

Solid-Solute Phase Equilibria in Aqueous Solutions, VIII: The Standard Gibbs Energy of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ **, ***

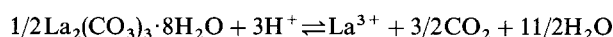
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Summary. The solubilities of lanthanum carbonate $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ in solutions S_0 ($[\text{H}^+] = H \text{ mol kg}^{-1}$, $[\text{Na}^+] = (I - H) \text{ mol kg}^{-1}$, $[\text{ClO}_4^-] = I \text{ mol kg}^{-1}$) at various fixed partial pressures of CO_2 have been investigated at 25.0°C . The hydrogen ion molality and the total molality of La(III) ion in equilibrium with the solid phase were determined by e.m.f. and analytical methods, respectively. The stoichiometric solubility constants

$$\log \star K_{ps0}^I = \log \{ [\text{La}^{3+}] p_{\text{CO}_2}^{3/2} [\text{H}^+]^{-3} \}$$

according to the overall reaction



have the values 10.23, 10.37, 10.58, 10.77 and 11.06 for $I = 0.1, 0.25, 1.0, 2.0$ and 4.0 mol kg^{-1} $(\text{Na})\text{ClO}_4$, respectively. The extrapolation to infinite dilution using the Pitzer equations resulted in a “thermodynamic” solubility constant:

$$\log \star K_{ps0}^0 = \log \{ ([\text{La}^{3+}] p_{\text{CO}_2}^{3/2} [\text{H}^+]^{-3}) (\gamma_{\text{La}^{3+}} \gamma_{\text{H}^+}^{-3}) a_{\text{H}_2\text{O}}^{11/2} \} = 9.57 \pm 0.05.$$

This in turn led to the Gibbs energy of lanthanite, $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, formation:

$$\Delta_f G_{298}^\ominus = -5048.4 \text{ kJ mol}^{-1}.$$

Keywords. Lanthanum carbonate; Pitzer model; Solubility.

Phasengleichgewichte zwischen Festkörpern und wäßrigen Lösungen, VIII: Die freie Bildungsenthalpie von $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$

Zusammenfassung. Die Löslichkeit von Lanthancarboxat $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ in Lösungen S_0 ($[\text{H}^+] = H \text{ mol kg}^{-1}$, $[\text{Na}^+] = (I - H) \text{ mol kg}^{-1}$, $[\text{ClO}_4^-] = I \text{ mol kg}^{-1}$) wurde bei 25.0°C und verschiedenen, konstanten Partialdrücken von CO_2 untersucht. Die Molalität der Wasserstoff- und die totale

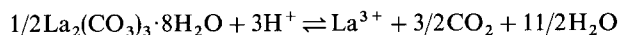
** Dedicated to Prof. Paul W. Schindler on the occasion of his 65th birthday

*** Part VII: [1]

Molalität der La(III)-Ionen im Gleichgewicht mit der festen Phase wurden potentiometrisch bzw. analytisch bestimmt. Für die stöchiometrischen Löslichkeitskonstanten

$$\log \star K_{ps0}^I = \log \{ [La^{3+}] p_{CO_2}^{3/2} [H^+]^{-3} \}$$

entsprechend der Gesamtreaktion



wurden bei $I = 0.1, 0.25, 1.0, 2.0$ und 4.0 mol kg^{-1} (Na)ClO₄, folgende Werte gefunden: 10.23, 10.37, 10.58, 10.77 und 11.06. Die Extrapolation auf unendliche Verdünnung mit Hilfe der Pitzer-Gleichungen führte zu einer „thermodynamischen“ Löslichkeitskonstante von:

$$\log \star K_{ps0}^0 = \log \{ ([La^{3+}] p_{CO_2}^{3/2} [H^+]^{-3}) (\gamma_{La^{3+}} \gamma_{H^+}^{-3}) a_{H_2O}^{11/2} \} = 9.57 \pm 0.05.$$

Mit dieser ergab sich die freie Bildungsenthalpie von Lanthanit La₂(CO₃)₃·8H₂O zu:

$$\Delta_r G_{298}^\ominus = -5048.4 \text{ kJ mol}^{-1}.$$

Introduction

Solubility studies of sparingly soluble metal carbonates contribute to fundamental as well as applied chemical research. Firstly, Gibbs energies of formation can be derived by appropriate combination of solubility constants and standard potentials, when both are measured in the same ionic medium [2] or extrapolated to infinite dilution. Secondly, thermodynamic information obtained thereby is since many decades used to predict the behaviour of the respective substances in industrially important reactions [3].

For the approach originally suggested by Schindler [4,5] to be applicable, reversible electrode potentials must be experimentally accessible in aqueous solutions of appropriate ionic strengths. However, only few metals meet this condition. Fortunately, the method of extrapolation can be improved considerably with the aid of the Pitzer equations [6]. Recently this was shown in the systems Na⁺-Y³⁺-ClO₄⁻-CO₂-H₂O [7] and Na⁺-Mg²⁺-ClO₄⁻-CO₂-H₂O [8].

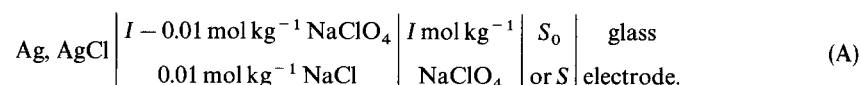
In the present work it was attempted to determine the solubility constant of lanthanite La₂(CO₃)₃·8H₂O at systematically varying ionic strengths. To avoid complications of side reactions, conditions were selected so as to minimize complex formation between lanthanum(III) ion and carbonate species. Information on solubility constants taken from the papers of Jordanov and Havezov [9], Ciavatta et al. [10], Ferri and Salvatore [11] and Firsching and Mohammadzadel [12] were compared with the results obtained in this work. Calculations were carried out with the Gibbs energy minimization program ChemSage [13] which uses the Pitzer model in the version of Harvie et al. [14] and, in addition, was recently improved by a general optimization routine [15].

Experimental

Lanthanite, La₂(CO₃)₃·8H₂O (99.99%), was either purchased from ABCR (Germany) and used directly, or lanthanum oxide (99.99% ABCR) was taken as starting material for its preparation following the procedure of Fischer et al. [16]. According to the latter, well crystallized La₂(CO₃)₃·8H₂O was prepared by adding slowly NH₄HCO₃ solution into the appropriate volume of 0.0067 mol kg⁻¹ La(NO₃)₃ solution at 0 °C, in a molar ratio La³⁺:HCO₃⁻ = 1:0.75. These lanthanum nitrate solutions

had been saturated with CO_2 for 12 hours at the same temperature prior to reaction. The precipitates were aged at 0°C for 3 or 4 days by continuously bubbling CO_2 through the suspensions. Finally the solid phases were filtered off, washed with water and air-dried. The products identified by X-ray diffraction analysis as lanthanite, agreed within the experimental error with the formula $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$. Pure carbon dioxide ($\geq 99.99\%$) and carbon dioxide/nitrogen mixtures (ca. 20%, 10% and 5% CO_2) were taken from cylinders. Sodium perchlorate (GR Merck) was recrystallized at 60°C .

Solutions S_0 ($[\text{H}^+] = H \text{ mol kg}^{-1}$, $[\text{Na}^+] = (I - H) \text{ mol kg}^{-1}$, $[\text{ClO}_4^-] = I \text{ mol kg}^{-1}$) were equilibrated with solid $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ at various fixed partial pressures of CO_2 . In the resulting solutions S the total molality of La(III) was determined complexometrically with *EDTA* as titrant and Xylenolorange as indicator. The pH or rather the hydrogen ion molality was followed using the galvanic cell (A).



At constant ionic strength the Nernst equation of cell (A) may be written as

$$E = E^\circ + \frac{RT \ln 10}{F} \log [\text{H}^+] + E_j, \quad (1)$$

where the liquid junction potential is essentially a linear function of $[\text{H}^+]$

$$E_j = -k[\text{H}^+]. \quad (2)$$

Under the pertinent conditions k can be determined experimentally or calculated from equations of varying complexity [17]. Moreover, in a definitive discussion of liquid junction potentials in similar systems, Hefter [18] concluded that for constant ionic medium junctions as in cell (A), E_j can be calculated by an approximate form of the Henderson equation (3); the limiting ionic conductivities λ_B^0 were taken from Robinson and Stokes [19].

$$E_j = -[\text{H}^+] \frac{RT}{F} \left\{ \frac{\lambda_{\text{H}^+}^0 - \lambda_{\text{Na}^+}^0}{I(\lambda_{\text{Na}^+}^0 - \lambda_{\text{ClO}_4^-}^0)} \right\}. \quad (3)$$

The e.m.f. was measured with a digital *pH* meter (ORION 940) and the solubility cell developed by Heindl and Gamsjäger was used [20]. Usually, after 48 hours of intimate contact between the solid lanthanum carbonate and the solutions, constant e.m.f. readings were obtained indicating equilibration. The solid material recovered from equilibrated solutions was occasionally checked X-ray diffractometrically, so as to make sure that no phase alterations had occurred.

Results

Solubility experiments have been carried out with commercially available $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ as well as with samples prepared according to Fischer et al. [16], the respective results agreed within the range of experimental errors. To ensure that true equilibrium was established, H and p_{CO_2} were varied to over a range of 10^{-1} to $10^{-3} \text{ mol kg}^{-1}$ and 1.0 to 0.05 atm, respectively (1 atm = $1.01325 \times 10^5 \text{ Pa}$). The pertinent data are summarized in Table 1. Plots of

$$\log \{ [\text{La}^{3+}]_{\text{tot}} \cdot p_{\text{CO}_2}^{3/2} \} \text{ versus pH}$$

were linear with an average slope of -3.01 ± 0.04 (see Fig. 1 and Table 2), according to the overall reaction (4)

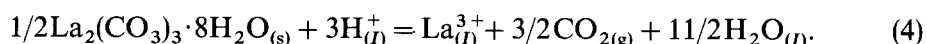


Table 1. Solubility of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ at 25 °C

| I mol kg ⁻¹ | P_{CO_2} atm | $[\text{H}^+]_{\text{ini}}$ mmol kg ⁻¹ | $-\log\left(\frac{[\text{H}^+]_{\text{eq}}}{\text{mol kg}^{-1}}\right)$ | $\frac{[\text{La}^{3+}]_{\text{tot}}^{\text{calc}}}{\text{mmol kg}^{-1}}$ | $\frac{[\text{La}^{3+}]_{\text{tot}}^{\text{exp}}}{\text{mmol kg}^{-1}}$ | $\log *K_{\text{ps0}}^I$ |
|-----------------------------|--------------------------|--|---|---|--|--------------------------|
| 0.10 | 0.9184 | 5.0 | 4.399 | 1.83 | 1.97 | 10.26 |
| | 0.9243 | 5.0 | 4.399 | 1.83 | 1.94 | 10.25 |
| | 0.9172 | 5.0 | 4.341 | 1.83 | 1.91 | 10.25 |
| | 0.1848 | 5.0 | 4.687 | 1.75 | 1.82 | 10.22 |
| | 0.1840 | 5.0 | 4.690 | 1.75 | 1.83 | 10.23 |
| | 0.0913 | 5.0 | 4.842 | 1.73 | 1.81 | 10.22 |
| | 0.9060 | 5.0 | 4.843 | 1.73 | 1.81 | 10.22 |
| | 0.0465 | 5.0 | 4.988 | 1.71 | 1.76 | 10.21 |
| | 0.0461 | 5.0 | 4.994 | 1.71 | 1.76 | 10.22 |
| 0.25 | 0.9236 | 10.0 | 4.287 | 3.47 | 3.75 | 10.38 |
| | 0.9174 | 10.1 | 4.290 | 3.51 | 3.59 | 10.37 |
| | 0.1850 | 10.1 | 4.640 | 3.43 | 3.57 | 10.37 |
| | 0.1839 | 10.1 | 4.643 | 3.43 | 3.51 | 10.37 |
| | 0.0917 | 10.0 | 4.788 | 3.37 | 3.68 | 10.37 |
| | 0.0917 | 10.0 | 4.783 | 3.37 | 3.59 | 10.35 |
| | 0.0918 | 10.0 | 4.789 | 3.37 | 3.57 | 10.36 |
| | 0.0463 | 10.1 | 4.941 | 3.39 | 3.47 | 10.36 |
| | 0.0462 | 10.1 | 4.936 | 3.39 | 3.48 | 10.35 |
| 1.00 | 0.9224 | 100.5 | 4.036 | 33.58 | 32.66 | 10.57 |
| | 0.9191 | 100.5 | 4.034 | 33.58 | 33.21 | 10.57 |
| | 0.9224 | 30.1 | 4.214 | 10.15 | 10.00 | 10.59 |
| | 0.9099 | 10.0 | 4.356 | 3.51 | 3.70 | 10.58 |
| | 0.9224 | 9.9 | 4.372 | 3.50 | 3.46 | 10.60 |
| | 0.9179 | 3.0 | 4.494 | 1.27 | 1.34 | 10.55 |
| | 0.9243 | 3.0 | 4.521 | 1.27 | 1.17 | 10.58 |
| | 0.1008 | 30.1 | 4.697 | 10.06 | 9.97 | 10.60 |
| | 0.1006 | 9.9 | 4.855 | 3.38 | 3.30 | 10.59 |
| 2.00 | 0.9366 | 100.0 | 4.089 | 33.39 | 34.44 | 10.76 |
| | 0.9228 | 100.0 | 4.095 | 33.39 | 34.11 | 10.77 |
| | 0.1015 | 100.0 | 4.581 | 33.35 | 33.71 | 10.78 |
| | 0.1014 | 100.0 | 4.577 | 33.35 | 33.73 | 10.77 |
| | 0.0462 | 100.0 | 4.752 | 33.35 | 33.73 | 10.78 |
| | 0.0463 | 100.0 | 4.755 | 33.35 | 33.61 | 10.79 |
| 4.00 | 0.9273 | 100.0 | 4.189 | 33.37 | 33.73 | 11.05 |
| | 0.9354 | 100.0 | 4.188 | 33.37 | 33.83 | 11.05 |
| | 0.1872 | 100.0 | 4.545 | 33.35 | 33.56 | 11.07 |
| | 0.1870 | 100.0 | 4.545 | 33.35 | 33.49 | 11.07 |
| | 0.0926 | 100.0 | 4.694 | 33.34 | 33.54 | 11.06 |
| | 0.0928 | 100.0 | 4.689 | 33.34 | 33.74 | 11.05 |
| | 0.0463 | 100.0 | 4.851 | 33.34 | 33.58 | 11.08 |
| | 0.0465 | 100.0 | 4.849 | 33.34 | 33.66 | 11.08 |

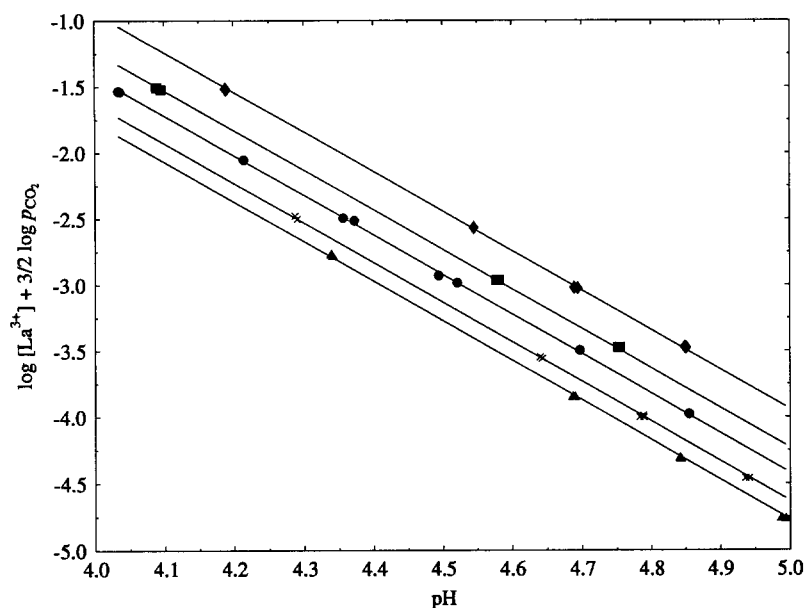


Fig. 1. Solubility of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ in $(\text{H}, \text{Na})\text{ClO}_4$ media at 25°C . $\blacktriangle I = 0.10$, $\times I = 0.25$, $\bullet I = 1.00$, $\blacksquare I = 2.00$, $\blacklozenge I = 4.00 \text{ mol kg}^{-1}$. For the sake of a clear visualization the solid lines were drawn with the theoretical slope = -3.0

Table 2. Auxiliary parameters for the determination of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ solubilities (25°C)

| $I/\text{mol kg}^{-1}$ | $k/\text{V kg mol}^{-1}$ | Slope | $-\log K_{pa_1}^I$ |
|------------------------|--------------------------|------------------|--------------------|
| 0.10 | 0.656 | -3.06 ± 0.01 | 7.61 |
| 0.25 | 0.262 | -3.03 ± 0.01 | 7.55 |
| 1.00 | 0.066 | -3.01 ± 0.03 | 7.55 |
| 2.00 | 0.033 | -2.97 ± 0.02 | 7.67 |
| 4.00 | 0.016 | -2.97 ± 0.02 | 7.95 |

The values of $[\text{La}^{3+}]_{\text{tot}}^{\text{calc}}$ were calculated using Eq. (5),

$$[\text{La}^{3+}]_{\text{tot}}^{\text{calc}} = \frac{1}{3}(H - h + K_{pa_1}^I \cdot p_{\text{CO}_2} \cdot h^{-1}), \quad (5)$$

where h refers to $[\text{H}^+]$ at equilibrium, and $K_{pa_1}^I$ is given by Eq. (6),

$$\log K_{pa_1}^I = \log \left\{ \frac{[\text{HCO}_3^-] \cdot [\text{H}^+]}{p_{\text{CO}_2}} \right\}. \quad (6)$$

The auxiliary parameters relevant for the calculation of solubility constants (k -values obtained from Eq. (3), slopes derived from the data of Fig. 1, and $-\log K_{pa_1}^I$ calculated with the Pitzer parameters given by Königsberger et al. [8]) are listed in Table 2, errors quoted are standard deviations. $[\text{La}^{3+}]_{\text{tot}}^{\text{exp}}$ and $[\text{La}^{3+}]_{\text{tot}}^{\text{calc}}$ in columns

Table 3. Solubility constants of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ (25 °C)

| $I/\text{mol kg}^{-1}$ | $\log *K_{ps0}^I$ | $\log(\gamma_{\text{La}^{3+}} \gamma_{\text{H}^+}^{-3})$ | $5.5 \log a_{\text{H}_2\text{O}}$ | $\log *K_{ps0}^0$ |
|------------------------|-------------------|--|-----------------------------------|-------------------|
| 0.10 | 10.23 ± 0.02 | -0.659 | -0.008 | 9.56 ₃ |
| 0.25 | 10.37 ± 0.01 | -0.789 | -0.020 | 9.56 ₁ |
| 1.00 | 10.58 ± 0.02 | -0.906 | -0.079 | 9.59 ₅ |
| 2.00 | 10.77 ± 0.01 | -0.964 | -0.161 | 9.64 ₅ |
| 4.00 | 11.06 ± 0.01 | -0.984 | -0.342 | 9.73 ₄ |

5 and 6 Table 1 are in fair agreement. Thus, the aqua ion, $\text{La}_{(\text{aq})}^{3+}$, predominates, while other La(III) species are negligible. This was also confirmed by calculations using the equilibrium constants given by Millero [21] and Pitzer parameters from [22].

In Fig. 2 the $\log *K_{ps0}^I$ values are plotted versus $I^{1/2}$. The experimental results up to $I = 1.0 \text{ mol kg}^{-1}$ ($\text{Na})\text{ClO}_4$ fall on the solid curve calculated with ${}^S\theta_{\text{Na},\text{La}}$ and $\psi_{\text{Na},\text{La},\text{ClO}_4}$ given by Kim and Frederick [23]. The dashed curve is obtained when the ternary mixing parameters are neglected. In this case, however, the calculated values deviate considerably from the experimental data already at $I = 1.0 \text{ mol kg}^{-1}$. Both curves extrapolate to

$$\log *K_{ps0}^0 = \log \{([\text{La}^{3+}]p_{\text{CO}_2}^{3/2}[\text{H}^+]^{-3})(\gamma_{\text{La}^{3+}}\gamma_{\text{H}^+}^{-3})a_{\text{H}_2\text{O}}^{1/2}\} = 9.57 \pm 0.05.$$

Experimental solubility constants, their standard deviations and the terms containing activity coefficients and water activities calculated with the Pitzer equations including ${}^S\theta_{\text{Na},\text{La}}$ and $\psi_{\text{Na},\text{La},\text{ClO}_4}$ are listed in Table 3. It should be emphasized that $5.5 \log a_{\text{H}_2\text{O}}$ is neither negligible nor independent of the ionic strength and has in any case to be taken into account, when lanthanite solubility constants determined in different ionic media are extrapolated to infinite dilution.

With the standard potential of La^{3+}/La taken from Nugent [24] (whose value agrees closely with that of Johnson [25]) and the CODATA values [26] for $\Delta_f G_{\text{CO}_2}^\ominus$ and $\Delta_f G_{\text{H}_2\text{O}}^\ominus$ the Gibbs energy of formation $\Delta_f G_{\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}}^\ominus$ can be calculated. Note that the experimental error in $\ln *K_{ps0}^0$ contributes only ca. $\pm 0.3 \text{ kJ mol}^{-1}$ to the overall uncertainty,

$$\begin{aligned} \Delta_f G_{\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}}^\ominus &= 2(\Delta_f G_{\text{La}^{3+}}^\ominus + 1.5\Delta_f G_{\text{CO}_2}^\ominus + 5.5\Delta_f G_{\text{H}_2\text{O}}^\ominus + RT \ln *K_{ps0}^0) \\ &= -5048.4 \text{ kJ mol}^{-1}. \end{aligned}$$

Discussion

As depicted in Fig. 2, $\log *K_{ps0}^I$ values determined at $I > 1.0 \text{ mol kg}^{-1}$ ($\text{Na})\text{ClO}_4$ start to deviate from the curve calculated with binary and ternary Pitzer parameters including ${}^S\theta_{\text{Na},\text{La}}$ and $\psi_{\text{Na},\text{La},\text{ClO}_4}$. Indeed most measurements of the osmotic coefficient for ternary $\text{NaClO}_4 + \text{La}(\text{ClO}_4)_3 + \text{H}_2\text{O}$ mixtures leading to these parameters have been carried out at ionic strengths below 1.0 mol kg^{-1} [27].

Ferri and Salvatore [11] use a very high ionic strength ($1 \text{ mol dm}^{-3} \text{ La}(\text{ClO}_4)_3$), consequently their and our results are difficult to compare. It should, however, again be pointed out that at high ionic strengths water activities have to be taken into account in the extrapolation procedure, hence the agreement might be incidental.

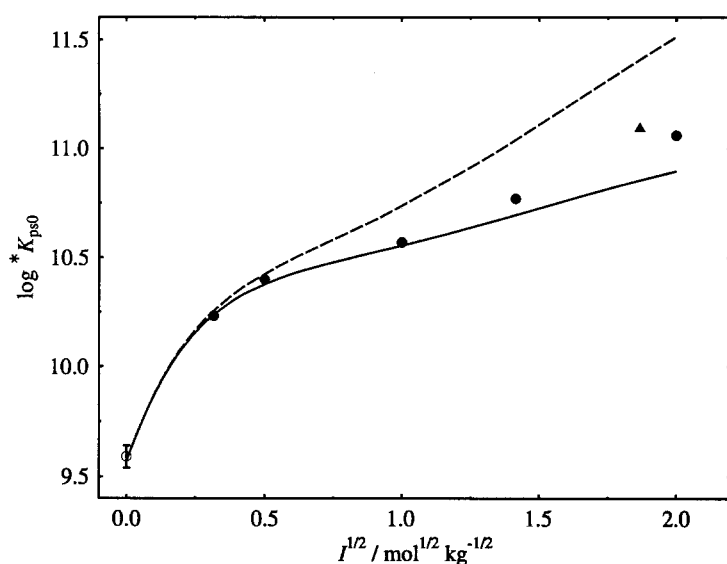


Fig. 2. Extrapolation of $\log *K_{ps0}$ ($\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$) to infinite dilution. The solid curve was calculated with ${}^s\theta_{\text{Na},\text{La}}$ and $\psi_{\text{Na},\text{La},\text{ClO}_4}$ given by Kim and Frederick [23]. The dashed curve is obtained when the ternary mixing parameters are neglected. ● this work; ▲ $I = 3.49 \text{ mol kg}^{-1}$, $\log *K_{ps0}^I = 11.10$ recalculated from [10]

From Fig. 2 it can be concluded that the solubility constant given by Ciavatta et al. [10] agrees reasonably well with the values of this work, provided both mass law expressions are calculated on the same (molality or molarity) basis.

The solubility constants found by Jordanov and Havezov [9] and Firsching and Mohammadzadel [12] are ca. 10 and 500 times respectively higher than the mean value found in this work. Such discrepancies can usually only be explained, when in fact different solid substances have been investigated. Therefore, it is assumed that Jordanov and Havezov as well as Firsching and Mohammadzadel determined the solubility of amorphous and/or more soluble lanthanum carbonate or hydroxide phases.

The results of this work can be summarized as follows:

1. The Pitzer equations are useful to extrapolate solubility constants $*K_{ps0}^I$ to zero ionic strength, particularly in simple cases where only one species as e.g. the aqua ion controls the overall solubility of the metal.
2. $*K_{ps0}^0$ values thus obtained lead to accurate Gibbs energies of formation.
3. Measurements carried out in a constant ionic medium may be used to calculate the respective value of the solubility at infinite dilution provided the ionic strength is not higher than ca. 1 mol kg^{-1} .
4. The ternary Pitzer parameters needed to predict solubilities at higher ionic strengths have still to be optimized. Once this has been achieved a wealth of already existing experimental information can be made to contribute to thermodynamic data banks.

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