with $m = 2$ are not so comparable among themselves; they furthermore involve much more uncertainty both as to structures and as to values of ionization constants.)

The similarities in Table I are both surprising and instructive. The acids here listed in the class $m = 1$, for example, are usually considered as unrelated, and if related, they are usually thought of as having widely different ionization constants, for the reason that they have never (to the writer's knowledge)[13] been grouped together in this fashion to bring out both the uniformity of their strengths and the similarity of constitution underlying this uniformity. The similarity is simply that the formal charge on the central atom is the same, and this seems to be the controlling factor for the aqueous ionization constant despite the variety of the elements represented, of their oxidation states and of the (analytical) formulas of the acids. The similarity of the first ionization constants of H_3PO_4, H_3PO_3 and H_3PO_2 has been noted by Yost and Russell (Table I, ref. ^{b}, p. 193), who remark that these are "unlike other series of acids (H_2SO_3, H_2SO_4, for example)." But H_2SO_4 (with $m = 2$, $n = 2$) and H_2SO_3 (with $m = 1$, $n = 1$) would not be expected to have similar values of K_1 at all, while the three phosphorus acids would, from this point of view, which may therefore be a useful one for correlation and systematization in general.

At any rate there may be a significant suggestion in the simplicity and uniformity of the ionization constants as arranged in Table I, that whatever the process of ionization may be in water solution, it is much less dependent upon the structure and constitution of the acid—as these are currently pictured, at least—than one would have expected. One wonders to what extent our ideas of these "structures" may be at fault, being possibly preconceived upon the assumption that the structure of the acid is the same as that of its salt, an apparently necessary consequence of the customary but arbitrary definition that an "acid" is something which "dissociates" in water solution to "give off" a proton; that an oxygen acid, in other words, is of necessity a hydrogen compound to begin with, whether we use the Arrhenius or the thermodynamically equivalent Brönsted point of view.

It is possible that a concept of ionization through coördination, more or less as originally suggested by Werner,[6] amounting to capture of hydroxyl ion and capture of proton as the acid and base ionization processes, respectively, might be developed, in which the emphasis would be laid upon the coördination requirements of the actual solute itself (SO_3) and not upon the structure of its ion ($SO_4^{=}$ or HSO_4^-) in its salts, as the determining factor for the ionization constant.

Summary

Critical examination of theoretical calculations of the aqueous ionization constants of inorganic oxygen acids shows that the treatment does not constitute a test of the fundamental assumption of a proton transfer from solute to solvent. An empirical correlation and grouping of these ionization constants based on the formal charge of the central atom and the number of non-hydroxyl oxygens in the acid, is presented. This grouping, apparently independent of the supposed "structures" of the acids, may indicate the need of a different picture of the process of ionization.

NEW YORK, N. Y. RECEIVED JANUARY 18, 194

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[13] The referee examining this paper kindly brought to the author's attention a book entitled "General Chemistry," by Linus Pauling (Edward Bros., Inc., Ann Arbor, Michigan, 1944), presenting a classification of ionization constants, based on coördination, which is in several respects similar to that in Table I.

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

The Influence of Dipolar Ions on the Solubility of Some Sparingly Soluble Salts

BY FANG-HSUIN LEE AND LI-KWON LUH

The interionic attraction theory applied to dipolar ions and real ions in solution has been formulated by Scatchard and Kirkwood.[1,2] This theory has been supported chiefly by experiments of Cohn.[3] Although much work has been done in finding the effect of varying the concentration of salts on the activity of amino acids, only few experiments have been done on influence of amino acids on the activity of salts. Solubility, f. p. and e. m. f. were the method chiefly used for the latter purpose. Among the amino acids glycine was the one most commonly used. The salts studied by previous workers are $NaCl$,[4,5] KCl,[6] $TlCl$,[4,7] $CaCl_2$,[4] $AgIO_3$,[8] $TlIO_3$,[9] $Ba(BrO_3)_2$,[8] $ZnCl_2$,[4] $Ca(IO_3)_2$[8] and $Pb(IO_3)_2$.[8]

According to Kirkwood, the solubility, S, of a sparingly soluble salt is related to the molality, m, of amino acid by the simplified experimental equation

$$\log S/S_0 = K(Z_+ \cdot Z_-/2)m \qquad (1)$$

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[1] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); *Chem. Rev.*, **19**, 275 (1936).

[2] G. Scatchard and J. G. Kirkwood, *Physik.*, 2, **33**, 297 (1932).

[3] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides." Reinhold Publishing Corp., New York, N. Y., 1943.

[4] N. R. Joseph, *J. Biol. Chem.*, **111**, 489 (1935).

[5] G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 1486 and 2314 (1934).

[6] R. M. Roberts and Kirkwood, *ibid.*, **63**, 1373 (1941).

[7] C. F. Failey, *ibid.*, **54**, 576 (1932).

[8] R. M. Keefer, H. C. Reiber and C. S. Bisson, *ibid.*, **62**, 2951 (1940); **63**, 689 (1941).

[9] C. F. Failey, *ibid.*, **55**, 4374 (1933).

where Z_+ and Z_- are the valences of the ions and K is a constant which is a function of radius of the dipolar ion and the sum of the mean radius of real ions and that of the dipolar ion. Although K varies to some degree from salt to salt, the slope of (log S) against m of salts of different valence types should bear approximately a relation with their valence. The above-mentioned list indicates that the salts are limited to 1-1 and 2-1 types only. *In this present work*, study was extended to 2-2 type salt with 1-1 type salt as reference. Thallium chloride and calcium sulfate were thus chosen and their solubilities determined in presence of glycine ranging from 0-1 molal.

Experimental

As to the chemicals used in this experiment, glycine was from Paul Lewis Laboratories and calcium sulfate from Merck Co. Thallium chloride was prepared from pure thallium sulfate. They were recrystallized twice.

For each solubility determination, a glycine solution of a certain known concentration was prepared. The solution was put in a Pyrex container to which an excess of salt was added. The solutions were shaken mechanically for six hours in a thermostat kept at 25.0 ± 0.1°. It has been found that saturation was reached during the time. The solution was then analyzed gravimetrically.

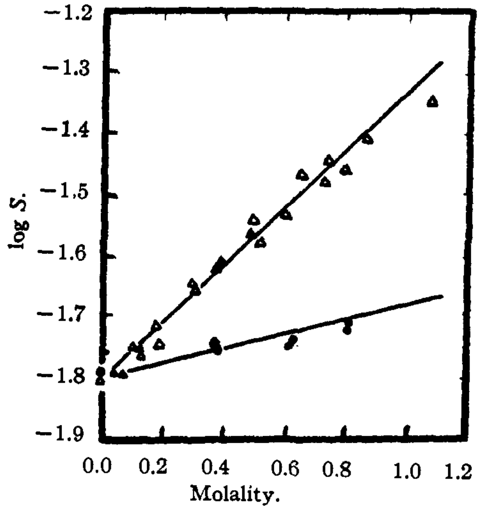

Fig. 1.—△, $CaSO_4$; ⊙, TlCl.

Results

TABLE I

I. Solubility of Thallium Chloride

Glycine, m	Solubility of TlCl (m)	− log S
0.0000	0.01594	1.798
.3619	.01798	1.745
.3849	.01777	1.750
.6060	.01788	1.748
.6169	.01820	1.740
.7978	.01913	1.718
.8008	.01953	1.709

II. Solubility of Calcium Sulfate

	Solubility of $CaSO_4$ (m)	
0.0000	0.01570	1.804
.0418	.01628	1.788
.0608	.01627	1.786
.1260	.01788	1.748
.1282	.01740	1.759
.1880	.01825	1.739
.3089	.02245	1.649
.3778	.02434	1.614
.4835	.02761	1.559
.5048	.02950	1.531
.6514	.03442	1.463
.7423	.03605	1.443
.8634	.03970	1.401
.0873	.04580	1.339
.1046	.01810	1.742
.1809	.01957	1.708
.2996	.02307	1.637
.3929	.02497	1.603
.5246	.02642	1.578
.6012	.02969	1.527
.7225	.03350	1.475
.7990	.03516	1.454

Discussion

The results collected in Table I are plotted in Fig. 1. It is seen that log S bears a linear relationship with m up to 1 m. The slope, (log S/S_0)/m, represents $K(Z_+ \cdot Z_-/2)$ in the equation (1). These are 0.11 and 0.47 for thallium chloride and calcium sulfate, respectively. The constant K calculated from these values comes out to be 0.22 and 0.24 in the respective order. Although values of K in the literature vary somewhat in a considerable range, our values of K for thallium chloride and calcium sulfate (0.22 and 0.24) check very closely to that of thallium chloride by e. m. f. method (0.22) and of sodium chloride by both e. m. f. and f. p. methods (0.24).

Acknowledgment.—The authors are very grateful to Mrs. Dorothy M. Needham of the British Council Cultural Scientific Office for her interest in this work and kindness in supplying the chemicals during the war period while these experiments were performed. They wish also to express their thanks to Professor J. G. Kirkwood for discussing this problem.

Summary

1. The solubilities, S, of thallium chloride and calcium sulfate in glycine ranging from 0–1 m have been determined at 25°.

2. The slope of (log S)/m for thallium chloride and calcium sulfate are 0.11 and 0.47 bearing out an approximate ratio, 1:4, as required by theoretical equation.

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RECEIVED APRIL 1, 1947