spite of the failure of the Debye limiting law to hold at concentrations as low as $0.0005\mu$.

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# ACTIVITY COEFFICIENTS OF ELECTROLYTES. IV. THE SOLUBILITIES OF LANTHANUM AND THALLOUS IODATES IN AQUEOUS SALT SOLUTIONS AND THE PRINCIPLE OF SPECIFIC INTERACTION[1]

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## 1. Introduction

The purpose of this investigation was to determine (a) whether or not the highly abnormal results (from the viewpoint of the present form of the Debye-Hückel Theory) obtained in this Laboratory by La Mer and Mason,[2] and since confirmed by Dr. Graham Cook,[3] for the solubilities of tri-univalent cobaltammines dissolved in solvents containing high valence anions were general phenomena, or simply specialized cases peculiar to the cobaltammine family; and (b) in how far Brönsted's principle of specific interaction would hold for other types of salt mixtures where the principle of ionic strength and the present form of the Debye-Hückel theory have proved to be inadequate.

To answer these questions the solubility of lanthanum iodate was measured, using aqueous solutions of the chlorides, nitrates and sulfates of potassium, sodium, magnesium, lanthanum and zinc as solvents. Lanthanum iodate is particularly suited for this study since $La^{+++}$ is the only trivalent cation, aside from the cobaltammine ions like $[Co(NH_3)_6]^{+++}$, which does not appreciably hydrolyze in aqueous solution. The neutrality of the lanthanum solutions was proved by colorimetric tests and by the fact that iodine was not liberated on addition of potassium iodide until free acid was added.

Similar studies were made of the solubility of thallous iodate in order to have a symmetrical uni-univalent salt with the same anion for comparison with lanthanum iodate.

These saturating salts are stable[4] and of an appropriate order of solubil-

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[1] Preliminary reports of this work were presented at the Detroit (September, 1927) and Swampscott (September, 1928) meetings of the American Chemical Society. The present paper is constructed from a Dissertation by F. H. Goldman submitted to The Faculty of Pure Science, Columbia University, in October, 1928, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] La Mer and Mason, THIS JOURNAL, **49**, 410 (1927).

[3] La Mer and Cook, *ibid.*, **51**, 2622 (1929).

[4] Sadolin, *Z. anorg. allgem. Chem.*, **160**, 133 (1927); see ref 5 c.

ity, the solubility of lanthanum iodate being 0.0008901 molar at 25°, while thallous iodate is 0.001844 molar. The latter is nine times as insoluble as thallous chloride, which has been much used by previous investigators.[5] The iodate can also be analyzed more accurately and more easily than the chloride. Thus one mole of thallous iodate reacting with potassium iodide furnishes six equivalents of iodine; while one mole of lanthanum iodate furnishes eighteen equivalents! Furthermore, it is possible to use solutions of salts with an ion in common as solvents, *e. g.*, lanthanum sulfate, lanthanum chloride, lanthanum nitrate, without causing the solubility to decrease below the point of analytical detection.

The only previous[6] solubility measurements on lanthanum iodate were made by Harkins and Pearce.[7] They measured the solubility of this salt in the presence of lanthanum nitrate, lanthanum ammonium nitrate and sodium nitrate. In utilizing these measurements to test the validity of the principle of ionic strength, Lewis and Randall[8] say, "Unfortunately an error seems to have slipped into the first two of these series" (lanthanum nitrate and lanthanum ammonium nitrate). This criticism adds particular interest to the study of this salt, since in the light of La Mer and Mason's investigations it is reasonable to suppose that the difficulty might be due to the failure of the principle of ionic strength and not to the data.

## 2. Theoretical

Debye and Hückel,[9] on the basis of the first approximation of the solution of the Poisson-Boltzmann equation, attempt to take "ion size" into account to explain the individual deviations from the limiting law which appear in the less highly dilute solutions. They get the following expression[10] for the activity coefficient of the solute

$$-\log_{10} f = \frac{\alpha' \, (-Z_1Z_2) \, \sqrt{\mu}}{1 + \text{``}a\text{''} \, \kappa} \qquad (1)$$

where "$a$" is the distance of closest approach of the ions in Å. ($10^{-8}$ cm.) units and $\kappa = 0.327 \times 10^8 \sqrt{\mu}$. This expression seems to hold very well for the lower valence types of salts up to concentrations of about $0.2\mu$, but is inadequate in the case of aqueous solutions where high valence ions of opposite sign are involved, as well as for most non-aqueous solutions.

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[5] (a) Bray and Winninghoff, This Journal, **33**, 1663 (1911); (b) Butler and Hiscocks, *J. Chem. Soc.*, 2554 (1926); (c) Randall and Chang, This Journal, **50**, 1535 (1928).

[6] Aside from the conductimetric measurements of Rimbach and Schubert, quoted in "International Critical Tables," Vol. IV, p. 227, where $S_0 = 0.00254$. This value is in error by 250%.

[7] Harkins and Pearce, This Journal, **38**, 2679 (1916).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 378.

[9] Debye and Hückel, *Physik. Z.*, **24**, 185, 343 (1923).

[10] See ref. 2, p. 417, Eq. 2. This equation contains a misprint. The fraction should read $1/(1 + x)$ not $x/(1 + x)$.

For extremely dilute solutions ($\kappa$ small), the denominator approaches unity, and Equation 1 reduces to the limiting law, which is independent of specific properties of the ions. In a saturated solution the activity coefficient of the solute is determined by the following relationship[11]

$$\log S/S_0 = \log f_0/f \tag{2}$$

$S$ is the solubility of the saturating salt in the salt solution under consideration; $S_0$ is the solubility of the saturating salt in pure water; $f_0$ is the activity coefficient of the saturating salt in water, which may arbitrarily be set equal to unity for a very slightly soluble salt, but can be determined by extrapolating the curve obtained in high dilution to infinite dilution.

The activity coefficient determined from Equation 2 is an observed value; that determined from Equation 1, a calculated value. From Equation 1 it can be seen that all deviations between the observed and calculated values of $\log f$, if negative, could be accounted for by assuming a larger value for "$a$." On the other hand, positive deviations could only be accounted for in this equation by assuming negative values of "$a$," which are physically absurd.

Gronwall, La Mer and Sandved[12] have recently obtained a complete solution of the Poisson-Boltzmann equation, whereby additional terms involving *only* the parameter "$a$" are introduced into Equation 1. This obviates the difficulty of negative values of "$a$," and they are thus able to account entirely for the discrepancies between theory and experiment *for salts of symmetrical valence types* up to values of $x = a\kappa$ equal to about 0.3, using values of "$a$" which are physically reasonable. The calculations for the unsymmetrical types studied by La Mer and Mason[2] are too complex for a complete theoretical treatment along these lines, but it appears likely that when the necessary numerical computations are available for these types, this purely mathematical extension will also account for most of these deviations.

In the meantime it is desirable to see how far the experimental results can be correlated with less complicated semi-empirical treatments, of which Brönsted's principle of specific interaction appears to be the most promising. For the development of this theory the reader must consult the original papers[13] and the preceding article.[3]

## 3. Preparation of Materials

**Lanthanum Iodate.**—Sixty grams of cerium-free lanthanum nitrate in solution and 130 g. of potassium iodate in solution were added dropwise and simultaneously to approximately fifteen liters of distilled water, the addition taking four to five hours. The mixture was thoroughly agitated by an electric stirrer and the stirring continued for three or four days. The precipitate was washed by decantation four times and then allowed to digest for two weeks in about two liters of water at 70° with stirring. The salt

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[11] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[12] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[13] (a) Brönsted, THIS JOURNAL, **44**, 877 (1922); (b) **45**, 2898 (1923); (c) *Trans. Faraday Soc.*, **23**, 416 (1927).

so obtained was "sedimented"[2] in a tall narrow cylinder (2 × 100 cm.) several times and the finer material remaining at the top each time was rejected.

**Thallous Iodate.**—Eighty grams of potassium iodate in solution and 100 g. of thallous nitrate were added dropwise and simultaneously to six liters of water at 60° with constant stirring. The precipitate was allowed to digest and the stirring continued. The salt was washed by decantation six times with water, after which it was placed in a beaker containing 500 cc. of water and allowed to digest on a hot-plate at 80°. It was then "sedimented" to obtain crystals of uniform size.

The same preparations of potassium, sodium, magnesium and lanthanum salts whose purification has been described in detail in the preceding paper (La Mer and Cook) were used in this work. In addition lanthanum sulfate, especially freed from cerium for us by the Welsbach Company, was used. Its "apparent" molecular weight was determined by precipitating a sample as oxalate, igniting, moistening with nitric acid and reigniting to the oxide. Kahlbaum's "Zur Analyse" zinc sulfate was dried to constant weight in an air-bath and kept in a desiccator over sulfuric acid.

The solubility measurements were performed with the same apparatus and with the same necessary precautions that have been described in detail in the first paper of this series.

Lanthanum iodate was determined by dissolving three grams of potassium iodide in 10 cc. of boiled water in a 500-cc. iodine flask, adding a 25-cc. aliquot of solution from a volumetric flask, then three rinsings with distilled water and finally 2 cc. of 9 *M* sulfuric acid. After standing for five minutes in the dark, the contents were then titrated with sodium thiosulfate from a weight buret, using starch as indicator. Duplicate determinations checked to one part in two thousand. The average deviation of eleven determinations of the solubility of lanthanum iodate in water extending over a period of five months was only nine parts in ten thousand. Equilibrium was checked by allowing a solution saturated at 35° to flow through a column of lanthanum iodate at 25°. No change in solubility was found when the saturated solution was allowed to run through the column a second time. Blanks on the potassium iodide were negative.

The thiosulfate solutions were restandardized each week against potassium permanganate and could be checked to 0.1%.[14]

When the same analytical method was tried for thallous iodate a difficulty was encountered. An insoluble yellow precipitate was obtained when sodium thiosulfate was added in the course of the titration. In the presence of thallous ion thiosulfate is reduced to thallous sulfide.[15]

The following modification was found satisfactory. Sodium arsenite was used instead of sodium thiosulfate; only one cc. of nine molar sulfuric acid was added. The flask was then placed in the dark for five minutes, fifty cc. of a solution containing 3 g. of sodium bicarbonate was added and the contents of the flask titrated with standard sodium arsenite, using starch as an indicator. The end-point was obtained by back titrating with standard iodine solution. Determinations differed from one another by not more than four parts in a thousand.

The sodium arsenite solution used was 0.0150 *N* and was prepared as a primary standard according to directions in Scott,[16] using Kahlbaum's "Zur Analyse" arsenious oxide, and checked against potassium permanganate.[17] The two methods agreed to one part in a thousand.

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[14] Bray and Miller, THIS JOURNAL, **46**, 2204 (1924).

[15] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Vol. V, p. 424.

[16] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, New York, **1920**, Vol. I, p. 240.

[17] Diess, *Chem.-Ztg.*, **38**, 413 (1914).

## 4. Discussion of Data

Table 1 gives the solubility of lanthanum iodate in aqueous solutions of potassium chloride, potassium sulfate and lanthanum nitrate. The concentrations of the solvent salts are given in Col. 2. Column 4 gives the value of the logarithm of the ratio of the solubility in the particular solvent, to the solubility in pure water, $S_0$. When the values $z_1 = 3$, $z_2 = -1$ and $\alpha' = 0.505$ are introduced, Equation 1 takes the limiting form

$$-\log f = 1.515\sqrt{\mu} \tag{3}$$

at 25° using 78.77 for $D$, the dielectric constant of water.

TABLE I

SOLUBILITY OF $La(IO_3)_3$

Sample No. 1

| No. of detns. | Moles/liter of added salt | Soly. in moles/liter | Log $S/S_0$ | $-$Log $f$ | $\mu$ | $\sqrt{\mu}$ | $-$Log $f$ (calcd.) | Log $f$ (obs.) —log $f$ (calcd.) |
|---|---|---|---|---|---|---|---|---|
| | | | | $H_2O$ | | | | |
| 11 | .... | 0.00089006 | ... | ... | 0.005340 | 0.07308 | 0.1107 | ...... |
| | | | | $K_2SO_4$ | | | | |
| 6 | 0.0002 | .00091666 | 0.01279 | 0.12349 | .006100 | .07810 | .1183 | +0.0052 |
| 4 | .0005 | .00097463 | .03934 | .1500 | .007347 | .08571 | .1299 | .0201 |
| 4 | .001 | .0010564 | .07429 | .1850 | .009337 | .09663 | .1464 | .0386 |
| 4 | .002 | .0012153 | .13536 | .2461 | .013293 | .1153 | .1747 | .0714 |
| 4 | .007 | .0016852 | .27718 | .3879 | .031110 | .1764 | .2672 | .1207 |
| 4 | .0125 | .0020272 | .35748 | .4682 | .04966 | .2228 | .3376 | .1306 |
| 4 | .02 | .0023675 | .42482 | .5355 | .07420 | .2724 | .4127 | .1228 |
| 4 | .05 | .0031871 | .55078[a] | .6615 | .16912 | .4112 | .6230 | .0385 |
| | | | | KCl | | | | |
| 2 | .001 | .00091128 | .01015 | .1203 | .006467 | .08042 | .1218 | − .0010 |
| 5 | .005 | .00097490 | .03959 | .1503 | .01085 | .1042 | .1578 | − .0075 |
| 4 | .01 | .0010322 | .06436 | .1751 | .01619 | .1272 | .1928 | − .0177 |
| 4 | .05 | .0013331 | .17552 | .2862 | .05800 | .2408 | .3649 | − .0787 |
| 2 | .1 | .0015713 | .24250[b] | .3532 | .1094 | .3308 | .5011 | − .1479 |
| 2 | .2 | .0018776 | .32423 | .4349 | .21127 | .4597 | .6964 | − .2615 |
| 2 | .5 | .0025641 | .45465[c] | .5653 | .51538 | .7179 | 1.088 | − .523 |
| 4 | 1.0027 | .0030547 | .53068[c] | .6414 | 1.021 | 1.010 | 1.531 | − .890 |
| 4 | 2.000 | .0037828 | .62356[c] | .7343 | 2.023 | 1.422 | 2.155 | −1.421 |
| | | | Log $\sqrt[4]{\frac{Ksp}{K_0sp}}$ | $La(NO_3)_3$ | | | | |
| | | | | Sample No. 3 | | | | |
| 7 | none | .0009482 | ... | ... | .005689 | .07543 | .1143 | ...... |
| 2 | .001667 | .0008347 | .0638 | .1781 | .01501 | .1225 | .1856 | − .0075 |
| 3 | .003333 | .0008101 | .1088 | .2231 | .02486 | .1577 | .2389 | − .0158 |
| 4 | .01667 | .0008696 | .2886 | .4029 | .1052 | .3243 | .4914 | − .0885 |
| 3 | .03333 | .0009398[d] | .3781 | .4920 | .2056 | .4534 | .6869 | − .1949 |

[a] $S_0$ = 0.0008967. [b] $S_0$ = 0.0008989. [c] $S_0$ = 0.0009000. [d] $S_0$ = 0.0009426.

TABLE II

SOLUBILITY OF $La(IO_3)_3$ AT 25° IN VARIOUS 0.1 $N$ SOLVENTS

Sample No. 2

| Solvent | No. of detns. | Solubility, mole/liter | Solvent | No. of detns. | Solubility, mole/liter |
|---|---|---|---|---|---|
| $S_0$ | 5 | 0.0009426 | $M$/10 $KNO_3$ | 4 | 0.001679 |
| $M$/30 $La_2(SO_4)_3$ | 2 | .001830 | $M$/10 $NaNO_3$ | 3 | .001654 |
| $M$/60 $La_2(SO_4)_3$ | 2 | .001532 | 5$M$/100 $K_2SO_4$ | 4 | .003370 |
| $M$/30 $La(NO_3)_3$ | 3 | .0009398 | 5$M$/100 $Na_2SO_4$ | 4 | .003326 |
| $M$/30 $LaCl_3$ | 4 | .0009233 | 5$M$/100 $MgSO_4$ | 2 | .002997 |
| $M$/10 NaCl | 2 | .001627 | 5$M$/100 $Mg(NO_3)_2$ | 4 | .001766 |
| $M$/10 KCl | 2 | .001648 | 5$M$/100 $MgCl_2$ | 4 | .001739 |

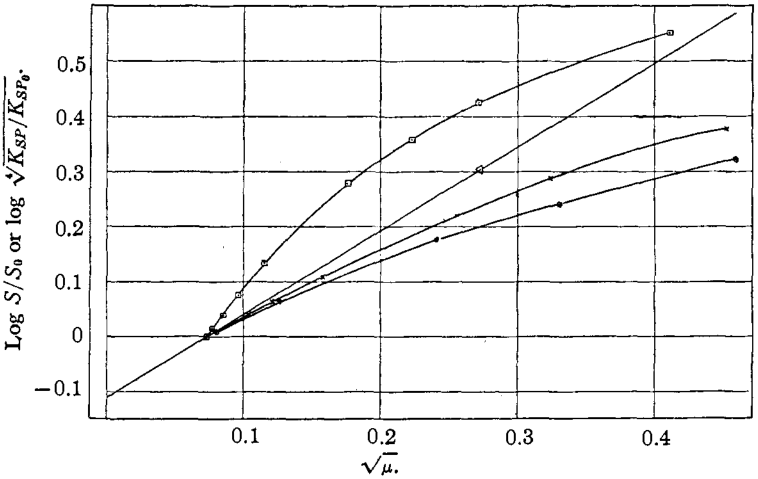
From this equation $-\log f_0 = 0.1107$. By introducing this value into Equation 2 we get the values for $-\log f$ given in Col. 5. Column 8 gives $-\log f$ calculated from Equation 3, and Col. 9 gives the difference between this value and the observed value.

It should be noted that of the three solvents in this table, potassium sulfate has the greatest effect on the solubility of lanthanum iodate. The solubility of lanthanum iodate is three and one-half times as great in a 0.1 $N$ solution of potassium sulfate as in pure water. In addition potassium sulfate exhibits marked positive deviations from the limiting law.

In the case of lanthanum nitrate, which has an ion in common with lanthanum iodate, it is necessary to consider the ratio of the stoichiometric solubility product constants[11] rather than the solubilities. Therefore in the case of lanthanum nitrate, Col. 3 represents $\log \sqrt[4]{Ksp/K_0sp}$. It is interesting to note that in changing the concentration of lanthanum nitrate from 0.003333 $M$ to 0.01667 $M$ the solubility of lanthanum iodate instead of decreasing, actually increases almost 6%, showing that in the case of a salt of high valence type the depression in solubility due to the common ion effect is soon obliterated by the more important factor, the change in the activity coefficient of the saturating salt. This is better seen by examining the data for the solubility of this salt in lanthanum sulfate, a (3,–2) solvent salt with an ion in common (see Table II). At sixtieth molar (0.1 $N$) the solubility is already 55% higher than in pure water!

These data should be of interest to the analytical chemist, especially when planning new procedures. For instance, before washing a precipitate with a salt solution having an ion in common, the point where minimum solubility occurs should be determined, instead of relying entirely on a stoichiometrical calculation of the solubility product.

The results in Table I are plotted in Fig. 1. The line marked "limiting tangent" is the limiting law of Debye and Hückel. From the figure it is evident that the curve for potassium sulfate does not fuse into the theoretical slope, but shows a maximum deviation, or "hump;" also that while the potassium chloride and lanthanum nitrate curves do fuse into the theoretical line, the latter deviates less than the former from the limiting law. This behavior is quite parallel to that observed by La Mer and Mason[2] (see their Figs. 2 and 3) using cobaltammines.



▽—Limiting tangent; ⊙—KCl; ⊡—$K_2SO_4$; ×—$La(NO_3)_3$.

Fig. 1.

The solubility of thallous iodate is given in Table III. The column headings have the same significance here as in Table I.

TABLE III

SOLUBILITY $TlIO_3$

Log $f_0$ = 0.02169; $-\log f = 0.505\sqrt{\mu}$ at 25°

| No. of detns. | Moles/liter of added salt | Soly. in mole/liter | Log $S/S_0$ | −Log $f$ | −Log $f$ calcd. | Log $f$(obs.) − log $f$ (calcd.) | $\mu$ | $\sqrt{\mu}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $H_2O$ | | | | |
| 15 | .... | 0.001844 | ... | ... | 0.02169 | ...... | 0.001844 | 0.04294 |
| | | | | $K_2SO_4$ | | | | |
| 4 | 0.001 | .001912 | 0.0157 | 0.0374 | .0354 | 0.0020 | .004912 | .07009 |
| 4 | .002 | .001958 | .0260 | .0477 | .0451 | .0026 | .007958 | .08921 |
| 4 | .005 | .002075 | .0513 | .0730 | .0660 | .0070 | .01708 | .1307 |
| 4 | .01 | .002193 | .0753 | .0970 | .0906 | .0064 | .03219 | .1794 |
| 4 | .013 | .002252 | .0868 | .1085 | .1026 | .0059 | .04125 | .2031 |
| 4 | .03 | .002513 | .1344 | .1561 | .1536 | .0025 | .09251 | .3042 |
| 4 | .03333 | .002544 | .1398 | .1615 | .1617 | − .0002 | .1025 | .3202 |
| 6 | .05 | .002747 | .1731 | .1948 | .1973 | − .0025 | .1527 | .3908 |
| 4 | .064 | .002877 | .1932 | .2149 | .2229 | − .0080 | .1949 | .4415 |
| 2 | .15 | .003520 | .2808 | .3025 | .3401 | − .0376 | .4535 | .6734 |
| 4 | .25 | .004028 | .3393 | .3610 | .4385 | − .0775 | .7540 | .8683 |
| 4 | .5 | .005128 | .4442 | .4659 | .6196 | − .1537 | 1.5051 | 1.227 |

TABLE III (*Concluded*)

| No. of detns. | Moles/liter of added salt | Soly. in mole/liter | Log $S/S_0$ | $-$Log $f$ | $-$Log $f$ calcd. | Log $f$(obs.) $-$log $f$ (calcd.) | $\mu$ | $\sqrt{\mu}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $KNO_3$ | | | | |
| 4 | .01 | .001987 | .0324 | .0541 | .0553 | $-$ .0012 | 0.01199 | 0.1095 |
| 3 | .02 | .002079 | .0521 | .0738 | .0750 | $-$ .0012 | .02208 | .1486 |
| 6 | .05 | .002270 | .0903 | .1120 | .1155 | $-$ .0035 | .05227 | .2286 |
| 4 | .1 | .002492 | .1308 | .1525 | .1617 | $-$ .0092 | .1025 | .3202 |
| 3 | .3 | .003126 | .2292 | .2509 | .2780 | $-$ .0271 | .3031 | .5505 |
| 2 | .5 | .003673 | .2993 | .3210 | .3584 | $-$ .0374 | .5037 | .7097 |
| 2 | 1.0 | .004821 | .4174 | .4391 | .5062 | $-$ .0671 | 1.0048 | 1.002 |
| | | | | $NaNO_3$ | | | | |
| 6 | 0.1 | .002486 | .1297 | .1514 | .1617 | $-$ .0103 | 0.1025 | 0.3202 |
| | | | | $Na_2SO_4$ | | | | |
| 4 | .03333 | .002543 | .1396 | .1613 | .1617 | $-$ .0004 | .1025 | .3202 |
| 4 | .05 | .002740 | .1720 | .1937 | .1973 | $-$ .0036 | .1527 | .3908 |
| | | | | $MgSO_4$ | | | | |
| 4 | .005 | .002068 | .0498 | .0715 | .0750 | $-$ .0035 | .02207 | .1486 |
| 5 | .01 | .002172 | .0711 | .0928 | .1037 | $-$ .0109 | .04217 | .2054 |
| 5 | .025 | .002387 | .1121 | .1338 | .1616 | $-$ .0278 | .1024 | .3200 |
| 3 | .05 | .002640 | .1558 | .1775 | .2273 | $-$ .0498 | .2026 | .4501 |
| | | | | KCl | | | | |
| 4 | .01 | .002005 | .0363 | .0580 | .0553 | .0027 | .01201 | .1487 |
| 4 | .02 | .002107 | .0579 | .0796 | .0751 | .0045 | .02211 | .1487 |
| 4 | .05 | .002335 | .1025 | .1242 | .1155 | .0087 | .05234 | .2288 |
| 4 | .10 | .002625 | .1534 | .1751 | .1618 | .0133 | .1026 | .3203 |
| | | | | $MgCl_2$ | | | | |
| 4 | .03333 | .002544 | .1398 | .1615 | .1617 | $-$ .0002 | .1025 | .3202 |
| 4 | .05 | .002744 | .1726 | .1943 | .1973 | $-$ .0030 | .1527 | .3908 |
| | | | | NaCl | | | | |
| 4 | .10 | .002620 | .1525 | .1742 | .1618 | .0124 | .1026 | .3203 |
| | | | | $Mg(NO_3)_2$ | | | | |
| 4 | .03333 | .002459 | .1250 | .1467 | .1617 | $-$ .0150 | .1025 | .3202 |
| 4 | .05 | .002621 | .1527 | .1744 | .1973 | $-$ .0229 | .1526 | .3906 |
| | | | | $ZnSO_4$ | | | | |
| 5 | .05 | .002789 | .1797 | .2014 | .2274 | $-$ .0260 | .2028 | .4503 |

Figure 2, which represented these results graphically, as in Fig. 1, shows the same type of curve in solutions of potassium sulfate but here the "hump" which was so pronounced in the case of lanthanum iodate, although present, is barely discernible. In the case of magnesium sulfate as solvent the deviations from the limiting law are negative and of the usual character.

Potassium chloride behaves differently with thallous iodate than with lanthanum iodate. The curve is a straight line exhibiting only positive deviations. At 0.1 *N* the solubility in potassium chloride solution is almost as great as that in potassium sulfate (see Table III). Sodium sulfate and sodium chloride show the same behavior as the potassium salts.

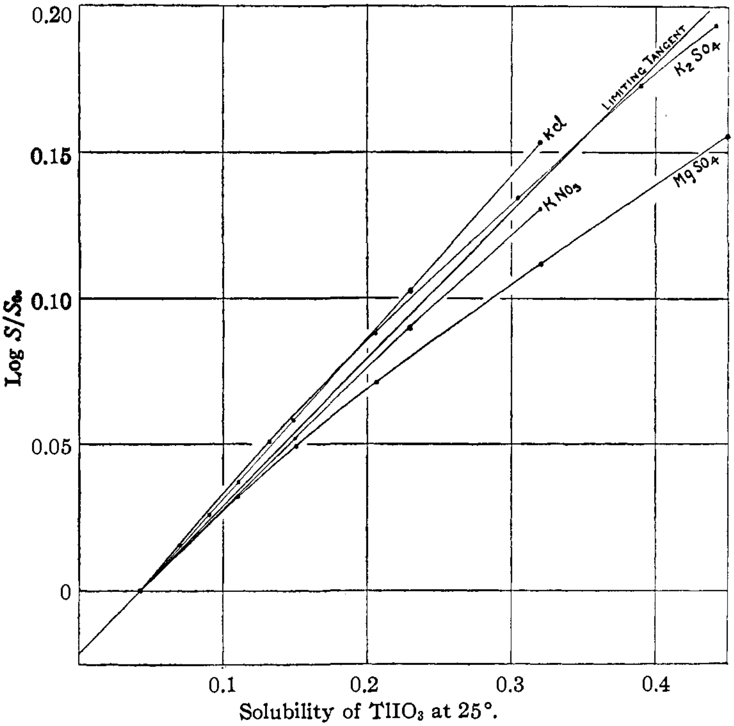


Fig. 2.

Table II contains the solubilities of lanthanum iodate in 0.1 *N* solvents, in order to determine the various solubility ratios for testing the principle of specific interaction.

TABLE IV

SOLUBILITY RELATIONS OF $La(IO_3)_3$ AT 25°

Harkins and Pearce, THIS JOURNAL, **38,** 2679 (1916) (Recalculated)

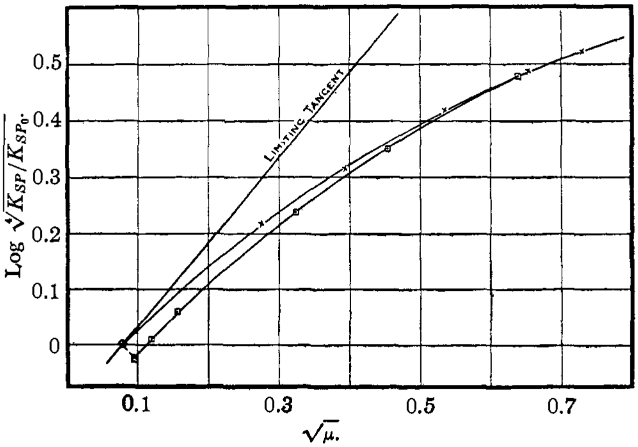
| No. | Concn. of added salt, millieq./1000 cc. | Concn. of added salt, mole/1000 cc. | Concn. of sat. salt, millieq./1000 cc. | Concn. of sat. salt, mole/1000 cc. |
|---|---|---|---|---|
| | Solvent $La(NO_3)_3 \cdot 2NH_4NO_3$, 3 equivalents = 1 mole | | | |
| 1 | 26.34 | 0.008780 | 2.8530 | 0.000951 |
| 2 | 56.682 | .018894 | 3.0470 | .001057 |
| 3 | 105.364 | .035121 | 3.4102 | .0011367 |
| 4 | 158.048 | .052683 | 3.69105 | .00123035 |
| 5 | 196.8375 | .0656125 | 3.9184 | .00130615 |
| 6 | 393.673 | .131224 | 4.8050 | .0016017 |
| 7 | 787.350 | .262450 | 6.1554 | .0020518 |
| 8 | 1574.700 | .5249 | 8.6904 | .0028968 |

Table IV (*Concluded*)

| No. | Concn. of added salt, millieq./1000 cc. | Concn. of added salt, mole/1000 cc. | Concn. of sat. salt, millieq./1000 cc. | Concn. of sat. salt, mole/1000 cc. |
|---|---|---|---|---|
| | | Solvent $La(NO_3)_3$ | | |
| 9 | 2.00 | .00067 | 2.5290 | .000843 |
| 10 | 5.00 | .001667 | 2.3905 | .0007968 |
| 11 | 10.00 | .003333 | 2.3477 | .0007826 |
| 12 | 50.00 | .01667 | 2.4960 | .0008320 |
| 13 | 100.00 | .03333 | 2.8086 | .0009362 |
| 14 | 200.52 | .06684 | 3.3586 | .001119 |

| No. | $\mu$ | $\sqrt{\mu}$ | Log $\sqrt[4]{\frac{K_{sp}}{K_{0sp}}}$ | −Log $f$ | −Log $f$ (calcd.) | Log $f$ (obs.) −Log $f$ (calcd.) |
|---|---|---|---|---|---|---|
| 1 | 0.07595 | 0.2756 | 0.2178 | 0.3378 | 0.4175 | −0.0797 |
| 2 | .1572 | .3965 | .3171 | .4371 | .6007 | − .1636 |
| 3 | .2878 | .3365 | .4188 | .5388 | .8127 | − .2739 |
| 4 | .4289 | .6549 | .4875 | .6075 | .9922 | − .3847 |
| 5 | .5327 | .7299 | .5230 | .6430 | 1.106 | − .463 |
| 6 | 1.060 | 1.030 | .6714 | .7914 | 1.560 | − .769 |
| 7 | 2.111 | 1.453 | .8269 | .9469 | 2.201 | −1.254 |
| 8 | 4.227 | 2.056 | 1.0142 | 1.134 | 3.115 | −1.981 |
| 9 | 0.009078 | 0.09528 | −0.0236 | 0.0964 | 0.1443 | −0.0479 |
| 10 | .01477 | .1215 | + .0110 | .1310 | .1840 | − .0530 |
| 11 | .02469 | .1571 | + .0609 | .1809 | .2380 | − .0571 |
| 12 | .1049 | .3240 | + .2379 | .3579 | .4909 | − .1330 |
| 13 | .2055 | .4535 | + .3495 | .4695 | .6870 | − .2175 |
| 14 | .4078 | .6386 | + .4820 | .6020 | .9674 | − .3654 |

Table IV contains Harkins and Pearce's[7] data for lanthanum iodate recalculated according to modern theory. Harkins and Pearce state their results only in terms of equivalents, which we interpret in the case of the



×—$La(NO_3)_3 \cdot 2NH_4NO_3$; ⊡—$La(NO_3)_3$.

Fig. 3.

double salt to mean three and not five equivalents per mole. The corresponding curves using lanthanum ammonium nitrate and lanthanum nitrate as solvent salts are given in Fig. 3. Except for the most dilute solutions the agreement with the principle of ionic strength is excellent. Lewis and Randall's failure to confirm their principle in this case evidently rests upon a miscalculation due to the unfortunate ambiguity attached to Harkins and Pearce's meaning of the term equivalent of double salt.

## 5. Solubility Ratios

Tables V and VI contain the solubility ratios for the saturating salts, $La(IO_3)_3$ and $Tl(IO_3)_3$, in various 0.1 *N* solvents to test the principle of specific interaction. If the equivalent concentration is the correct scale

TABLE V

$LA(IO_3)_3$ SOLUBILITY RATIOS. ALL CONCENTRATIONS ARE AT 0.1 *N* TO TEST THE THEORY OF SPECIFIC INTERACTION

| Cation | $NO_3/Cl$ | Ideal value | $SO_4/NO_3$ | Ideal value | $SO_4/Cl$ | Ideal value |
|---|---|---|---|---|---|---|
| K | 1.019 | 1.000 | 2.007 | 1.281 | 2.045 | 1.281 |
| Na | 1.017 |  | 2.011 |  | 2.044 |  |
| Mg | 1.015 |  | 1.697 | 1.232 | 1.723 | 1.232 |
| La | 1.014 |  | 1.449 | 1.202 | 1.468 | 1.202 |

| Anion | K/Na | Ideal value | K/Mg | Na/Mg | Ideal value | K/La | Na/La | Ideal value | Mg/La | Ideal value |
|---|---|---|---|---|---|---|---|---|---|---|
| $NO_3$ | 1.015 | 1.000 | 0.951 | 0.936 | 0.780 | 0.727 | 0.716 | 0.634 | 0.765 | 0.813 |
| Cl | 1.013 |  | .948 | .935 |  | .723 | .714 |  | .763 |  |
| $SO_4$ | 1.013 |  | 1.124 | 1.110 | .812 | 1.007 | .994 | .675 | .896 | .832 |

TABLE VI

$TlIO_3$ SOLUBILITY RATIOS. CONCENTRATION 0.1 *N* TO TEST THEORY OF SPECIFIC INTERACTION

| Cation | $NO_3/Cl$ | Ideal value | $SO_4/NO_3$ | $SO_4/Cl$ | Ideal value |
|---|---|---|---|---|---|
| K | 0.949 | 1.000 | 1.102 | 1.046 | 1.086 |
| Na | .949 |  | 1.102 | 1.046 |  |
| Mg | .955 |  | 1.007 | 0.962 | 1.072 |

| Anion | K/Na | Ideal value | K/Mg | Na/Mg | K/Zn | Na/Zn | Ideal value | Zn/Mg | Ideal value |
|---|---|---|---|---|---|---|---|---|---|
| $NO_3$ | 1.002[a] | 1.000 | 0.951 | 0.949 | ... | ... | 0.921 | ... | 1.000 |
| Cl | 1.002 |  | .957 | .955 | ... | ... |  | ... |  |
| $SO_4$ | 1.003 |  | 1.040 | 1.038 | 0.985 | 0.982 | 0.933 | 1.056 |  |

[a] Brönsted (ref. 13 a, p. 889) obtains 1.005 for this ratio in the presence of Cl and $ClO_3$ ions using praseo iodate as the saturating salt. On the basis of Hall and Harkins' values for the freezing point depression of $KIO_3$ and $NaIO_3$, the principle of specific interaction predicts a value of 1.004 for this ratio. Using Equations 18 and 19 of ref. 13 a we obtain a value of 1.036 for the ratio of interaction for iodate ion; $r_{\text{I}} = r_{IO_3}(Na/K)$ and a value of 0.986 for $r_{\text{u}} = r(Na/K)$ the salting out ratio for Na/K, taking $R_{\text{I}} = 1.004$ and $R_{\text{III}}$ (the K/Na solubility ratio for $La(IO_3)_3$) = 1.013 from Table V. The agreement between our value for $r(Na/K) = 0.986$ and Brönsted's value (1.011) is not entirely satisfactory.

for these comparisons regardless of the valence type of the solvent, then the ratio within each individual column should be constant. The bracketed values correspond to ratios for which the primary Milner effect is identical, as indicated by the ideal value for the ratio as given by the Debye limiting law. The data substantiate the conclusion of the previous paper that the ratios are constant at 0.1 $N$ only when the ideal value remains unchanged; also that a comparison of the activity deviation coefficients instead of the total activity coefficient at the same equivalent concentration will not yield constant ratios in all cases since variation in the ratios which occurs is very much greater than the corresponding change in the ideal value.

On the other hand, limiting the comparisons only to solvent ratio types which should have the same ideal value, we find the principle of specific interaction to be confirmed, as witnessed by the constancy of the bracketed values. In Table V the greatest discrepancy (0.5%) occurs for the $NO_3$/Cl ratio in passing from the K to the La salts.

The $SO_4/NO_3$ and $SO_4$/Cl ratios agree to within 0.2 and 0.05%, respectively, in changing the common cation from K to Na. Since the observed values (2.007 and 2.045) differ markedly from the ideal value (1.281), indicating highly specific effects for the $SO_4$ ion as opposed to the $NO_3$ or Cl ion, we must look upon this agreement as an excellent proof that the individual specific interactions are restricted to the ions of opposite sign at least up to 0.1 $N$. The constancy of the cation ratios of the type K/Mg and Na/La when changing the common anion from $NO_3$ to Cl is significant for the same reasons, since in previous tests the observed ratios and the ideal ratios have been almost identical, that is to say, the systems chosen have obeyed the Debye limiting law quite closely or have exhibited similar deviations from it.

Table VII gives the solubility ratios for $TlIO_3$ in solvents of various types at the same ionic strength. According to the Lewis and Randall principle of ionic strength,[8] all the ratios should be unity, which is obviously not the case. Although at 0.1 $\mu$ the ratios approach their corresponding ideal values somewhat more closely than at 0.1 $N$, this is partly due to the fact that the higher valence solvents are more dilute in the former case. On the other hand, the constancy of the ratios within a given group is not as good in Table VII as in Table VI. Thus the $NO_3$/Cl ratio for Mg differs

TABLE VII

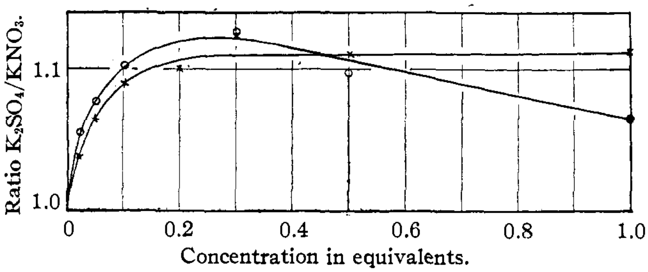
$TlIO_3$ SOLUBILITY RATIOS

Concentration (ionic strength) $\mu$ = 0.1 to test principle of ionic strength. Ideal value 1.000 for all.

| | $NO_3$/Cl | $SO_4/NO_3$ | $SO_4$/Cl | | K/Na | K/Mg | Na/Mg |
|---|---|---|---|---|---|---|---|
| K | 0.949 | 1.021 | 0.969 | $NO_3$ | 1.002 | 1.013 | 1.011 |
| Na | .949 | 1.023 | .971 | Cl | 1.002 | 1.032 | 1.030 |
| Mg | .967 | 0.9707 | .938 | $SO_4$ | 1.000 | 1.066 | 1.065 |

by only 0.6% from the identical values for Na and K as cations at 0.1 $N$, while the corresponding difference amounts to 1.8% at 0.1 $\mu$. Likewise, the K/Mg and Na/Mg ratios in the presence of $NO_3$ and Cl differ by 0.6% at 0.1 $N$, whereas the difference becomes 1.9% at 0.1 $\mu$.

Bray and Winninghoff[5a] and Butler and Hiscocks[5b,18] have determined the solubility of thallous chloride in the presence of potassium sulfate and potassium nitrate as solvent salts. From these data the ratio $[S_{TlCl(K_2SO_4)}]/S_{TlCl(KNO_3)}]$ can be calculated at different concentrations of added salts.



X—TlCl; O—$TlIO_3$.

Fig. 4.

These results appear in Table VIII and are plotted in Fig. 4 together with our data on thallous iodate. Values interpolated from the solubility curves are given in parentheses. Up to 0.3 $N$ the principle of specific interaction is confirmed as well as could be expected when we note that many of the ratios are obtained by combining data from different observers.

TABLE VIII

COMPARISON OF SPECIFIC INTERACTION RATIOS FOR TLCL AND $TLIO_3$

TlCl

| Added salt, equiv. | $K_2SO_4/KCl$ | $K_2SO_4/KNO_3$ | $KCl/KNO_3$ |
|---|---|---|---|
| 0.02 | (1.02) x/o | 1.037 x/x | (1.02) o/x |
| .05 | 1.073 x/o | 1.064 x/x | 0.991 o/o |
| .10 | 1.066 x/o | 1.090 x/x | 1.023 o/x |
| .20 | (1.04) x/o | (1.10) x/o | 1.063 o/o |
| .30 | (1.04) x/o | 1.124 x/x | (1.08) o/x |
| .50 | (0.957) x/o | (1.11) x/o | 1.163 o/o |
| 1.0 | ........ | 1.127 x/o | ........ |
| 1.0 | ........ | 1.112 x/x | ........ |

x = Bray and Winninghoff; o = Butler and Hiscocks.

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[18] Inadvertently an error crept into the printing of the solubilities of TlCl in $ZnSO_4$. The following corrected values were obtained through communication with Dr. J. A. V. Butler.

SOLUBILITY OF TLCL IN $ZnSO_4$ AT 25°

| Moles/liter of $ZnSO_4$ | 0.05 | 0.1 | 0.3 | 0.5994 |
|---|---|---|---|---|
| Solubility | 0.02059 | 0.02279 | 0.02770 | 0.03203 |

TABLE VIII (*Concluded*)

Our data on $TlIO_3$

| Added salt, equiv. | $K_2SO_4/KCl$ | $K_2SO_4/KNO_3$ | $KCl/KNO_3$ |
|---|---|---|---|
| 0.02 | 1.041 | 1.055 | 1.013 |
| .05 | (1.046) | (1.076) | 1.029 |
| .10 | 1.046 | 1.102 | 1.053 |
| .30 | ... | 1.126 | ... |
| .50 | ... | 1.097 | ... |
| 1.0 | ... | 1.064 | ... |

## Summary and Conclusions

The activity coefficients of lanthanum and thallous iodates have been determined in aqueous solutions of the chlorides, nitrates and sulfates of potassium, sodium, magnesium and lanthanum at 25° by solubility measurements. The usual form of the Debye-Hückel theory does not account for the behavior of a high valence salt like lanthanum iodate in $K_2SO_4$ solutions. The data show uniformly positive deviations from the Debye-Hückel limiting law and do not fuse into the theoretical curve at least down to concentrations as low as 0.0002 mole of added salt. This behavior is consequently to be looked upon as a general phenomenon and not an isolated one confined to the cobaltammine family. Saturating salts of the (1,–1) type like $TlIO_3$ exhibit positive deviations in sulfate solvents but to a far less marked degree than with $La(IO_3)_3$.

Harkins and Pearce's data for $La(IO_3)_3$ dissolved in $La(NO_3)_3$ as solvent are substantially correct. Lewis and Randall's suggestion that their data for $La(NO_3)_3 \cdot 2NH_4NO_3$ as solvent are in error is not justified and evidently arises from a misinterpretation of the term equivalent of double salt used by Harkins and Pearce.

Brönsted's principle of specific interaction has been tested at 0.1 $N$ concentrations for both saturating salts in various valence types of solvents. Excellent agreement with the requirements of this principle is found whenever the solubility ratios compared at the same equivalent concentration also involve the same ratio of ionic strengths even though the ratios deviate markedly from the ideal value predicted by the Debye limiting law as in the case where sulfates or higher valence cation solvents are involved. The solubility ratios for TlCl and for $TlIO_3$ have been compared for a number of solvents at various concentrations.

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