[CONTRIBUTION NO. 606 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

ACTIVITY COEFFICIENTS OF ELECTROLYTES.
III. THE PRINCIPLE OF SPECIFIC INTERACTION IN MIXTURES OF HIGH VALENCE ELECTROLYTES[1]

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RECEIVED FEBRUARY 6, 1929 PUBLISHED SEPTEMBER 5, 1929

1. Introduction

One of the most promising attempts to account for the specific deviations from the laws of uniform behavior of given valence type which individual strong electrolytes exhibit at concentrations other than those of extreme dilution, was presented by Brönsted[2] in a paper entitled "The Principle of Specific Interaction of Ions," published previous to the appearance of the theory of Debye and Hückel.[3] The purpose of this investigation was to subject this principle to a more extended test by studying mixtures of higher valence types of salts than in previous tests, in order to determine its limits of applicability. The fundamental physical assumption of the principle of specific interaction is that those specific effects which are due to electric forces should occur only between ions of *opposite* sign, since they approach each other closely while the electrical interaction between ions of *like* sign may be considered uniform, since on the average these ions are far apart.

This postulate may be expressed as follows.[2,3] If we let A_1B and A_2B represent two solvent salts with an anion in common (B), and having the same *equivalent* concentration, and let X represent an arbitrary cation and Y an arbitrary anion, present in small amount in the two solvents, then

$$\frac{f_{X(A_1B)}}{f_{X(A_2B)}} = F\,(A_1, A_2) \tag{1a}$$

and

$$\frac{f_{Y(A_1B)}}{f_{Y(A_2B)}} = F\,(A_1, A_2, Y) \tag{2a}$$

That is, the *ratio of the activity coefficients*, *f*, of the same cation in two equally strong solutions having an anion in common is a *function* only *of the nature of the two cations of the solvents;* the ratio of the activity coefficients of the same anion in two equally strong solutions having an anion in common is a function of the nature of the cation considered and the cations

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[1] The material for this paper is constructed from a dissertation submitted by R. Graham Cook to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, May, 1928. An abstract was presented before the Division of Physical and Inorganic Chemistry at the Swampscott (September, 1928) Meeting of the American Chemical Society.

[2] Brönsted (a) THIS JOURNAL, **44,** 877 (1922); (b) **45,** 2898 (1923).

[3] For a review and summary see La Mer, *Trans. Am. Electrochem. Soc.*, **50,** 631 (1927).

of the two solvents. By equally strong solutions here is meant solutions of the same *equivalent* concentration, that is, where the total number of charges, irrespective of sign, is the same in each solution.

When solvents of the type AB_1 and AB_2, where the cation is common, are employed, Equations 1a and 2a become

$$\frac{f_{X(AB_1)}}{f_{X(AB_2)}} = F\,(B_1, B_2, X) \tag{1b}$$

$$\frac{f_{Y(AB_1)}}{f_{Y(AB_2)}} = F(B_1, B_2) \tag{2b}$$

As a result of these equations we should have the following solubility relations, when we take AgCl, AgBr and TlCl as simple examples of uni-univalent saturating salts for purposes of illustration, and KNO_3, $NaNO_3$, $NaClO_3$, etc., to represent the aqueous solvents in which they are dissolved, namely,

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(NaNO_3)}} = \frac{S_{AgCl(KClO_3)}}{S_{AgCl(NaClO_3)}} = \frac{S_{TlCl(KNO_3)}}{S_{TlCl(NaNO_3)}} = \text{---} \tag{3}$$

and similarly when the terms cations and anion are interchanged

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(KClO_3)}} = \frac{S_{AgCl(NaNO_3)}}{S_{AgCl(NaClO_3)}} = \frac{S_{AgBr(KNO_3)}}{S_{AgBr(KClO_3)}} \tag{4}$$

2. Plan of the Investigation

Although considerable experimental data[2,4] have been accumulated in support of the theory, the evidence has been confined to the use of solvent salts of the simple uni-univalent type, with the exception of an important series of measurements[2b] involving Na_2SO_4 and NaCl as the solvents for two (1, − 1) and two (1, − 2) types of saturating salts having the ion $[Co(NH_3)_4C_2O_4]^+$ as cation.

In no case have any of the tests involved solubility data where the ions of opposite sign in the solute and solvent salts (*i. e.*, X and B, and Y and A) were both of a valence higher than unity. Such a test is of particular interest since La Mer and Mason[5] found extremely marked deviations from the Debye limiting law under these conditions even at very high dilutions. They found entirely normal results for the solubility of (3, − 1) salts involving the luteo cobaltic cation in the presence of solvent salts containing univalent anions, but when they employed sulfate solvents, the experimental curve for $-\log f$, when plotted against the square root of the ionic strength, gave no evidence of fusing into the limiting law of Debye and Hückel. If it can be shown that the principle of specific interaction holds at 0.1 N concentrations for these salts, then one should have little fear in applying it to mixtures which obey the present form of Debye theory.

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[4] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[5] La Mer and Mason, THIS JOURNAL, **49**, 363 (1927). See also the next paper of this series, *ibid.*, **51**, 2632 (1929), where the same behavior is found for $La(IO_3)_3$.

Because of the important theoretical significance of this result, we first repeated La Mer and Mason's measurements at low concentrations on independently and freshly prepared salts (Parts 5 and 6). It also seemed desirable to determine whether or not the solubility ratios, when B_1 and B_2 were of different valence, retained the same numerical value when the common solvent cation A was changed in valence; and similarly when the common anion B was changed in valence and the solvents cations A_1 and B_2 are of different valence. If the equivalent concentration is the appropriate scale for comparisons regardless of the valence type of solvent, then no change should occur in these cases. Such a result, however, would conflict with the Debye-Hückel theory, for this theory predicts that the contribution due to primary Milner effect (ideal value dependent only on valence type and independent of specific properties) is proportional to the ionic strength and not to the equivalent concentration.

We should expect, therefore, to obtain constant ratios only when the ratios of the ionic strengths of the solvents remain unchanged at the same equivalent concentration. This proves to be the case.[6]

3. Experimental

The saturating salts employed in this investigation were (1) luteo-cobaltic di-ammino tetra-nitro cobaltiate, $Co(NH_3)_6[Co(NH_3)_2(NO_2)_4]_3$, which we shall represent hereafter by the symbol "LN_3" (S_0, the solubility in moles per liter in pure water, is 1.64×10^{-4}); (2) luteo-cobaltic di-ammino di-nitro oxalo cobaltiate, $Co(NH_3)_6[Co(NH_3)_2(NO_2)_2C_2O_4]_3$, symbol, "$LOn_3$" ($S_0 = 0.826 \times 10^{-4}$); (3) luteo-cobaltic ferricyanide, $Co(NH_3)_6Fe(CN)_6$, symbol, "LF" ($S_0 = 0.30 \times 10^{-4}$); and (4) luteo-cobaltic cobalticyanide, $Co(NH_3)_6Co(CN)_6$, symbol, "LC" ($S_0 = 0.22 \times 10^{-4}$). The first two, the tri-univalent salts, were employed in that part of the investigation where the conclusions of La Mer and Mason[4] were to be tested. All four were used as saturating salts for the experimental test of the specific interaction theory. The LN_3 salt became so soluble in tenth normal salt solutions that it was not possible to run a whole series of measurements on the same sample of saturating salt, and only a few measurements were made on this salt. On the other hand, it was possible to measure the solubility of the LOn_3 salt in a complete series of solvent salts, using the same sample throughout.

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[6] Brönsted, ref. 2b, p. 2908 recognized the error in assuming that the primary Milner effect is determined by the equivalent concentration, but since he finds, p. 2909, "that the identity of values found by comparing two isotopic salts with a common cation appears only when the equivalent concentration is used" and "not at the same molar concentration or ionic strength"—a conclusion which our data also support (see data for $TlIO_3$ in the following paper)—it seemed desirable to obtain data bearing on this point in hopes of discovering an appropriate scale or scales for purposes of comparison. As far as we are aware no data bearing on this question have been presented.

The method used and the various precautions to be observed in carrying out the solubility determinations have been described in detail previously.[7] The original thesis should be consulted for further details concerning these measurements.

4. Preparation of Materials

Luteo-cobaltic Nitrate.—This salt was prepared by the iodine method of Biltz[8] and recrystallized from dilute nitric acid, washed with water containing a little nitric acid and finally thoroughly washed with 95% ethyl alcohol. It was dried in the oven at 100°.

Ammonium Di-ammino Tetra-nitro Cobaltiate.—The method given by Jörgensen[9] was followed. The salt was twice recrystallized from water and allowed to dry spontaneously.

Ammonium Di-ammino Di-nitro Oxalo Cobaltiate.—This salt was obtained by adding to a solution of the above salt a solution of oxalic acid, in the correct molecular proportions according to the direction of Jörgensen.[10] It was once recrystallized from water. The luteo-cobaltic saturating salts were prepared from the above salts by methods previously described.[6,11]

Salts of Potassium and Sodium.— Potassium nitrate, potassium chloride, potassium sulfate, sodium chloride, sodium nitrate and sodium sulfate: the best "c. p." grades obtainable were twice recrystallized from redistilled water, dried in the oven at 120°, ground in an agate mortar and dried again at 120° for twenty-four hours.

Salts of Magnesium.—Concentrated solutions of all salts gave no qualitative tests for calcium, barium, strontium, sodium, potassium or ammonium ions as impurities, except magnesium chloride, which contained very small amounts of ammonia, as described later.

Magnesium Sulfate.—A "c. p." product was twice recrystallized, dried in the oven at 50° for three days, then kept in a desiccator over phosphorus pentoxide for a week. The "apparent" molecular weight of the hydrate was determined by igniting a weighed sample to constant weight in a crucible, thus determining the magnesium as magnesium oxide. It was kept in a glass-stoppered bottle sealed with paraffin.

Magnesium Chloride.—Of all the solvent salts employed, this was the only one which was found to contain ammonium salts in appreciable amounts. A sample of Kahlbaum's "zur Analyse" grade was found to have the least amount of ammonia present. A 100-cc. aliquot of 0.1 N $MgCl_2$ solution contained ammonia equivalent to 0.15 cc. of 0.02073 N HCl. Thus one liter of the salt solution would contain only 0.5 mg. of NH_3. A stock solution of the $MgCl_2$ was made up, the chloride determined by titrating against 0.1034 N silver nitrate solution (Mohr method), and the solution diluted to 0.1000 N and re-checked against the silver nitrate solution before use.

Lanthanum Salts.—Samples of the hydrated salts were obtained from the Welsbach Company, who especially purified the salts to free them from cerium and other rare earths. Tests for cerium by the sensitive hypochlorite method[12] gave negative results.

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[7] La Mer, King and Mason, This Journal, **49**, 363 (1927).

[8] Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, Inc., New York, **1909**, p. 176.

[9] Jörgenson, *Z. anorg. Chem.*, **17**, 476 (1898). See also Thomas, "Complex Salts," Blackie and Son, Ltd., Glasgow, **1924**, p. 116.

[10] Jörgensen, *Z. anorg. Chem.*, **11**, 445 (1896).

[11] Jörgensen, *ibid.*, **5**, 179 (1894).

[12] Baxter, Tani and Chapin, This Journal, **43**, 1080 (1921).

Lanthanum Nitrate.—The apparent molecular weight of the hydrated salt was determined by igniting a weighed sample to lanthanum oxide.

Lanthanum Chloride.—The apparent molecular weight of this hydrate was determined by analyzing for chloride by the Mohr method. All salts were kept in glass-stoppered bottles sealed with paraffin.

Water.—Distilled water was redistilled over potassium permanganate acidified with phosphoric acid, through a block tin condenser, with steam escaping. The combined ammonia and indicator "blank" on water prepared in this manner amounted to 0.04–0.05 cc. of 0.02073 *N* HCl for a 100-cc. aliquot. The water was stored in pyrex "resistance glass" bottles, but never for a period longer than a week or ten days.

5. The Data at High Dilution

The solubility relations of two tri-univalent cobaltammines in very high dilutions of aqueous potassium sulfate at 25° are given herewith.

TABLE I

LUTEO-COBALTIC DI-AMMINO TETRA-NITRO COBALTIATE, LN_3

HCl = 0.01031 *N*. Sample aliquot, 100 cc. Water blank, 0.06 cc.

Solvent	No. of detns.	Av. cc. of HCl, corr.	Av. dev.	Soly. in moles per liter × 10^4	μ	$\sqrt{\mu}$	Log S/S_0
Water	8	19.10	0.03	1.641	0.0009852	0.03139	...
K_2SO_4							
0.0002 *M*	3	20.80	.01	1.787	.001672	.04089	0.0371
.0005 *M*	3	23.18	.02	1.991	.002695	.05191	.0841
.0010 *M*	5	26.05	.03	2.238	.004343	.06590	.1348

TABLE II

LUTEO-COBALTIC DI-AMMINO DI-NITRO OXALO COBALTIATE, LON_3

HCl = 0.01031 *N*. Sample aliquot, 200 cc. Water blank, 0.11 cc.

Solvent	No. of detns.	Av. cc. of HCl corr.	Av. dev.	Soly. in moles per liter × 10^4	μ	$\sqrt{\mu}$	Log S/S_0
Water	8	19.22	0.03	0.8255	0.0004953	0.02226	...
K_2SO_4							
0.0002 *M*	3	21.50	.01	0.90236	.001154	.03397	0.0487
.0005 *M*	3	24.13	.01	1.036	.002122	.04607	.0989

The column "Av. cc. of HCl" gives the average amount of acid used to neutralize the ammonia distilled for the number of determinations indicated in the second column. "Av. dev." represents the average deviations of the individual determinations from this average. The fifth column gives the solubility of the saturating salt in moles per liter at 25 ± 0.007°. μ is the ionic strength. The last column gives the values for the relation log S/S_0, where "S" is the solubility of the saturating salt in the neutral salt solution and "S_0" the solubility in pure water.

6. Discussion of Results

The values obtained for the solubility of the present preparations of the two luteo-cobaltic salts in pure water agree with those found by La Mer and Mason for the LN_3 salt within 0.6%, and for the LOn_3 salt within 0.2%.

Similarly, their results, in which they found marked deviations from the theory given by Debye and Hückel for the case where these two cobalt-ammine salts were dissolved in potassium sulfate solutions, have been confirmed. The deviations have been found to persist down to even more dilute solutions, namely, to a solution of 0.0002 *M* K_2SO_4. In the figure the values of log S/S_0 are plotted against the square root of the ionic strength. I represents the curve for the LN_3 salt, II the curve for the LOn_3 salt, while the dotted lines represent the curves demanded by the limiting law for the respective salts. The experimental curves give no evidence whatever of fusing into the theoretical at the highest dilutions possible with this salt. The initial slopes of these experimental curves for

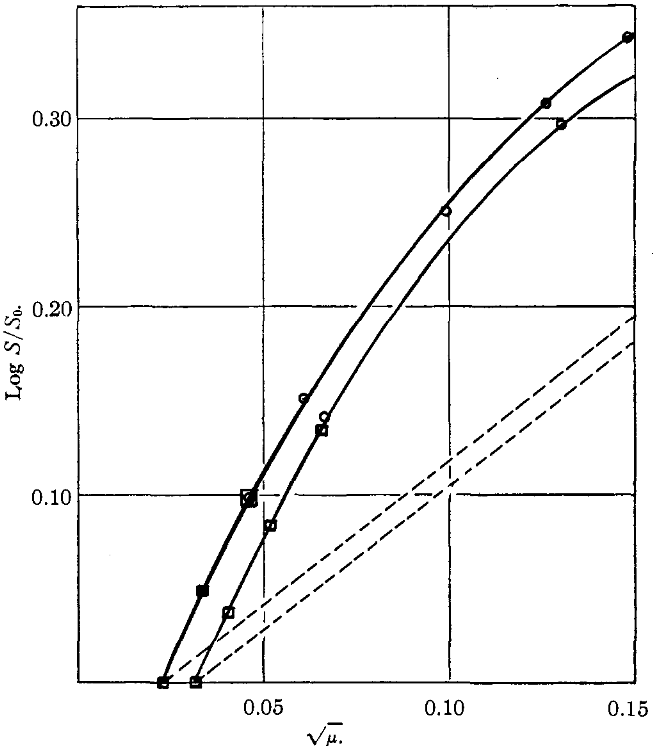

Fig. 1.—The solubility effects of potassium sulfate on luteo-cobaltic diammino tetranitro cobaltiate, I, and luteo-cobaltic diammino dinitro oxalo cobaltiate, II, at high dilution. The upper curve is II, the lower I. The dotted lines represent the slopes of the Debye–Hückel limiting law for each salt. ⊡, This investigation; ⊙, La Mer and Mason.

the highly dilute regions (μ = 0.0005–0.002, and 0.001–0.0027) give "apparent" values for the constant α' of 1.4, which is nearly three times the theoretical value at 25°, namely, 0.504.[5,7]

7. The Data at 0.1 *N* Concentration

Table III

	Luteo-cobaltic Di-ammino Di-nitro Oxalo Cobaltiate $Co(NH_3)_6[Co(NH_3)_2(NO_2)_2C_2O_4]_3$		Luteo-cobaltic Cobalticyanide[a] $Co(NH_3)_6Co(CN)_6$	
Solvent salt solns., all 0.1 *N*	No. of detns.	Molar soly. × 10^4	No. of detns.	Molar soly. × 10^4
KNO_3	12	2.030	3	1.978
KCl	4	2.006	2	2.018
K_2SO_4	5	3.438	5	5.920
$NaNO_3$	4	1.954	3	1.864
NaCl	3	1.935	6	1.857
Na_2SO_4	4	3.348	3	5.623
$Mg(NO_3)_2$	3	1.928	3	2.415
$MgCl_2$	3	1.905	3	2.381
$MgSO_4$	3	2.818	3	4.619
$La(NO_3)_3$	3	2.615	3	3.301
$LaCl_3$	3	2.590	2	3.384

[a] For measurements on this salt at high dilution see Brönsted and Brumbaugh, This Journal, **48,** 2015 (1926).

Table IV

Luteo-cobaltic Di-ammino Tetra-nitro Cobaltiate

$Co(NH_3)_6[Co(NH_3)_2(NO_2)_4]_3$

Solvent salt solns., all 0.1 *N*	No. of detns.	Molar soly. × 10^4
KNO_3	3	3.790
KCl	5	3.753
K_2SO_4	4	6.432

Table V

Luteo-cobaltic Ferricyanide

$Co(NH_3)_6Fe(CN)_6$

Solvent salt solns., all 0.1 *N*	No. of detns.	Molar soly. × 10^4
KNO_3	6	2.739
KCl	6	2.789
$NaNO_3$	4	2.572
NaCl	2	2.577

For measurements on this salt at high dilution see ref. 7.

Table VI

Solubility Ratios at 0.1 *N* Concentrations

Saturating salts Type	Salt	Cation present	NO_3/Cl	Ideal value	SO_4/Cl	SO_4/NO_3	Ideal value
(3, −1)	LON_3	K	(a) 1.012	1.000	(f) 1.714	(j) 1.694	1.281
		Na	1.010		1.730	1.714	
		Mg	1.012		1.479	1.461	1.229
		La	1.010		(1)	(1)	
(3, −1)	LN_3	K	1.010		1.713	1.697	1.281
		Av. =	1.011				

TABLE VI (*Concluded*)

Saturating salts Type	Salt	Cation present		NO_3/Cl	Ideal value		SO_4/Cl		SO_4/NO_3	Ideal value
(3, −3)	LC	K	(b)	0.980	1.000	(g)	2.934	(k)	2.993	2.102
		Na		1.004			3.028		3.017	
		Mg		1.014			1.940		1.913	1.854
		La		0.976			(*a*)		(*a*)	
(3, −3)	LF	K		0.982			(*b*)		(*b*)	
		Na		0.998			(*b*)		(*b*)	
			Av. =	0.992						

TABLE VII

SOLUBILITY RATIOS AT 0.1 N CONCENTRATIONS

Saturating salts Type Salt	Anion present		K/Na	Ideal value		K/Mg	Ideal value		K/La	Ideal value
(3, −1)LOn_3	NO_3	(c)	1.039	1.000	(h)	1.053	0.780	(l)	0.776	0.634
	Cl		1.037			1.053			0.775	
	SO_4		1.027			1.220	0.814		(1)	
(3, −3)LC	NO_3	(d)	1.061	1.000	(i)	0.819	0.476	(m)	0.599	0.255
	Cl		1.087			0.848			0.596	
	SO_4		1.053			1.282	0.539		(*a*)	
(3, −3)LF	NO_3	(e)	1.065	1.000		(*b*)			(*b*)	
	Cl		1.082			(*b*)			(*b*)	

[a] Not determined, see Section 8. [b] Not determined.

8. Discussion of Results

Tables III, IV and V give the respective solubilities in 0.1 N solutions of the solvents indicated. It was impossible to include lanthanum sulfate as one of the solvent salts since crystals of some less soluble salt, possibly a double salt, separated out. Table VI summarizes the anion solubility ratios for the four saturating salts; also the ideal values for the ratios as predicted by the Debye-Hückel limiting law. Table VII gives the cation ratios in the presence of the common anions.

According to Equations 1 and 2, the bracketed groups labeled (a), (b), (c), etc., designate groups within which the ratios should be identical if the principle of specific interaction holds for all valence types of solvents at the same equivalent concentration. The numerical values in group (a) are not necessarily equal to those in group (b) since they represent ratios for two different valence types of saturating salts. Groups (c), (d) and (e) of Table VII should be constant within each group but not necessarily to each other, since here the anions of the saturating salts are different (Equation 2a).

If the principle of ionic strength were true at 0.1 N concentrations, all of the values in groups (a), (b), (c), (d) and (e) should be equal to unity, which is obviously not the case; the deviations from this principle vary from 2.7 to 8.7% for groups (c), (d) and (e), while the corresponding variations from the principle of specific interaction are 0.2% for NO_3^- to Cl^- in group (c) to 3.4% between Cl and SO_4 in group (d). Table III contains the most striking departure from the ionic strength principle which we have ever noted. The solubilities of the (3, −3) LC salt change from 2.381 to $5.920.10^{-4}$ mole liter in passing from 0.1 N $MgCl_2$ to 0.1 N K_2SO_4. The ionic strengths of the solvents are identical yet the ratio of the solubilities is 2.55 instead of 1.00.

In considering groups (f), (g), (j), (h), (k) and (i), where the ratios involve ions of different valence, it will be observed that the values remain constant only when the ideal values as given by the Debye limiting law also remain constant. In other words, *it is only when the ratios of the ionic strengths of the solvents remain constant, as well as the equivalent concentrations, that the numerical comparisons of principle of specific interaction can be applied.*

The solubility ratios for SO_4/Cl or SO_4/NO_3 change by 25% for LOn_3 and by 35% for LC, when the common univalent cation (K or Na) is exchanged for the bivalent cation Mg. A similar result holds for the cation ratios K/Mg in Table VII when the common anion changes from NO_3 or Cl to SO_4.

According to the Debye-Hückel theory, one might expect that this difficulty could be avoided by making all comparisons at the same ionic strength but, as can be pointed out more clearly in the next paper with $TlIO_3$, this procedure does not seem to work in agreement with the earlier statement of Brönsted.[13]

Nor does the equally plausible scheme of comparing *only the activity deviations* at the same equivalent concentrations, instead of the total activity coefficient, assist very materially. The reader may readily verify this statement by dividing the observed ratios in Tables VI and VII by the corresponding ideal values to eliminate the change in primary Milner effect. The change in the ideal values with valence type is too small to bring about the desired constancy.

Accepting the restriction that the valence types of the solvents must be chosen such that the comparisons do not involve a change in the ideal value, our data furnish some excellent confirmations of the principle of specific interaction. Thus the NO_3/Cl, SO_4/Cl and SO_4/NO_3 ratios are identical for the LN_3 and LOn_3 salts within 0.2% in the presence of K ion, as they should be, since the saturating salts contain the same cation (verification of Equations 1 and 2). This confirmation is particularly significant in view of the fact that not only are the ratios quite different from the ideal values for 0.1 N levels, but the Debye limiting law breaks down completely for both of these salts at such small additions as 0.0002 M K_2SO_4 (Parts 5 and 6).

Although the values in group (b) show slight variations when the common cation changes from K to Mg and finally to La, it should be noted that

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[13] Ref. 2 a, p. 2909; see ref. 6.

changing the anion of the saturating salt from C^{---} to F^{---} produces a variation of only 0.2% in the presence of K and of 0.6% in the presence of Na. The constancy of the K/La and K/Mg ratios when the common anion is changed from NO_3 to Cl also deserves mention in extending the limits of applicability to higher valence types of solvents.

Since the saturating salts involve two different valence types, we can calculate the ratios of the interaction coefficients r_i of chlorides and nitrates, and of sulfates and chlorides, on the luteo cobaltic ion from the values given in Table VI by the methods outlined in detail by Brönsted,[14] and also, the ratios of the salting out coefficients (r_u).

The products of r_u by r_i give r_f, the ratios of the activity coefficients. These calculations yield.

TABLE VIII[a]

CHLORIDE/NITRATE RATIOS

In presence of cation	r_i	r_u	r_f
K^+	0.883	1.043	0.921
Na^+	0.976	1.016	0.992
Mg^{++}	1.008	1.010	1.018
La^{+++}	0.872	1.045	0.911
	CHLORIDE/SULFATE RATIOS		
K^+	8.60	1.001	8.60
Na^+	9.39	0.988	9.28

[a] The ratios of the interaction coefficients do not appear to be entirely independent of the other ions in the solution, as demanded by the principle. The nature of the calculation, however, makes the values extremely sensitive to small errors in the measurements, so that the disagreements may not be as marked as appears at first sight. Using (1, −1) and (1, −2) as saturating salts, Brönsted found the salting out ratio $r_u(Cl/SO_4)$ to be about 1.01, while our ratios based on (3, −1) and (3, −3) saturating salts are 1.00 and 0.99 in the presence of K and Na, respectively.

Summary and Conclusions

The principle of specific interaction has been given an extensive experimental test by means of solubility measurements on high valence types of mixtures, using (3, −1) and (3, −3) saturating salts in the presence of (1, −1), (1, −2) (2, −1), (2, −2) and (3, −1) types of solvent salts at 0.1 *N* concentrations. It is shown that the principle can be extended to higher valence solvents provided that comparisons are restricted to types in which the ratio of the ionic strengths remains unchanged when changing the common solvent ion at the same equivalent concentration.

The results of La Mer and Mason, in which they found very marked deviations from the limiting law of Debye and Hückel at high dilutions when the ions of opposite sign are of high valence, have been confirmed.

The principle of specific interaction retains its validity in these cases in

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[14] Ref. 2 a, pp. 885 ff.

spite of the failure of the Debye limiting law to hold at concentrations as low as 0.0005μ.

NEW YORK, N. Y.

[CONTRIBUTION NO. 607 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

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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RECEIVED FEBRUARY 6, 1929 PUBLISHED SEPTEMBER 5, 1929

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.