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Effect of Pressure on the Dissociation of the $(LaSO_4)^+$ Complex Ion[1]

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Electrical conductance as a function of pressure up to 2000 atm has been measured on aqueous solutions of lanthanum sulfate at 25° at seven concentrations from 0.0002 to 0.0082 equiv/l. The effect of pressure on the dissociation constant of the $(LaSO_4)^+$ complex ion pair was calculated using three different methods. At atmospheric pressure $\Delta V°$ ranged from -21.2 to -26.2 ml/mole and at 2000 atm $\Delta V°$ ranged from -6.8 to -11.8 ml/mole depending on the method used and concentration. Based on the atmospheric pressure value of $\bar{V}_2° = -23.8$ for $La_2(SO_4)_3$ the partial molal volume of the $(LaSO_4)^+$ ion at the lowest concentration is -0.9 to 0.2 ml/mole.

The very small partial molal volume assigned by Owen and Brinkley[2a] to the La^{3+} ion, $\bar{V}_i° = -38.3$ ml/mole relative to the H^+ ion for which $\bar{V}_i° = 0$ ml/mole, suggested to F. H. F. that there might be an even greater effect of pressure on $La_2(SO_4)_3$ than was observed for $MgSO_4$[2b] or $MnSO_4$.[3]

Measurements of the electrical conductivity were made on aqueous solutions of $La_2(SO_4)_3$ at 25° in essentially the same manner as for $MgSO_4$. It was possible to use Pyrex connected electrodes throughout the measurements with a small correction (10^{-6} atm^{-1}) for the coefficient of linear compression of Pyrex.[4]

Lanthanum chloride was prepared from Lindsay lanthanum oxide in the manner of Nathan,[5] while the lanthanum sulfate purchased from K and K Laboratories was recrystallized once, also after Nathan. Reagent grade potassium chloride and potassium sulfate were obtained from Mallinckrodt and Matheson Coleman and Bell, respectively. All solutions were within ±0.2 pH unit of the conductance water (pH 5.8).

Results

Ratios of equivalent conductivities as a function of pressure are shown in Table I. By making use of earlier data[6,7] obtained at 1 atm, values for equivalent conductance as a function of pressure were calculated using the ratios in Table I and are shown in Table II. In Table III measurements to 2000 atm on KCl solutions obtained in the 30-ml cylindrical Teflon cell show agreement to within 0.1% with those obtained in a 12-cc spherical Pyrex cell.

Table I: Λ_P/Λ_1 for Aqueous Solutions of $La_2(SO_4)_3$ at 25°

P,	mequiv/l.						
atm	0.2	0.3	0.6	1.2	2.4	3.1	8.2
250	1.036	1.044	1.056	1.064	1.072	1.074	1.078
500	1.063	1.078	1.102	1.119	1.135	1.139	1.147
750	1.082	1.106	1.140	1.166	1.190	1.198	1.213
1000	1.096	1.125	1.169	1.206	1.239	1.249	1.274
1250	1.104	1.140	1.193	1.239	1.292	1.296	1.326
1500	1.107	1.149	1.209	1.263	1.314	1.330	1.372
1750	1.107	1.153	1.222	1.283	1.342	1.361	1.411
2000	1.103	1.156	1.231	1.299	1.365	1.387	1.447

If c is concentration of the solute in equivalents, then the dissociation constant for the reaction

$$LaSO_4^+ \rightleftarrows La^{3+} + SO_4^{2-} \quad (1)$$

may be expressed as follows[8]

$$K = [(c/3 - x)(c/2 - x)/x]\pi^f \quad (2)$$

(1) This paper represents results of research sponsored by the Office of Naval Research.

(2) (a) B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, **29,** 461 (1941); (b) F. H. Fisher, *J. Phys. Chem.*, **66,** 1607 (1962).

(3) F. H. Fisher and D. F. Davis, *ibid.*, **69,** 2595 (1965).

(4) L. H. Adams, *J. Am. Chem. Soc.*, **53,** 3780 (1931).

(5) C. C. Nathan, W. E. Wallace, and A. L. Robinson, *ibid.*, **65,** 790 (1943).

(6) F. H. Spedding and S. Jaffe, *ibid.*, **76,** 882 (1954).

(7) I. L. Jenkins and C. B. Monk, *ibid.*, **72,** 2695 (1950).

(8) At atmospheric pressure the difference between molar and molal units will be neglected.

Table II: Λ_p, Equivalent Conductance for Aqueous $La_2(SO_4)_3$ Solutions at 25°

P, atm	mequiv/l. 0.2	0.3	0.6	1.2	2.4	3.1	8.2
1	119.0[c]	109.5[c]	94.7[c]	80.7[a]	67.1[b]	63.3[b]	48.8[b]
250	123.3	114.3	100.0	85.9	71.9	68.0	52.6
500	126.5	118.0	104.4	90.3	76.2	72.1	56.0
750	128.8	121.1	108.0	94.1	79.8	75.8	59.2
1000	130.4	123.2	110.7	97.3	83.1	79.1	62.2
1250	131.4	124.8	113.0	100.0	86.7	82.0	64.7
1500	131.7	125.8	114.5	101.9	88.2	84.2	67.0
1750	131.7	126.3	115.7	103.5	90.0	86.2	68.9
2000	131.3	126.6	116.6	104.8	91.6	87.8	70.6

[a] I. L. Jenkins and C. B. Monk, *J. Am. Chem. Soc.*, **72**, 2695 (1950). [b] F. H. Spedding and S. Jaffe, *ibid.*, **76**, 882 (1954). [c] Interpolated graphically from combined data of *a* and *b*.

Table III: Comparison of KCl Conductance Ratios Λ_p/Λ_1 for Two Cells at 25.00 ± 0.02° and 10-kc Bridge Frequency

P, atm	Teflon cell[a]	Glass cell[b]
250	1.0090	1.0094
500	1.0145	1.0147
750	1.0175	1.0178
1000	1.0177	1.0180
1250	1.0167	1.0168
1500	1.0133	1.0134
1750	1.0086	1.0087
2000	1.0028	1.0025

[a] Λ_p/Λ_1 average over five concentrations of KCl from 0.0005 to 0.02 *M* measured in 30-ml cylindrical Teflon cell with parallel Pyrex-spaced platinum electrodes coated with platinum black. [b] Λ_p/Λ_1 for 0.02 *M* KCl measured in 12-ml spherical Pyrex cell with parallel shiny platinum electrodes.

where x is the concentration in equivalents of the $(LaSO_4)^+$ complex ion and π^f is the activity coefficient product.

Calculations were made using the mixture rule in which the solution is regarded as a mixture[9] of a 1–2 salt, $(LaSO_4)_2SO_4$, at equivalent concentration x and the 3–2 salt, $La_2(SO_4)_3$, at equivalent concentration $c - 3x$. The observed equivalent conductance of the solution is written then as

$$\Lambda_{obs} = (x/c)\Lambda_{12} + (c - 3x)/c\Lambda_{23} \quad (3)$$

where the Λ_{12} and Λ_{23} are calculated from theory and x is solved for by successive approximations. The activity coefficient product is[6]

$$\pi^f = [(f_{32\pm})^{5/2}/(f_{12\pm})^{3/2}] \quad (4)$$

where

$$-\log f_{ij\pm} = (A|z_iz_j|\sqrt{I})/(1 + B\mathring{a}\sqrt{I}) \quad (5)$$

and the ionic strength $I = 2.5c - 6x$.

Calculations of x and K were made using three different methods as follows.

Method a: The Davies–Otter–Prue equation with appropriate modifications for pressure-dependent terms[2b]

$$\Lambda = \Lambda^\circ - [(R\Lambda^\circ/\{1 + B\mathring{a}\sqrt{I/2}\}) + E] \times (\sqrt{I}/\{1 + B\mathring{a}\sqrt{I}\}) \quad (6)$$

was used to calculate the equivalent conductance. Bjerrum distances (at atmospheric pressure) of 21.4 A for the 3–2 and 7.14 A for the 1–2 salt were used for $\mathring{a}$ and the same pressure dependence was applied as in the $MgSO_4$ work.

Method b: Equation 6 was used but distances of $\mathring{a}$ = 5 A for the 3–2 and $\mathring{a}$ = 3.6 A for the 1–2 salt were used; these are the same values that Spedding and Jaffe used.

Method c: The Onsager equation[9]

$$\Lambda = \Lambda^\circ - [R\Lambda^\circ + E]\sqrt{I} \quad (7)$$

was used to calculate the equivalent conductance and the $\mathring{a}$ distances of 5 and 3.6 A were used in the activity coefficient calculation.

The pressure-dependent forms of eq 6 and 7 were used to calculate x and K as a function of pressure in a manner similar to that described earlier,[2b] and the results for x in molar units are shown in Table IV. The molal dissociation constant, K_m, shown in Table V was obtained by dividing the values of K in molar units by the ratio of the density of water at pressure P to that at atmospheric pressure.

From the equation[2a]

$$(\partial \ln K_m/\partial p)_{T,m} = -(\Delta V^\circ/RT) \quad (8)$$

values of ΔV° are calculated corresponding to the three different methods and are shown in Table VI.

The pressure dependence of infinite dilution equivalent conductivity, Λ°_p, for the $La_2(SO_4)_3$ was determined from the equation

$$\Lambda_p{}^\circ{}_{[La_2(SO_4)_3]} = \Lambda_p{}^\circ{}_{[LaCl_3]} + \Lambda_p{}^\circ{}_{[K_2SO_4]} - \Lambda_p{}^\circ{}_{[KCl]} \quad (9)$$

The Λ_p° values for the La^{3+} and $SO_4{}^{2-}$ ions were calculated using the KCl transference number data of Wall and Gill.[10] It was assumed that their transference number data to 1000 atm could be extrapolated linearly to 2000 atm. The Jenkins and Monk[7] value for

(9) C. W. Davies, "Ion Association," Academic Press, New York, N. Y., 1962.

(10) F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **59**, 278 (1955).

Table IV: Concentration ($\times 10^3$, equiv/l.) of $LaSO_4^+$ in Aqueous $La_2(SO_4)_3$ at 25°

P, atm	mequiv/l. of $La_2(SO_4)_3$ 0.2	0.3	0.6	1.2	2.4	3.1	8.2
a	0.015	0.031	0.088	0.22	0.54	0.72	2.3
b 1	0.015	0.030	0.086	0.22	0.53	0.70	2.2
c	0.015	0.030	0.085	0.21	0.52	0.69	2.2
500	0.011	0.025	0.073	0.19	0.48	0.65	2.1
	0.011	0.024	0.070	0.18	0.47	0.63	2.1
	0.011	0.023	0.069	0.18	0.46	0.61	2.0
1000	0.009	0.020	0.061	0.17	0.43	0.59	2.0
	0.008	0.019	0.058	0.16	0.41	0.56	1.9
	0.008	0.018	0.057	0.15	0.40	0.54	1.8
1500	0.007	0.016	0.052	0.15	0.40	0.54	1.9
	0.007	0.015	0.049	0.14	0.37	0.50	1.7
	0.007	0.015	0.048	0.13	0.36	0.48	1.6
2000	0.006	0.014	0.045	0.13	0.36	0.49	1.8
	0.006	0.013	0.041	0.12	0.33	0.45	1.6
	0.006	0.012	0.040	0.12	0.32	0.43	1.5

[a] Data obtained using the Davies–Otter–Prue conductance equation with $\mathring{a}$ calculated from Bjerrum's equation, $\mathring{a} = |Z_1Z_2|e^2/2\epsilon KT$. [b] Data obtained using the Davies–Otter–Prue conductance equation, but with $\mathring{a}$ = 5 A for the 3–2 case and $\mathring{a}$ = 3.6 A for the 2–1 case. [c] Data obtained using the basic Onsager conductance equation.

Table V: Dissociation Constant K_m ($\times 10^4$) for Aqueous $La_2(SO_4)_3$ at 25°

P, atm	mequiv/l. of $La_2(SO_4)_3$ 0.2	0.3	0.6	1.2	2.4	3.1	8.2
a	2.4	2.1	2.0	2.0	2.0	2.0	1.9
b 1	2.4	2.1	2.0	1.9	1.8	1.8	1.6
c	2.4	2.2	2.1	2.0	1.9	1.9	1.8
500	3.6	3.2	3.1	3.1	3.0	3.1	3.1
	3.7	3.2	3.1	3.0	2.8	2.8	2.6
	3.8	3.3	3.2	3.1	3.0	3.0	2.9
1000	5.2	4.6	4.4	4.3	4.3	4.5	4.6
	5.4	4.7	4.4	4.3	4.1	4.1	3.8
	5.6	4.8	4.6	4.5	4.3	4.5	4.5
1500	6.5	5.9	5.7	5.6	5.6	5.9	6.2
	6.9	6.1	5.8	5.6	5.4	5.5	5.2
	7.1	6.4	6.0	5.9	5.8	6.0	6.3
2000	8.0	7.6	7.3	7.2	7.2	7.5	8.0
	8.6	8.0	7.6	7.2	7.0	7.2	6.9
	8.9	8.4	8.0	7.7	7.6	8.0	8.4

[a] See footnote a of Table IV. [b] See footnote b of Table IV. [c] See footnote c of Table IV.

Table VI: $-\Delta V°$ (ml/mole) for Aqueous $La_2(SO_4)_3$ at 25°

P, atm	mequiv/l. 0.2	0.3	0.6	1.2	2.4	3.1	8.2
a	22.9	21.6	21.2	21.5	22.7	22.6	25.3
b 1	23.7	22.2	21.7	22.0	23.1	23.0	25.2
c	24.0	22.4	22.0	22.4	23.6	23.6	26.2
500	18.9	18.5	18.3	18.4	19.2	19.3	21.3
	19.6	19.2	18.9	19.0	19.7	19.8	21.5
	19.9	19.5	19.2	19.4	20.3	20.4	22.6
1000	14.9	15.5	15.4	15.3	15.7	16.0	17.3
	15.6	16.2	16.1	15.9	16.3	16.6	17.8
	15.8	16.5	16.5	16.4	16.9	17.3	19.0
1500	10.8	12.5	12.6	12.2	12.2	12.6	13.4
	11.5	13.2	13.3	12.9	12.9	13.4	14.1
	11.8	13.5	13.7	13.4	13.5	14.1	15.4
2000	6.8	9.4	9.7	9.1	8.7	9.3	9.4
	7.4	10.2	10.5	9.9	9.5	10.2	10.4
	7.7	10.5	10.9	10.4	10.1	10.9	11.8

[a] See footnote a of Table IV. [b] See footnote b of Table IV. [c] See footnote c of Table IV.

Table VII: Equivalent Conductivities at Infinite Dilution as a Function of Pressure

P, atm	$La_2(SO_4)_3$	La^{3+}	SO_4^{2-}	$LaSO_4^-$
1	149.5	69.5	80.0	23.2
250	150.4	69.8	80.6	23.3
500	150.6	69.4	81.2	23.1
750	150.6	69.2	81.4	23.1
1000	150.0	68.6	81.4	22.9
1250	149.6	68.2	81.4	22.7
1500	148.9	67.4	81.5	22.5
1750	147.5	66.3	81.2	22.1
2000	146.3	65.4	80.9	21.8

$\Lambda°_{LaSO_4^+}$ of 23.2 is used rather than the value of 40.0 proposed by Spedding and Jaffe[6] because this value yielded values of K_m which showed less concentration dependence. The pressure dependence of the $LaSO_4^+$ ion was taken to be the same as for $\Lambda_P°$ for $La_2(SO_4)_3$.

Results for pressure dependence of equivalent conductance at infinite dilution are shown in Table VII. The original data for $La_2(SO_4)_3$ solution are shown in Table VIII.

Discussion

It is seen from Table V that regardless which method is used, K_m at atmospheric pressure approaches values in the neighborhood of 2.4×10^{-4} at low concentration, in agreement with the results of Spedding and Jaffe.[6] The Davies–Otter–Prue equation used with the Bjerrum distances appears to give K values slightly less concentration dependent than for the other methods.

Table VIII: Copy of Original Conductivity Data for Aqueous Solutions of $La_2(SO_4)_3$ at 25°; Teflon Cell with Pyrex Bar between Electrodes: Cell Constant 0.457, Measured at 0.02 *M* KCl

P, atm	10^3 equiv/l. of $La_2(SO_4)_3$: 0.2046	0.3072	0.6144	1.206	2.412	3.072	8.190	H_2O
	Conductivity in μmhos							
1	53.88	76.31	131.2	217.1	361.2	433.4	880.7	2.31
250	56.73	80.81	140.3	233.9	391.6	470.8	960.0	2.70
500	59.16	84.69	148.4	248.9	419.5	505.1	1033.5	3.11
750	61.22	88.08	155.3	262.2	444.6	536.7	1103.8	3.59
1000	63.01	90.87	161.1	274.1	467.6	565.3	1171.0	4.09
1250	64.53	93.35	166.4	284.5	488.1	590.9	1229.8	4.64
1500	65.85	95.45	170.7	293.2	505.7	613.5	1284.5	5.26
1750	66.94	97.18	174.4	300.8	521.2	633.5	1332.3	5.88
2000	67.85	98.73	177.6	307.2	534.7	650.9	1376.8	6.52
1[a]	54.11	76.42	131.4	217.1	361.3	433.8	883.8	2.59

[a] Readings taken the day after the pressure run.

At atmospheric pressure there is at most only a 5% difference in the $\Delta V°$ values obtained by the three methods. At the highest pressures and highest concentration the largest difference in the $\Delta V°$ values occur.

The atmospheric pressure values of $\Delta V°$ are of the same order as observed for NH_4OH[11] and organic solutions[12] and very close to the value of -23.4 ml/mole calculated by Owen and Brinkley[2a] for water. It is not known if a possible multistate configuration[13,14] exists similar to that of $MgSO_4$ or $MnSO_4$ or if there exists only one form of the $(LaSO_4)^+$ ion pair. There is some indication that the rare earth sulfates show large ultrasonic absorption[15] but until detailed experimental results are available, it is not possible to make an interpretation incorporating acoustic data.

Based on values of partial molal volume assigned by Owen and Brinkley[2a] to La^{3+} of -38.3 ml/mole and SO_4^{2-} of $+14.5$, the partial molal volume of the $(LaSO_4)^+$ ion pair at atmospheric pressure and at the lowest concentration varies from -0.9 to $+0.2$ ml/mole depending upon the method used to calculate theoretical values of equivalent conductance.

(11) S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, New York, N. Y., 1957, p 151.

(12) A. Disteche and S. Disteche, *J. Electrochem. Soc.*, **112**, 350 (1965).

(13) F. H. Fisher, *J. Phys. Chem.*, **69**, 695 (1965).

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(15) G. Atkinson, private communication.