

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEW HAMPSHIRE]

The Activity and Osmotic Coefficients of Aqueous Solutions of Lanthanum Chloride at 25°

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The present communication is concerned with the calculation of the activity and osmotic coefficients of lanthanum chloride in aqueous solution at 25°. These quantities have been calculated from the vapor pressures of the aqueous solutions obtained by the isotonic method of Robinson and Sinclair.¹

Experimental Details

Apparatus.—The apparatus employed was the same as that described by Mason and Gardner² except for a few minor alterations. Six glass weighing bottles with ground-in stoppers were employed instead of the nickel crucibles. The metal tee tube was replaced by a brass needle valve to which was soldered the female half of a brass union. The male half of the union was connected by means of rubber tubing to the vacuum line. Another male half of the union interchangeable with the first was soldered shut and served to keep water out of the valve during immersion in the thermostat.

All measurements were carried out in a water thermostat at 25 ± 0.01°. The temperature was determined by thermometers checked against thermometers calibrated by the Bureau of Standards.

Lanthanum Chloride.—The lanthanum salt had been prepared carefully by repeated recrystallization. The chloride was prepared from the oxalate by ignition to the oxide and solution of this in redistilled, arsenic free hydrochloric acid. The chloride so prepared was then twice recrystallized by concentration of the aqueous solution and shaking out with hydrogen chloride gas at 0°. It was then carefully air-dried at 50° and placed for several weeks in a vacuum desiccator over potassium hydroxide. Examination of the solutions with the hand spectroscope and by chemical test showed the absence of other rare earths. The lanthanum chloride was dissolved in water to make a concentrated solution which was carefully analyzed gravimetrically for chloride content. This solution was then weighed out into the weighing bottles as needed.

Potassium Chloride.—The best c. p. grade of potassium chloride was twice recrystallized from conductivity water and then dried for twenty-four hours at 120°. This salt was weighed directly into the weighing bottles.

Results

Three samples of each concentration of lanthanum chloride solution were allowed to come to isopiestic equilibrium with three samples of the reference, potassium chloride solution. The data obtained are, therefore, in each case the mean of

three determinations. These data are given in Table I.

TABLE I
CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE (m_1) AND LANTHANUM CHLORIDE (m_2)

m_1	m_2	m_1	m_2
0.2157	0.1091	2.5870	1.0272
.4298	.2281	2.8414	1.0967
.5697	.3063	3.2548	1.2071
.7399	.3895	3.4075	1.2472
1.0312	.5069	3.4381	1.2574
1.4362	.6603	3.5795	1.2908
1.7105	.7548	3.7674	1.3381
1.7321	.7618	3.8541	1.3595
2.0895	.8767	3.8814	1.3663
2.4924	.9985	4.1533	1.4317
		4.2776	1.4573

It was found that forty-eight hours were sufficient for equilibrium between the concentrated solutions. For the dilute solutions it was necessary to run them as long as four days to obtain equilibrium. Concentrations below 0.1 m would not come to equilibrium in any length of time. This is in accordance with the experience of Robinson and Jones³ for higher valence types.

The data given in Table I were plotted, m_1 vs. m_2 , on a large scale. Values of m_1 and m_2 were then obtained from this curve at round concentrations of lanthanum chloride. The vapor pressures of these isopiestic solutions were then obtained by calculation from the equation

$$R = (p_0 - p)/mp_0$$

The values of R for this calculation were obtained from a large scale plot of the values given by Robinson and Sinclair¹ for potassium chloride solutions.

The values of the activities of the water in the solutions were then calculated from the equation $a_1 = p/p_0$.

The osmotic coefficient ϕ was calculated by means of the equation $\phi = (55.51/4m_2) \ln p_0/p$. These data are all given in Table II.

The activity coefficients of the lanthanum chloride in the solutions were calculated by the method of Randall and White⁴ using the value 2.81 as the

(1) Robinson and Sinclair, *THIS JOURNAL*, **56**, 1830 (1934).

(2) Mason and Gardner, *J. Chem. Ed.*, **13**, 188 (1936).

(3) Robinson and Jones, *THIS JOURNAL*, **58**, 959 (1936).

(4) Randall and White, *ibid.*, **48**, 2514 (1926).

TABLE II

VAPOR PRESSURES, OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS OF LANTHANUM CHLORIDE SOLUTIONS

m_2	ρ , mm.	a_2	φ	γ obsd.	γ calcd.
0.0	23.756 ^a	1.000	1.000	1.000	1.000
.1	23.609	0.9938	0.860	0.318	0.309
.2	23.467	.9878	.849	.269	.269
.3036	23.321	.9817	.837	.247	.254
.5	22.986	.9676	.915	.250	.249
.7	22.586	.9508	1.001	.272	
1.0	21.860	.9202	1.154	.322	
1.2	21.283	.8959	1.271	.376	
1.4	20.642	.8689	1.393	.446	
1.5	20.290	.8541	1.459	.491	

^a "International Critical Tables," Vol. III, p. 210.

zero intercept on the $h/m_2^{1/2}$ axis, which was calculated from the value for the dielectric constant for water obtained by Wyman.⁵ The calculated values are tabulated as $\gamma_{\text{obsd.}}$ in Table II. In order to provide some means of comparison with existing data the values of the activity coefficients obtained by this means have been plotted with similar values for lanthanum nitrate obtained from Landolt-Börnstein.⁶ This plot, which also contains the values of the osmotic coefficients obtained, is shown in Fig. 1.

The constants A and B have been calculated for the Hückel equation⁷

$$\log \gamma = -\frac{1.068\sqrt{12c}}{1 + A\sqrt{12c}} + \frac{B(12c) - \log(1 + 0.072m)}{1 + A\sqrt{12c}}$$

A and B were found to be 1.096 and 0.02027, respectively. These values were used in the Hückel equation to calculate the activity coefficients of the lanthanum chloride solutions for which the densities had been determined by Mason and Leland.⁸ The values which were obtained from the calculation are given as $\gamma_{\text{calcd.}}$ in Table II.

The value of A obtained gives a tentative value

(5) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(6) Landolt-Börnstein-Roth-Scheel, "Tabellen," (5) II Ergänzungsband, Verlag Julius Springer, Berlin, 1931, p. 1123.

(7) Hückel, *Physik. Z.*, **26**, 93 (1925).

(8) Mason and Leland, *THIS JOURNAL*, **57**, 1507 (1935).

of 4.7×10^{-8} cm. for the mean distance of approach "a."

The values obtained follow the general trend noted for all electrolytes, namely, a minimum in the curve when the activity coefficient is plotted against the ionic strength. They are, of course, open to the criticism of some uncertainty due to possible variation of the graphical integration below 0.1 molal. This is, however, unavoidable with this method which is not applicable with accuracy below this concentration.

Summary

1. The vapor pressures of aqueous solutions of lanthanum chloride have been determined by the isopiestic method, using potassium chloride for the reference substance.

2. The activity and osmotic coefficients of the

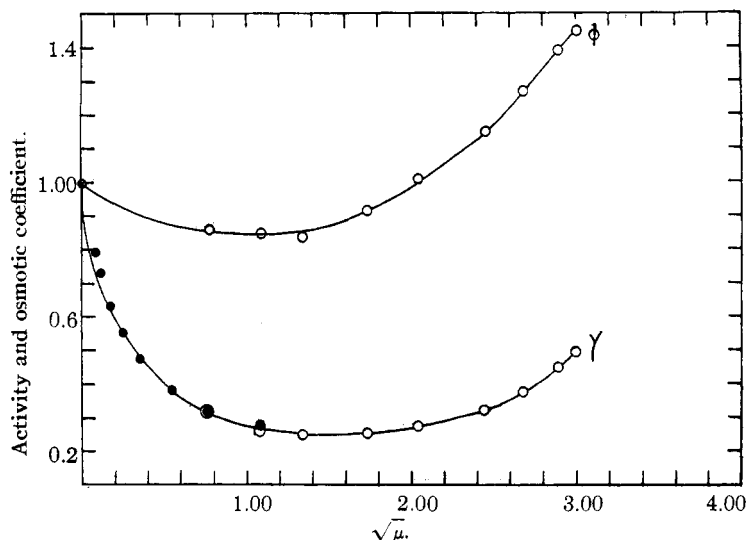


Fig. 1.—Activity and osmotic coefficients: O, LaCl_3 ; ●, $\text{La}(\text{NO}_3)_3$.

lanthanum chloride solutions have been calculated from the vapor pressure data.

3. The activity coefficient of lanthanum chloride in aqueous solution may be calculated by Hückel's equation, which is

$$\log \gamma = -\frac{1.068\sqrt{12c}}{1 + 1.096\sqrt{12c}} + 0.02027(12c) - \log(1 + 0.072m)$$

for lanthanum chloride solutions.

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