

Single-Ion Activities of Lanthanum Chloride in Aqueous Solution

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Single-Ion activity coefficients of lanthanum and chloride ions in aqueous 0.1–1.4 molal lanthanum chloride solutions at 25 °C have been determined by a liquid-junction approach. For either sort of ion, obedience is found to $\ln f_i = -z_i^2 A c^{1/3} + (z_i^2/r_i) B c$, where A and B are constants common to the ions of the salt, c is the salt molarity of the solution and z_i and r_i are the ion charge number and the effective ion radius, respectively. This is interpreted by a combined quasi-lattice and ion-hydration excess energy treatment.

True single-ion activity coefficients (γ_i) are obtainable by a double-layer approach.¹ Convenient single-ion activity coefficients (γ'_i), defined by eqn. (1)

$$\gamma'_i = \gamma_i r^{-z_i/2} \quad (1)$$

where z_i is the ionic charge number (with sign) and r means γ_+/ γ_- for potassium chloride in pure saturated solution of this salt, are obtainable by a liquid-junction approach.² The two approaches have recently been tested against each other for aqueous solutions of sodium sulfate.³ This testing is satisfactory at low concentration, favours the liquid-junction approach at higher concentration and shows r to be close to unity at 25 °C.

For aqueous single-salt solutions, rational (mol fraction) activity coefficients are obtained from molal ones by eqn. (2):

$$f_i(\text{or } f'_i) = (1 + (v x / 55.51)) \gamma_i(\text{or } \gamma'_i) \quad (2)$$

where v is mol of ions per mol salt and $x/55.51$ is the mol ratio of salt to water in the solution.⁴ From studies of alkali-metal halide solutions,^{5,6} it appears that such activity coefficients for the ions

of single-salt solutions at medium to high concentration are well represented by equations like eqn. (3)

$$\ln[f_i(\text{or } f'_i)] = -A_i(c/c^\circ)^{1/3} + B_i(c/c^\circ) \quad (3)$$

where A_i and B_i are salt and ion dependent constants (25 °C, 1 atm) and c/c° is the dimensionless salt molarity of the solution. The two right-hand terms of this equation have been ascribed to quasi-lattice ion-ion interaction and hydration energy loss, respectively.^{5,6} In the linear term, m/m° may replace c/c° .

The present work pursues the above description by studies on aqueous solutions of the 3:1 salt lanthanum chloride. Main aims are to test the applicability of eqn.(3) for such solutions and to have more information on the constants A_i and B_i of this equation. By having stable, quite large and spherical ions with little tendency to complex each other or to hydrolyze water,⁷ lanthanum chloride is a suitable salt for the present studies.

EXPERIMENTAL

The experimental work comprises measurements of the liquid-junction containing equilibrium potential (E') of the Ag/AgCl electrode in aqueous 0.1–1.4 molal LaCl₃ solutions against the saturated calomel electrode under isothermal conditions at 25 °C. From such data, the convenient molal activity coefficient (γ_-) of the chloride ion is obtained by eqn. (4)

$$\gamma'_- = \frac{m^\circ}{m_-} \exp\left[-\frac{F}{RT}(E' - \Delta\phi - E^\circ + 0.241\text{V})\right] \quad (4)$$

where m_-/m° is the dimensionless chloride ion molality concerned, E° is the standard molal

hydrogen-scale potential of the Ag/AgCl electrode, and $\Delta\phi = \phi_t - \phi_r$ is the liquid-junction potential difference between the test solution (ϕ_t) and the saturated KCl solution of the calomel reference electrode (ϕ_r), all at 25 °C.² In the present work, 0.222 V has been used for E° ,⁸ and $\Delta\phi$ has been estimated from the Henderson equation⁹ with limiting mobility data⁸ for the ions.

The convenient molal activity coefficient (γ'_\pm) is obtained from eqn. (5)

$$\gamma'_\pm = \gamma_\pm^4 / (\gamma'_\pm)^3 \quad (5)$$

using presently determined values for γ'_\pm and tabulated data⁸ for the mean molal ionic activity coefficient (γ_\pm). These activity coefficients are all stoichiometric bare-ion ones.

The solutions were made from high purity lanthanum chloride (ROC/RIC) and twice distilled water. They were deoxygenated with purified and premoistened nitrogen. The measurements were performed with equipment and procedures essentially as previously described.²

RESULTS

The results of the present work are summarized in Table 1, which also gives the previous⁸ mean-ion data utilized. The activity data have been transferred to the mol-fraction scale by means of eqn. (2), the molality data to the molarity scale by means of solution density data,⁷ and the outcome analyzed for the applicability of eqn. (3). In this analysis,⁵ a search is made for a value of A_i which best makes $\ln f_i + A_i(c/c^\circ)^{1/3}$ a linear function of c/c° (with emphasis on the salt molarity range 0.1–1.0). The slope of this function is B_i .

Such testing results are given and illustrated in Figs. 1 and 2. Except for some deviation at high

Table 1. Data for aqueous lanthanum chloride solutions at 25 °C (see text).

m/m°	c/c°	$\Delta\phi/mV$	E'/mV	γ'_-	γ'_+	γ_\pm
0.1	0.0995	0.3	22.8	0.66	0.034	0.314
0.2	0.1985	1.7	8.0	0.62	0.024	0.274
0.3	0.297	2.7	-0.3	0.59	0.023	0.263
0.5	0.493	4.3	-10.2	0.56	0.028	0.266
0.7	0.686	5.5	-17.0	0.55	0.040	0.285
1.0	0.970	6.9	-25.2	0.56	0.078	0.342
1.4	1.339	8.4	-34.6	0.60	0.23	0.470

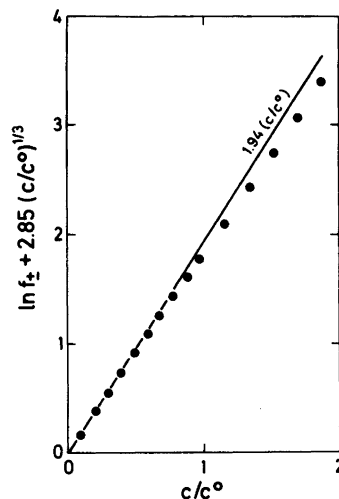


Fig. 1. Tests on the applicability of eqn. (3) to f_\pm (with best fitting value for A_\pm).

concentration, they essentially show obedience to eqn. (3) with the parameter values:

$$A_+ = 8.55 \text{ and } B_+ = 6.43 \quad (6a)$$

$$A_- = 0.95 \text{ and } B_- = 0.44 \quad (6b)$$

$$A_\pm = 2.85 \text{ and } B_\pm = 1.94 \quad (6c)$$

for the cation, the anion and the hypothetical mean-ion, respectively, of lanthanum chloride in

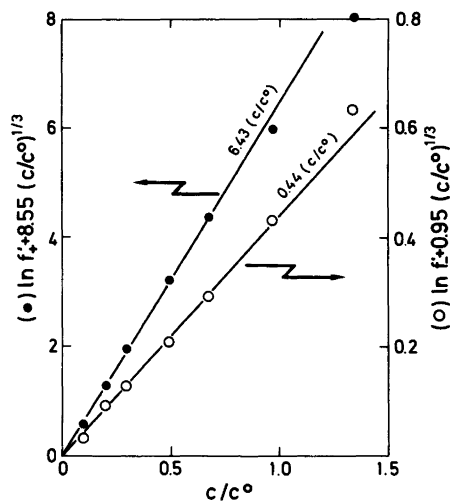


Fig. 2. Tests on the applicability of eqn. (3) to f_+ and f_- (with best fitting values for A_+ and A_-).

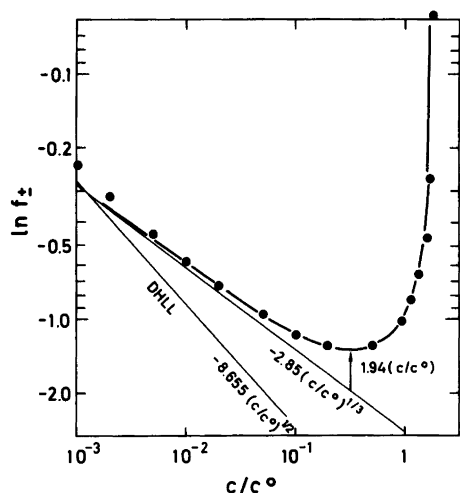


Fig. 3. Log-log plot of $\ln f_{\pm}$ vs. c/c° for lanthanum chloride in water at 25 °C. Curve is $-2.85(c/c^{\circ})^{1/3} + 1.94(c/c^{\circ})$. DHLL means Debye-Hückel limiting law.

aqueous single-salt solutions at 25 °C. The lines in Fig. 2 should respectively give $\ln f_{+} = -(3/2)\ln r$ and $\ln f_{-} = (1/2)\ln r$ at $c/c^{\circ} = 0$. That the lines essentially go through origo, supports that r be close to unity.

In Fig. 3, a log-log plot of $\ln f_{\pm}$ (from tabulated data⁸) vs. c/c° is given and compared to a curve

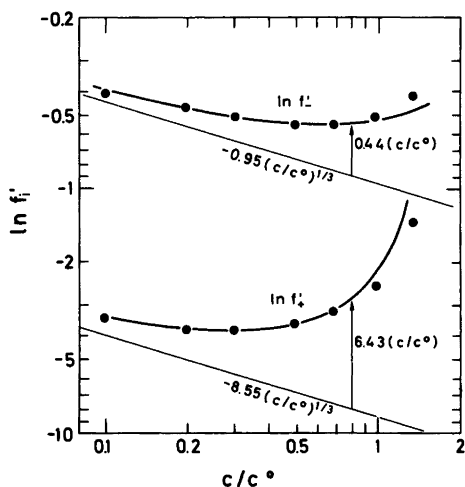


Fig. 4. Log-log plot of $\ln f_i$ vs. c/c° for lanthanum chloride in water at 25 °C. Curves are $-A_i(c/c^{\circ})^{1/3} + B_i(c/c^{\circ})$ with noted values for A_i and B_i .

for the function $-2.85(c/c^{\circ})^{1/3} + 1.94(c/c^{\circ})$ over an extended concentration range. The experimental data clearly follow this function well in the molarity range 10^{-2} –1. At higher concentrations, the above noted deviation is seen. At lower concentrations, another deviation appears towards approaching obedience to the Debye-Hückel limiting law (DHLL). In Fig. 4, analogous comparisons are made for the single-ion data over the concentration range covered.

DISCUSSION

Over an extended concentration range, (about 10^{-2} –1 M) the mol-fraction activity coefficients (f_{+} , f_{-} , f_{\pm}) of lanthanum chloride in aqueous solution clearly follow eqn. (3) with a negative cube-root term and a positive linear term. This matches what has previously been found for alkali-metal halides,^{5,6} and makes this behaviour a more general one for strong electrolytes (ionophores). Since the activity coefficient (by $\mu_i^{\text{ex}} = RT \ln f_i$) represents excess energetic interactions over ideal ones ($\mu_i^{\text{ex}} = \mu_i - \mu_i^{\text{id}}$) for the dissolved ions, the two observed terms may be associated with electrostatic ion-ion interactions and remaining less ideal ion-water interactions by $\mu_i^{\text{ex}} = \mu_i^{\text{el}} + \mu_i^{\text{c}}$ with $\mu_i^{\text{el}} = -RTA_i(c/c^{\circ})^{1/3}$ and $\mu_i^{\text{c}} = RTB_i(c/c^{\circ})$.

A negative cube-root term is expected from quasi-lattice treatment of ion-ion interactions,¹⁰ provided the quasi-lattice type (the quasi-Madelung constant) and the effective dielectric constant be concentration independent. This is qualitatively satisfactory, but gives much room for possible deviations. From lattice energy (or Güntelberg charging) considerations,⁶ one furthermore may expect $A_{+}:A_{-}:A_{\pm} = z_{+}^2:z_{-}^2:|z_{+}z_{-}|$ for a single-salt solution. In the present case, this means 9:1:3, which fully agrees with the experimental results [see eqns.(6a)–(6c) above].

A positive linear term is expected from a Born-charging treatment of ion hydration,⁶ provided the effective dielectric constant involved (ϵ) be related to the one for pure water (ϵ_w) by $\epsilon_w/\epsilon = 1 + \delta c$, where δ is a constant. For single-salt solutions, the static dielectric constant appears to vary somewhat like this up to quite high concentration.¹¹ Also this is qualitatively satisfactory, but needs more elaboration. The Born-charging treatment furthermore gives $B_{+}/B_{-} =$

$(z_+^2/r_+)/z_-^2/r_-)$, where r_+ and r_- are the effective radii of the dissolved cation and anion, respectively. With the results of eqns. (6a) and (6b), one hence obtains $r_+/r_- = 0.62$ for the dissolved ions of lanthanum chloride. The corresponding Pauling radius ratio is 0.635.

The present results and their matching with simple expectations lend confidence to the possibility and profitability of determining single-ion activity data. The work moreover supports the applicability of a combined quasi-lattice and hydration energy treatment of ionic activity coefficients at medium to high electrolyte concentration.

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