

[CONTRIBUTION NO. 645 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. V. THE PRINCIPLE OF SPECIFIC INTERACTION IN CADMIUM AND MAGNESIUM SULFATE AND CHLORIDE SOLVENTS

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In two recent papers^{1,2} from this Laboratory, it has been demonstrated that the principle of specific interaction, which Brönsted has shown to be valid for low valence types of solvents, can be extended to solvents containing higher valence types of strong electrolytes, provided the ratios of the ionic strengths of the two solvents of different valence types remain unaltered on varying the common solvent ion at the same equivalent concentration. Such a restriction is demanded by the Debye-Hückel theory. It is remarkable that Brönsted's principle was found to be valid in complex mixtures where the Debye-Hückel equations are incapable of accounting for the results.

In the first paper cited this aspect of the principle was tested by comparing the solubility ratios of the saturating salt thallos iodate, and also lanthanum iodate, when the anion of the solvent salt was changed from sulfate to chloride at 0.1 *N* concentrations. The significant ratios were usually constant to 0.2% (maximum 0.6%) in the presence of potassium or sodium as cation. In the specific case of lanthanum iodate the ratios for (SO₄/Cl)K and (SO₄/Cl)Na were 2.045 and 2.044, respectively, data which confirm the principle in a striking manner.

The corresponding (SO₄/Cl)Mg ratio was 1.723 but since the ionic strength ratio for (SO₄/Cl) is different in the presence of magnesium as contrasted with potassium and sodium at the same equivalent concentration, the ratio in the presence of magnesium cannot be expected to equal that in the presence of potassium or sodium.

On the other hand the (SO₄/Cl) ratios for magnesium salts should be the same as for the cadmium salts, *if both* behave as strong electrolytes, for any given saturating salt and for two saturating salts with a common anion like thallos iodate and lanthanum iodate the (Mg/Cd) ratios should be identical for both saturating salts irrespective of the common anion of the solvent salts.

Since it is generally recognized that cadmium chloride is abnormal in its behavior as a strong electrolyte as judged by transference, conductance and osmotic measurements, a comparison of the (SO₄/Cl) solubility ratios in the presence of Mg and of cadmium is of interest since a comparison of the same ratios in the presence of potassium and sodium has demonstrated the validity of the principle involved.

¹ La Mer and Goldman, *THIS JOURNAL*, 51, 2632 (1929).

² La Mer and Cook, *ibid.*, 51, 2622 (1929).

Experimental

The reader is referred to the previous publications² of this series for the details of the preparation of the thallos iodate and lanthanum iodate and the apparatus used in making the solubility measurements. The magnesium sulfate solutions were prepared by weighing out twice recrystallized salt dried to the anhydrous state. The magnesium and cadmium chloride solutions were prepared by diluting to 0.1 *N* solutions whose strength had been determined by titration for chloride content by the Mohr method.

Cadmium sulfate crystals recrystallized from J. T. Baker's c. p. salt were analyzed electrolytically and found to conform to the formula $\text{CdSO}_4 \cdot \text{H}_2\text{O}$.³

The experimental results are summarized in Table I. The quantities after the = signs refer to the arithmetic mean of the deviations from the average of the individual data. The ratios computed in Table II should therefore be precise to about 1%. The so-called ideal values for the ratios are calculated from the Debye-Hückel limiting law and are submitted only

TABLE I
SUMMARY OF SOLUBILITIES OF THALLOUS IODATE AND OF LANTHANUM IODATE IN 0.1 NORMAL AQUEOUS SOLVENTS AT 25° IN MICROMOLES (10^{-6} M./L.) PER LITER

Solvent	Detns.	Soly. of ThIO_3 in mole/liter $\times 10^6$	Detns.	Soly. of $\text{La}(\text{IO}_3)_3$ in mole/liter $\times 10^6$
H_2O	5	1819 \pm 6	5	939.1 \pm 1.2
MgSO_4 (0.05 <i>M</i>)	8	2625 \pm 7	4	3010 \pm 4
CdSO_4 (.05 <i>M</i>)	5	2798 \pm 3	5	3205 \pm 9
MgCl_2 (.05 <i>M</i>)	5	2755 \pm 9	6	1768 \pm 7
CdCl_2 (.05 <i>M</i>)	4	2708 \pm 2	4	1689 \pm 6

TABLE II
SOLUBILITY RATIOS AT 0.1 *N* CONCENTRATIONS AT 25°

Cation present	SO_4/Cl	Ideal value	Anion present	Mg/Cd	Ideal value
ThIO ₃ as Saturating Salt					
Mg	0.953	} 1.072	SO ₄	0.938	} 1.000
Cd	1.033		Cl	1.017	
La(IO ₃) ₃ as Saturating Salt					
Mg	1.703	} 1.232	SO ₄	0.939	} 1.000
Cd	1.898		Cl	1.047	

³ The details of this procedure have been worked out by Mr. W. G. Parks and will be submitted shortly for publication. The method is precise to 0.01%. This work which deals with the e. m. f. of the cell $\text{Cd}(\text{Hg})-\text{CdSO}_4(m)-\text{PbSO}_4-\text{Pb}(\text{Hg})$ shows that cadmium sulfate is virtually completely ionized at least up to 0.01 *m*, since the activity coefficients of cadmium sulfate can be accurately accounted for between $m = 0.0005$ to $m = 0.01$ by the Gronwall, La Mer and Sandved [*Physik. Z.*, 29, 358 (1928)] extension of the Debye-Hückel theory using a constant value of 3.6 Å. for the single parameter "*a*," and the assumption that the dielectric constant is equal to that of pure water. If cadmium sulfate is incompletely dissociated, the influence of this factor is inappreciable up to 0.01 *m* when electrostatic influences are properly calculated.

as a guide to the extent to which the ratio deviates from the ideal limiting value. Only those ratios having the same ideal value should be identical according to the restatement of the principle of specific interaction.

The fact that $(\text{Mg}/\text{Cd})\text{SO}_4$ ratios for thallos iodate and lanthanum iodate are sensibly identical, *i. e.*, 0.938 and 0.939, is most gratifying. The $(\text{SO}_4/\text{Cl})\text{Mg}$ ratios, however, are uniformly 1% lower than are the values previously reported by La Mer and Goldman.¹ Aside from possible inaccuracies in the determination of the solubilities, this is most likely to be ascribed to possible constant error in determining the chloride concentration of the solvents to be 0.1 *N* by the Mohr methods. Unfortunately we have not had an opportunity to repeat this phase of the work to establish the source of this 1% discrepancy. Granting, however, even this limit of uncertainty, it seems very improbable that the 8 and 11% differences in the $(\text{SO}_4/\text{Cl})\text{Mg}$ ratio as compared to the $(\text{SO}_4/\text{Cl})\text{Cd}$ ratio for the two saturating salts can arise from analytical error alone. We therefore conclude that the specific interaction principle does not hold when considering such an atypical electrolyte as cadmium chloride, though in view of the marked abnormality which this salt exhibits it is surprising that the principle holds as well as it does.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

**THE HYDROLYSIS EQUILIBRIA OF
TRIPHENYLCHLOROMETHANE AND
TRIPHENYLBROMOMETHANE. THE FREE ENERGY OF SOME
REACTIONS OF TRIPHENYLCHLOROMETHANE,
TRIPHENYLBROMOMETHANE AND TRIPHENYLCARBINOL**

By J. O. HALFORD

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The standard free energy of a reaction is related to the equilibrium constant by the familiar equation, $\Delta F^\circ = -RT \ln K$, and the two functions may be taken as alternative expressions of the tendency of the reaction to take place. However, the standard free energy is more significant, since it is related more directly to the fundamental properties of the substances involved in the reaction, and permits a wider application of the results. One advantage is that the intention to express results as free energies usually leads to experiments so carried out that the data may be applied not only to the reaction measured but to a number of related reactions as well. Certain difficulties may arise as a result, for with a given reaction the conditions most favorable to the production and measurement of equilibrium are not, in general, the best conditions for the determination of free energy relations. This is particularly true