TABLE III

COMPARISON OF CALCULATED WITH ACTUAL VALUES

Integral	Exp. 1		Exp. 2		Exp. 3	
	Actual	Computed	Actual	Computed	Actual	Computed
$\frac{1}{2t}\left[\int_{-\infty}^{x_2} x^2 \frac{\partial n}{\partial x}\, dx + \int_{x_{96}}^{\infty} x^2 \frac{\partial n}{\partial x}\, dx\right]$	0.448	0.446	0.536	0.534	1.655	1.615
$\frac{1}{2t}\left[\int_{x_2}^{x_9} x^2 \frac{\partial n}{\partial x}\, dx + \int_{x_{89}}^{x_{96}} x^2 \frac{\partial n}{\partial x}\, dx\right]$	.627	.628	.757	.757		
$\frac{1}{2t}\left[\int_{x_9}^{x_{89}} x^2 \frac{\partial n}{\partial x}\, dx\right]$	.621	.621	.757	.757		
$\frac{1}{2t}\int_{-\infty}^{\infty} x^2 \frac{\partial n}{\partial x}\, dx$	1.694	1.695	2.050	2.048	3.600	3.568

TABLE IV

COMPARISON OF REDUCED FOURTH MOMENTS

	Exp. 1		Exp. 2	
	Actual	Computed	Actual	Computed
D^2_{4m}	2.964×10^{-14}	2.951×10^{-14}	4.325×10^{-14}	4.252×10^{-14}
σ_D	0.30×10^{-7}	0.27×10^{-7}	0.35×10^{-7}	0.23×10^{-7}

moments calculated for different portions of the curves are presented in Table III. The computed values were obtained by the use of eq. 6 and 7. The last integral in eq. 6 was evaluated from the positions of fringes 96 and 98.[7] The actual values were calculated using eq. 10.

$$\int_{x_j}^{x_i} x^2 \frac{\partial n}{\partial x}\, dx = \Sigma 2t\ X_k D_k \left[\lambda^k{}_i - \lambda^k{}_j\right] \tag{10a}$$

$$\frac{D_l}{D_m} = \left(\frac{Z^m}{Z^l}\right)^2 \tag{10b}$$

$$\sum_k x_k H(Z^k{}_j\ ) = \frac{j = {}^1/_2 J}{{}^1/_2 J} \tag{10c}$$

X_k is the weight fraction of component k. Equations 10b and c were solved numerically by double interpolation in the "Tables of Probability Functions." Difficulties with signs for λ and Γ are perhaps best avoided by considering all variables involved as being positive and separating any integrals crossing the zero axis into two integrals.

Table IV compares the reduced fourth moments and the σ_D calculated from the eq. 8 and 9 with the actual values.

Discussion

Most of the error in the computation arises from the first and last integrals in eq. 6.

The above results suggest that one can compute reduced second moments which are within 0.1% of the correct values for systems in which there is not too large a range of diffusion constants. It is also possible to obtain useful information about the amount of dispersion in the system by comparing the reduced second and fourth moments. Experiment 3 (see Table II) corresponds to a highly improbable situation: *e.g.*, a protein contaminated with 10% of a low molecular weight polypeptide. In this case the error is considerably larger than 0.1%.

Preliminary experiments with polydisperse systems[8] indicated that data obtained at different times during the run are reproducible to 0.1–0.2%. A final evaluation of the accuracy obtainable with actual polydisperse systems will have to be made on the basis of model experiments.

Although the calculations involved are laborious, there will be systems for which the extra effort will be justified. It may be possible to make use of high speed calculators.

PEARL RIVER, N. Y.

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(7) No definite rule can be given for choosing the optimum fringes for calculating the last integral of eq. 6. In general one should use for the second fringe the highest numbered fringe or fractional fringe for which accurate measurements can be made.

(8) S. L. Burson, Jr., M. J. Fahrenbach, L. H. Frommhagen, B. A. Riccardi, R. A. Brown, J. A. Brockman, H. V. Lewry and E. L. R. Stokstad, THIS JOURNAL, **78**, 5874 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS]

The Apparent Molar Refraction of Lanthanum Perchlorate in Aqueous Solution

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The apparent molar refraction, dispersion, volume and the partial molal volume of lanthanum perchlorate in aqueous solution have been determined. The results have been interpreted in terms of the Fajans theory as well as by Böttcher's modified refraction equation.

Introduction

The chemistry of the lanthanon elements has assumed new importance by the recognition of their relationship to the actinides, and accurate measurements of chemical and physical properties of the lanthanons has made possible helpful predictions and extrapolations to the actinides. A quantity which has received little attention for these elements

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(1) Taken from the M.S. thesis of Norman W. Silcox, Univ. of Mass., June, 1955.

is molar refraction. Differences between adjacent members of the series may be expected to be small but any differences or trends within the series should be largely attributable to the differences in the 4f electron shells and to the accompanying change in nuclear charge. The rare-gas-type lanthanum ion is isoelectronic with the barium ion, can be compared readily with ions which have been subjected to considerable study and therefore makes possible an extension of the well-known theoretical interpretations of refraction developed by K. Fajans and co-workers.[2]

In 1925 Heydweiller[3] reported the molar refraction of the aqueous lanthanum ion to be 1.61 cc. in a nitrate solution. Extrapolation to infinite dilution from his data is unreliable. A value of 3.24 cc. for R_{D_3} for the lanthanum ion was found by Roberts[4] for a 3.1916 *m* nitrate solution but only one concentration was measured. No other refraction measurements of aqueous solutions have been reported. The symmetrical structure, low deformability and non-complexing properties of the perchlorate ion suggested that lanthanum perchlorate would be a suitable compound for this study.

Experimental

Materials.—The lanthanum material used in this work was isolated by recrystallization procedures from crude monazite oxides. Traces of non-rare earth impurities were removed by precipitation with hydrogen sulfide followed by several precipitations of lanthanum oxalate with recrystallized oxalic acid. The final oxalate precipitate was ignited to oxide in platinum. Spectrographic, spectrophotometric and chemical tests showed that impurities could not be present in excess of 0.01% and probably were much less. The perchloric acid used was analytical reagent grade (J. T. Baker). Water for dilution of the stock solution was triply distilled in an all Pyrex still, once from alkaline permanganate and once from acidic solution. The specific resistivity was 4.4 × 10^{-6} ohm cm.

Preparation of the Solutions.—The lanthanum oxide was slurried with water and treated with an amount of concentrated perchloric acid insufficient to cause complete solution. The mixture was boiled, kept just below the boiling point for two days, cooled, filtered through a fine sintered glass funnel and the clear solution stored in a Pyrex flask. Dilutions were prepared using weight burets for both stock solution and water. All weighings were done by transposition with calibrated weights and tares. Vacuum corrections were applied, the air density being calculated from measured temperature, humidity and barometric pressure.[5] The stock solution was analyzed by precipitation with oxalic acid and ignition of the oxalate to oxide in the usual way. The concentrations of the dilute solutions were calculated from the dilution data. A check analysis of the most dilute solution established the validity of this procedure within 1.3 p.p.t.

Density.—Solution densities were determined with bicapillary pycnometers of about 20-ml. capacity. These pycnometers were calibrated with water and permitted an accuracy of 1 × 10^{-5} in the density of the solutions. Temperature was controlled to 25.00 ± 0.01°. The reported densities are the average of two independent fillings.

Refractive Index.—The refraction measurements were made with a Zeiss Pulfrich Refractometer. Values for the refractive index of the prism for 25.00° and for the seven helium spectral lines were calculated from the manufacturer's values for 20° and other spectral lines. The resultant values were shown to be accurate by measurement of water and test pieces. The micrometer screw was calibrated against the graduated circle for three different positions and found to have negligible error. The zero point correction was applied to all measurements. The glass cell was attached to the prism by Duco household cement and thermostatic water was circulated through the prism and cell jackets, the temperature of the sample being recorded as the average reading of two Beckmann thermometers placed in the water line on either side of the prism. Temperature was controlled to 25.00 ± 0.005°. Samples were transferred from the pycnometers directly to the cell by means of air pressure and the filled cell was closed immediately to prevent evaporation. The light source was a helium discharge tube operated at ten thousand volts.

The entire experimental procedure was tested using analytical reagent quality potassium chloride. The molar refraction agreed within 0.01 cc. with values reported by Kruis and Geffcken[6] for comparable concentrations.

TABLE I

COMPOSITION, DENSITY, APPARENT MOLAR AND PARTIAL MOLAL VOLUMES OF LANTHANUM PERCHLORATE SOLUTIONS AT 25.00°

Soln.	Molarity	Density, g./ml.	App. molar vol., Φ, (ml.)	Partial molal vol., $\overline{V}$ (ml.)
I	2.839	1.90435 ± 2.5 × 10^{-5}	118.06	124.91
II	2.109	1.67750 ± 1.2 × 10^{-5}	115.00	121.80
III	1.363	1.44314 ± 1.0 × 10^{-5}	110.35	116.53
IV	0.6515	1.21397 ± 1.5 × 10^{-5}	104.69	109.41
V	0.0901	1.02759 ± 1.0 × 10^{-5}	98.96	100.83
Extrap. to c = zero			95.1	95.1
Water		0.99708 (standard)		

TABLE II

REFRACTIVE INDEX OF LANTHANUM PERCHLORATE SOLUTIONS AND WATER AT 25.00°

Wave length, Å.	H_2O	I	II	III	IV	V
4472	1.33872	1.43870	1.41584	1.39048	1.36451	1.34243
4713	1.33724	1.43695	1.41414	1.38892	1.36296	1.34094
4921	1.33613	1.43565	1.41287	1.38769	1.36176	1.33980
5016	1.33565	1.43507	1.41235	1.38715	1.36129	1.33935
5876	1.33240	1.43131	1.40868	1.38364	1.35790	1.33609
6678	1.33027	1.42891	1.40637	1.38137	1.35570	1.33394
7065	1.32949	1.42804	1.40548	1.38049	1.35191	1.33314

TABLE III

APPARENT MOLAR REFRACTION OF LANTHANUM PERCHLORATE, CC./MOLE

Wave length, Å.	I	II	III	IV	V	c = zero[b]
4472	43.68	43.92	43.90	43.79	43.69	43.68
4713	43.55	43.79	43.79	43.66	(43.48)	43.61
4921	43.45	43.70	43.69	43.55	(43.29)	43.38
5016	43.41	43.66	43.65	43.53	43.49	43.36
5876	43.14	43.39	43.37	43.27	(43.30)	43.17
5893[a]	43.14	43.38	43.37	43.26	43.19	43.16
6678	42.98	43.24	43.23	43.11	43.04	43.01
7065	42.92	43.17	43.16	43.07	(42.88)	42.92
Infinity[b]	42.43	42.70	42.67	42.56	42.49	42.46

[a] Graphical interpolation. [b] Graphical extrapolation: values for infinite wave length by a plot of $1/R$ *vs.* square of frequency; values for c = zero by graphical extrapolation as in Fig. 1.

Discussion of Results

Lorentz–Lorenz Refraction of $La(ClO_4)_3$ as a Function of Concentration and Wave Length.—The apparent molar refraction of lanthanum perchlorate was calculated by the method of

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[2] This theory is to be found in the series "Refractometric Investigations" by Fajans, *et al.* See ref. (11) for a listing of many of these papers.

[3] A. Heydweiller, *Physik. Z.*, **26**, 526 (1925).

[4] J. E. Roberts, M.S. thesis, Univ. of New Hampshire, 1944.

[5] P. F. Weatherill, THIS JOURNAL, **52**, 1938 (1930).

[6] A. Kruis and W. Geffcken, *Z. physik. Chem.*, **B34**, 1 (1936).

Geffcken[7] and the resulting values are shown in Table III. When these results were plotted by the reciprocal plotting method of Wulff[8] a series of straight lines resulted from which the apparent molar refraction at infinite wave length was found by extrapolation. These values for infinite wave length as well as those for selected finite wave lengths are plotted in Fig. 1 to show the concentration dependence.

The accuracy of the results may be estimated by taking the difference between values for any two solutions and for each wave length. Such differences should be constant or show a regular change. The maximum ranges found for these solutions are: I–II, 0.03 cc.; II–III, 0.03 cc.; III–IV, 0.07 cc.; IV–V, 0.05 cc.; V-zero, 0.11 cc. These values may be taken as maximum errors and the graphical processes may be expected to minimize them. The probable error in the extrapolated quantity may be reasonably taken as ±0.06 cc./mole. This also affects the value of the hydration effect.

The possible accuracy decreases with decrease in concentration and some values for solution V, which is about at the minimum concentration for which the method is applicable, contain relatively large errors. These values are enclosed in parentheses in Table III and were not used in the extrapolation. Further measurements in the very dilute range would be required to attain higher accuracy.

In terms of the Fajans theory, the slight positive slope, dR/dc in Fig. 1 for c between zero and 2 molar, may be interpreted as representing the displacement of water of hydration on the lanthanum ion. The negative slope between 2 and 2.8 molar may be due to interaction between lanthanum and perchlorate ions to form loosely bound ion pairs.

Lorentz–Lorenz Refraction and Dispersion of Free and Hydrated La^{3+} Ions.—To evaluate the hydration effect for the lanthanum ion

$$\Delta R_{\text{Hyd.}} = R_{\text{aq.}} - R_{\text{gas}}$$

its refractions in the infinitely dilute aqueous solution and in the "free gaseous ion" are compared, at the same wave length (Na "D" line). Using 13.24 cc. as the refraction of the aqueous perchlorate ion[9]

$$R_{\text{La}^{+++}\text{aq.}} = R_{\text{La(ClO}_4)_3} - 3R_{\text{ClO}_4^-} = 43.16 - 39.72 = 3.44 \text{ cc./mole}$$

$R_{\text{La}^{+++}}$ gas can be obtained by extrapolation of the gradation of the values for isoelectronic ions[10] as

$$1.15_6 R_{\text{Ba}^{++}}/R_{\text{La}^{+++}} = R_{\text{Cs}}/R_{\text{Ba}^{++}} = 1.38_1$$

Hence $R_{\text{La}^{+++}\text{gas}} = 3.96$ cc./mole. From this, the hydration effect $\Delta R_{\text{Hyd.}} = 3.44 - 3.96 = -0.52$ cc./mole.

The hydration effect for the triply-charged lanthanum ion may be expected to be greater in absolute value than that for the isoelectronic barium ion, *i.e.*, more negative than −0.36 cc./mole.[11] The upper limit is less certain but may be estimated by comparison with the Mg^{++}/Al^{+++} case for which the hydration effects are −2.10[12] and −2.66[9,12] cc./mole, respectively. The change in hydration effect on going from Ba^{++} to La^{+++} may be expected to be less than 0.56 cc. and probably proportionally less, *i.e.*, less than (0.36)(0.56)/2.10 = 0.096 cc. Therefore the ΔR_{Hyd} for La^{+++} should certainly be less than 0.92 cc. and probably less than 0.46 cc. in absolute value. In view of the uncertainty of ±0.06 cc. in the extrapolation, the experimental value of −0.52 cc. is in satisfactory agreement with these estimates.

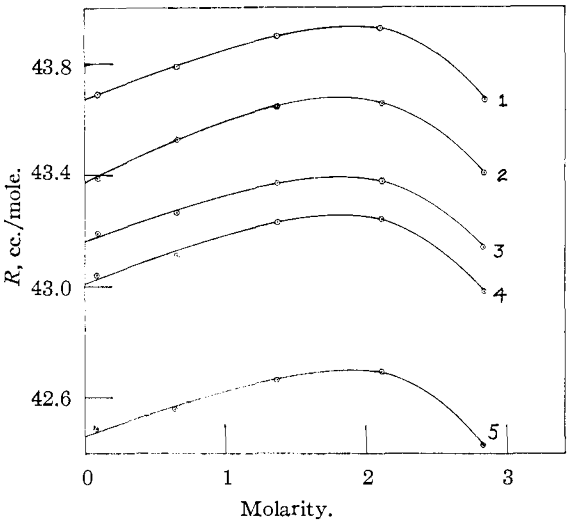

Fig. 1.—Concentration dependence of the apparent molar refraction of lanthanum perchlorate at various wave lengths: (1) 4472 Å.; (2) 5016 Å.; (3) 5893 Å.; (4) 6678 Å.; (5) extrapolated to $\lambda = \infty$.

The apparent molar dispersion may be evaluated from the data. $R_D - R_\infty = 43.16 - 42.46 = 0.70$ cc./mole. Taking 0.23 cc. as the molar dispersion of the perchlorate ion,[11] the apparent molar dispersion of the aqueous lanthanum ion is 0.01 cc./mole. This is satisfactory in view of the value of 0.02 cc./mole reported for the aqueous barium ion.[11]

Calculations by Böttcher's Method.—In the Fajans interpretation of the Lorentz–Lorenz refractions, deviations from additivity were associated with interactions of ions with each other and with water molecules. This interpretation has been questioned by Böttcher[13,14] and it was claimed initially that the deviations were completely eliminated when a corrected equation was used. Later it was concluded that the "Fajans effect" still exists in potassium fluoride and aluminum chloride. The corrected equation considers that the internal field at the position of the molecules has a different value than in the intervening spaces and is different for various kinds of particles. This equation takes the form

$$\frac{(n^2 - 1)(2n^2 + 1)}{12\pi n^2} = N_0\alpha_0^* + N_s\alpha_s^*$$

$$\alpha^* = \frac{\alpha}{1 - f\alpha} \text{ and } f = \frac{1}{r_3} \times \frac{2n^2 - 2}{2n^2 + 1}$$

in which n is the refractive index, N_0 and N_s are concentrations of water and salt, respectively, α is the polarizability and r is a constant best inter-

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[7] W. Geffcken, *Z. physik. Chem.*, **B5**, 81 (1929).

[8] P. Wulff, *ibid.*, **B21**, 370 (1933).

[9] K. Fajans and R. Luhdeman, *ibid.*, **B29**, 150 (1935), Table II.

[10] K. Fajans, *ibid.*, **B24**, 103 (1934). Table IV modified to include later data of G. Damköhler, *ibid.*, **B27**, 130 (1934).

[11] N. Bauer and K. Fajans, THIS JOURNAL, **64**, 3023 (1942).

[12] K. Fajans, *Z. physik. Chem.*, **B24**, 103 (1934).

[13] C. J. F. Böttcher, *Rev. trav. chim.*, **65**, 39 (1946).

[14] C. J. F. Böttcher and T. G. Scholte, *ibid.*, **70**, 209 (1951).

preted as the distance of closest approach of the molecules or ions. Using 1.38 Å. as the value of r for water,[15] it is found from the present data that the value 3.04 Å. for lanthanum perchlorate gives equal polarizabilities for extremes of concentration. The resultant values of α and the corresponding refraction $R = 4/3\pi N\alpha$ are shown in Table IV.

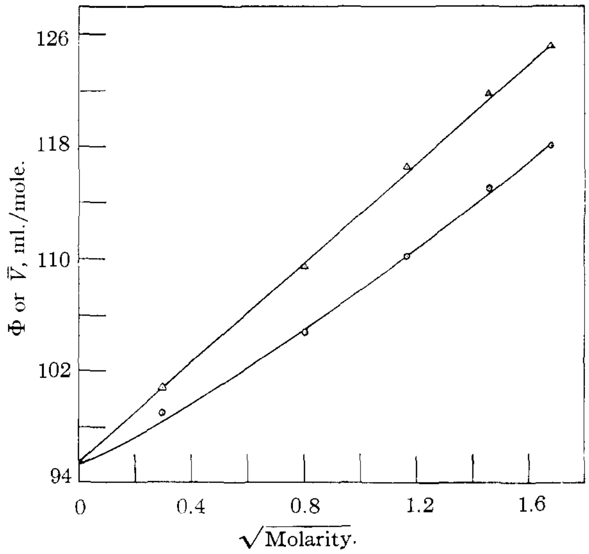

Fig. 2.—Apparent molar (⊙) and partial molal (△) volumes of lanthanum perchlorate.

The slight deviations from constancy of the refraction values calculated by this method are in the same direction as those of the Lorentz–Lorenz refraction but of only about half the magnitude. Since the value of r must be adjusted to fit the data, this equation is essentially empirical and values calculated with it are best interpreted as representing a lower limit of the polarizability. Furthermore, small changes in r have a relatively large effect on α. Brown's conclusion[16] that the success of Böttcher's method is the result of cancellation of errors indicates that little significance can be attached to these values. For comparisons of similar materials, the Lorentz–Lorenz equation which does not contain an arbitrary parameter is satisfactory.

TABLE IV

POLARIZABILITY CALCULATED BY BÖTTCHER'S EQUATION

Soln.	$\alpha s \times 10^{23}$, cc./molecule	R, cc./mole
I	1.4856	37.71
II	1.4910	37.85
III	1.4896	37.81
IV	1.4851	37.70
V	1.4856	37.71

Apparent Molar Volume.—The apparent molar volumes of lanthanum perchlorate are shown in Table I and Fig. 2. By extrapolation to infinite dilution the value 95.1 ml./mole is obtained and by use of the quantity 44.5 ml./eq. for the apparent volume of the perchlorate ion,[17] the apparent molar volume of the lanthanum ion was found to be −38.4 ml./mole. This large negative value indicates that the lanthanum ion exerts strong constrictive forces on the water molecules and is in close agreement with the value −38.3 cc./mole given by Owen and Brinkley.[18]

From the density data, the partial molal volumes were calculated using the convenient equations of Harned and Owen,[19] and are listed in Table I. When these data are plotted against $c^{1/2}$ a linear relationship is found (Fig. 2) as is commonly observed for strong electrolytes. The solutions, however, were not sufficiently dilute to serve as an adequate test of the limiting law.

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AMHERST, MASS.

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[15] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1944, p. 304.

[16] W. F. Brown, Jr., *J. Chem. Phys.*, **18**, 1193, 1200 (1950).

[17] K. Fajans and O. Johnson, THIS JOURNAL, **64**, 668 (1942).

[18] B. B. Owen and S. R. Brinkley, *Chem. Revs.*, **29**, 461 (1941).

[19] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.