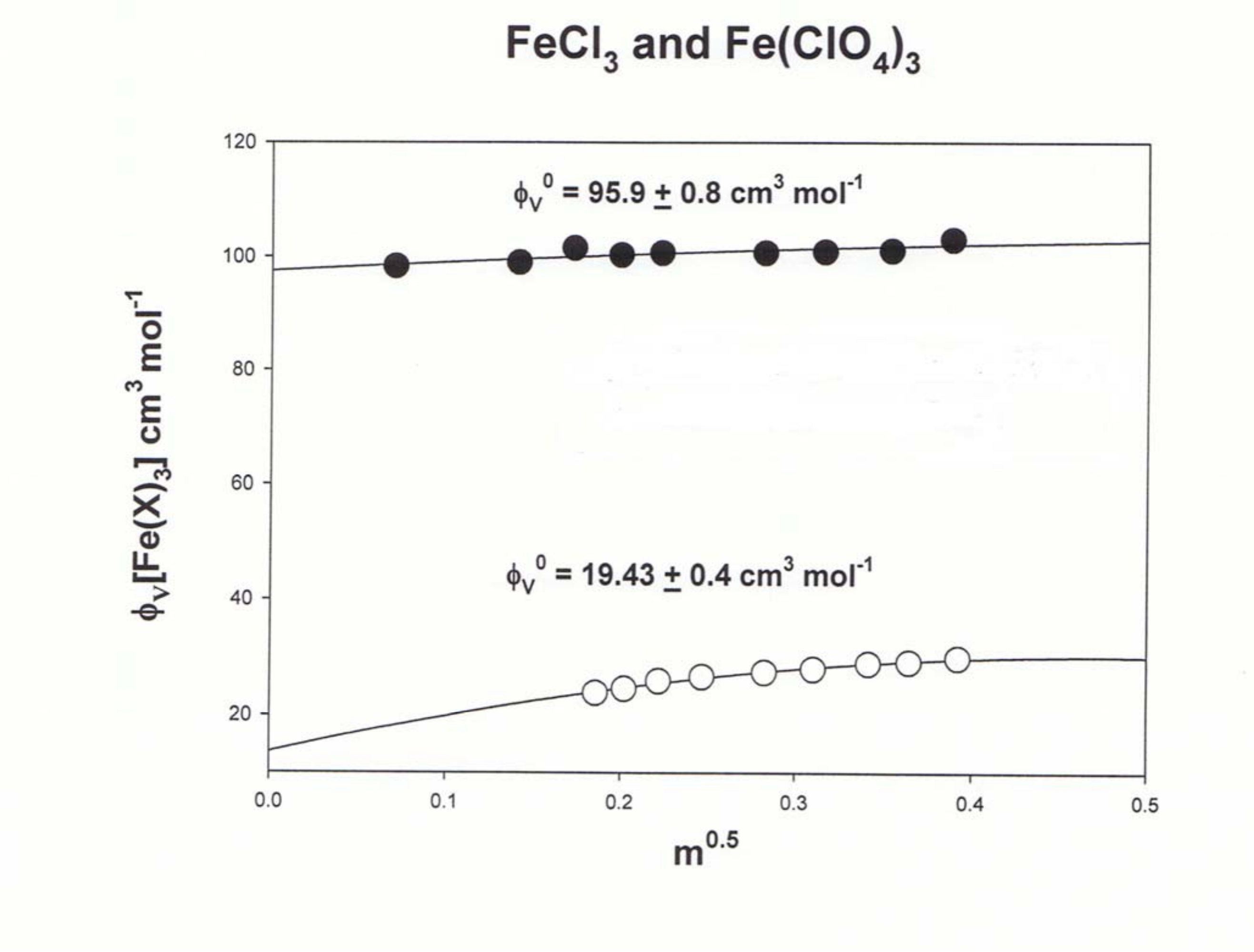

Fig. 2[20]-Extrapolation at infinite dilution of the apparent molal volumes of $FeCl_3$ (○) and $Fe(ClO_4)_3$[7] (●).

Our result of $\overline{V^{0}_{Fe+2}}$ = -2.45 ± 0.9[cm^3 $mole^{-1}$] is relatively different from measurements appeared in previously published work. This it is to be considered a preliminary observation since more work is needed to clarify the influence of the pH and the effect of the ionic buffer in the determination of the partial molar volume at infinite dilution of the metal ion. We feel that the differences between the determination of the partial molar volume at infinite dilution presented in this study and the ones from previous investigators are substantially related to the differences in experimental conditions under which this work was carried, and the ones used in the other available experimental studies[7,12,19]. These differences include the range of pH (2-3 in this work *vs* 5-8 in others), the choice of the ionic buffer (HCl in this work *vs* $HClO_4$ or HNO_3 in others), and possibly oxidative environment between (in acidic conditions $E°_{clo4/cl} > E°_{NO3-/NO2} > E°_{Fe+3/Fe+2}$).

The work by Millero[3] is an estimate of the molar partial volume of iron (II) at infinite dilution from critical parameters and may be less reliable due to the lack of information available in the literature on this topic at the time of publication. Since the broad interest in the chemistry of iron in seawaters, this study is only a first step of a re-evaluation of thermodynamic properties of iron water based solutions. Further work is needed to study the temperature dependence of the partial molar volumes of iron (III) and iron (II) and to theoretically quantify the effect of these newly proposed values on the estimation of the activity coefficients for the iron salts at different pressures.

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