

terms, however, this information does not need to be very exact. For the effect of water transfer, for example

$$\int_{\alpha}^{\beta} t_w \left( d \ln a_w - \frac{z_w}{z_s} d \ln a_s \right) = \int_{\alpha}^{\beta} \frac{u_w}{0.018 \sum_j z_j u_j m_j} d \ln a_w \quad (33)$$

The ratio  $u_w/0.018$  will usually be nearly constant. The sum  $\sum_j z_j u_j m_j$  is  $1/\mathcal{F}$  times the conductance of the membrane, which ordinarily is a monotone function of  $\ln a_w$ , so the value of the integral lies between

$$\left( \frac{u_w}{0.018 \sum_j z_j u_j m_j} \right)_{\alpha} \ln \frac{a_w \beta}{a_w \alpha} \text{ and } \left( \frac{u_w}{0.018 \sum_j z_j u_j m_j} \right)_{\beta} \ln \frac{a_w \beta}{a_w \alpha}$$

and is probably not far from their average.

Similarly, in the expression for an ion

$$\int_{\alpha}^{\beta} t_i \left( d \ln a_i - \frac{z_i}{z_s} d \ln a_s \right) = \int_{\alpha}^{\beta} \frac{u_i m_i}{\sum_j z_j u_j m_j} \left( d \ln a_i - \frac{z_i}{z_s} d \ln a_s \right) \quad (34)$$

$u_i$  is nearly constant and  $\sum_j z_j u_j m_j$  is  $1/\mathcal{F}$  times the conductance of the membrane. For ions of the same sign as the membrane,  $m_i$  will usually be small. Except for the case of biionic potential, the standard  $S$  may usually be chosen so that every other  $m_i$  is small. The correcting term vanishes, of course for  $S$  itself.

The Teorell-Meyer and Sievers method of splitting the potential into two Donnan potentials and a Henderson liquid function potential loses the advantage of separating the potential into a main term and deviation terms. The simplifying assumptions which they make would, however, lead to their result by this method also. This is not true of the later treatments involving activity coefficients. Obviously a membrane potential is like an electrode potential in that it cannot be expressed completely in terms of mean activities. However, the important error in these earlier treatments arises from the neglect of water transfer.

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## The Preparation of Monosilicic Acid

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Monosilicic acid has been prepared as a 0.1  $M$  solution at  $pH$  3 by the reaction of crystalline sodium metasilicate with a slurry of the hydrogen form of a cation-exchange resin at about  $0^{\circ}$ . Polymerization occurs at this temperature, even at this optimum  $pH$ . Based on the degree of polymerization of the silicic acid formed, it has been concluded that silicate ions are monomeric in crystalline hydrated metasilicate, but are partially polymerized in an aqueous solution of this salt. In a solution of sodium orthosilicate, the silicate ions are essentially monomeric.

The preparation of monosilicic acid by the hydrolysis of silicon tetrachloride in the presence of silver oxide has been previously reported by Willstätter.<sup>1</sup> Moreover, monosilicic acid has been prepared by Kraut<sup>2</sup> by dissolving sodium metasilicate,  $Na_2SiO_3 \cdot 6H_2O$ , in various acid solutions. These authors have shown that monosilicic acid is most stable in dilute acidic solutions of about  $pH$  2-3.

Based on this background, a new method of preparing a relatively pure solution of this unstable compound has been devised: pulverized, hydrated, crystalline sodium metasilicate is treated with an aqueous slurry of a cation-exchange resin in the hydrogen form at  $0^{\circ}$ .<sup>3</sup> The liberated monosilicic acid is stabilized at  $pH$  3 by a trace of acid in the solution. This method has the advantages that the procedure is simple, and there is obtained a solution of the monomer free from electrolytes, except for the small amount of acid required as a stabilizer.

### Experimental

Materials used were as follows: J. T. Baker C.P. sodium metasilicate,  $Na_2SiO_3 \cdot 9H_2O$  ( $SiO_2$ ,  $19.67 \pm 0.06\%$ ;  $Na_2O$ ,  $20.27 \pm 0.05\%$ , fluoride, less than 1 p.p.m.); the hydrogen form of the cation-exchange resin "Nalcite" HCR (National Aluminate Corp.) was prepared by regenerating the sodium form of the resin with 5% sulfuric acid, followed by

thorough washing with distilled water, air drying, and screening to obtain a fraction between 16 and 24 mesh.

**Determination of Molecular Weight.**—The cryoscopic method was used to determine the degree of polymerization, D.P., of silicic acid solutions, using a Heyden-Hahn cryoscopic thermometer, and an apparatus similar to that used by Adams<sup>4</sup> and Robertson and LaMer.<sup>5</sup> Briefly, the procedure consisted of measuring the freezing point depression of a silicic acid solution, and calculating the D.P. from

$$D.P. = \frac{(1.86)M}{x}$$

where  $x$  is the freezing point depression due to the silicic acid in  $C^{\circ}$ , and  $M$  is the molality of silicic acid in the solution.

The apparatus used to measure freezing point depression consisted of a box 14" square and 21" high, lined with 3" of insulation, and containing an inner steel box 8" square and 16" high. Centered upright in the bottom of this inner box was a stainless steel cylinder 10" deep and 3.25" diameter, open at the top, serving as a housing for a thermos flask. The section of the inner block above the cylinder was fitted with a tray 8" square and 6" deep, through which ran 3 stainless steel pipes, permitting entry of the thermometer, the inlet and sampling tube, and the stirring handle.

To determine the zero reading (or blank), the tray and space around the thermos housing were filled with cracked ice and ice-water. The thermos was partially filled with 200 g. of cracked ice (prepared from distilled water) and 220 ml. of distilled water previously cooled to  $0 \pm 0.2^{\circ}$ . The ice-water mixture was occasionally stirred with an 8" stainless steel rod, having a loop in the lower end. When equilibrium had been reached (about half an hour), the zero reading was taken. The freezing point depression

(1) Richard Willstätter, *et al.*, *Ber.*, **62**, 2027 (1929).

(2) Heinrich Kraut, *ibid.*, **64**, 1709 (1931).

(3) R. K. Iler, U. S. Patent 2,588,389, assigned to E. I. du Pont de Nemours & Co., Inc.

(4) Leason H. Adams, *This Journal*, **37**, 481 (1915).

(5) Campbell Robertson and Victor K. LaMer, *J. Phys. Chem.*, **35**, 1954 (1931).

of the sample was determined as follows: Water in the thermos flask was completely removed through the suction tube extending to the bottom of the thermos, and replaced with a wash solution of 200 ml. of the sample previously adjusted to  $0.0 \pm 0.2^\circ$ . This was stirred, and the liquid was again removed and replaced with another 200 ml. of the sample. The thermometer readings were taken every three to five minutes (occasionally stirring) until a steady temperature had been reached. The degree of polymerization of the silicic acid in the sample was then calculated, after obtaining an analysis for silica in the solution by evaporating a sample of the solution to dryness, igniting, weighing and fuming off the silica with HF, igniting and reweighing. A correction was made for the freezing point depression due to the sulfuric acid, by measuring a blank solution containing an amount of sulfuric acid equivalent to that present in the silicic acid solution.

The accuracy of the method was considered adequate, since check readings over a 24-hour period with 0.100 *M* solution of mannite were all  $0.186 \pm 0.003^\circ$ , corresponding to the known freezing point constant for water.

**The Preparation of Monosilicic Acid from Crystalline Sodium Silicate.**<sup>3</sup>—In a typical preparation of 0.1 *M* solution of monosilicic acid (0.6% SiO<sub>2</sub>), 200 g. of air-dried resin was slurried in 1 liter of 0.0050 *M* H<sub>2</sub>SO<sub>4</sub> in a Pyrex beaker, cooled to 2°, and vigorously agitated with a high speed, air-driven stirrer, and 30.6 g. of pulverized crystalline Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O was added over about 15 minutes at a uniform rate. The pH of the mixture (as determined by a Beckman Model G pH meter) was never allowed to exceed 3.5. Filtration gave a clear solution having a pH of 2.6. The degree of polymerization of the silicic acid so obtained was about 1.1.

The pH of the solution could be adjusted, when desired, by the addition of solid sodium metasilicate, or sulfuric acid, in either case with vigorous agitation.

**The Preparation of Silicic Acid from an Aqueous Solution of Sodium Silicate.**<sup>3</sup>—Several attempts were made to prepare monosilicic acid from aqueous solutions of sodium metasilicate, but in no case was a degree of polymerization lower than 1.5 obtained. Since the solid hydrated sodium metasilicate gave essentially monomer, it is evident that some polymerization of metasilicate ions to disilicate must occur in aqueous solution.

The details for the preparation of silicic acid from aqueous sodium metasilicate solutions are: 400 ml. of 0.20 *M* Na<sub>2</sub>SiO<sub>3</sub> solution was added through a capillary tube to a slurry of 400 ml. of 0.01 *M* H<sub>2</sub>SO<sub>4</sub> and 150 g. of exchange resin. During the reaction, the temperature was maintained at 2°, and the pH below 2.5. After addition of silicate solution, the slurry was filtered and the degree of polymerization of the silicic acid found to be 1.5.

**Preparation of Monosilicic Acid from Sodium Orthosilicate.**<sup>3</sup>—Monosilicic acid, having a degree of polymerization of about 1.1, has been prepared from sodium orthosilicate either by dissolving crystalline sodium orthosilicate in a slurry of ion-exchange resin in dilute H<sub>2</sub>SO<sub>4</sub>, or by adding sodium orthosilicate solution through a capillary tube.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY AT CLARK UNIVERSITY]

## Stability of Metal Chelates. VI. Nitrilotricarboxylic Acids

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The acid dissociation constants of nitrilodiaceticpropionic acid, nitrilodipropionicacetic acid, nitrilotripropionic acid, and the stabilities of the corresponding chelates formed with Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Zn<sup>+2</sup>, Cd<sup>+2</sup> and Mg<sup>+2</sup> ions were studied at 30° in 0.1 *M* aqueous potassium chloride solution. Relationships are given for calculation of the chelate stability constants by the Bjerrum method. Acid dissociation constants and equilibrium constants for the 1:1 chelates are reported, and the results are interpreted in the light of certain factors recognized as having a bearing on the stability of chelate compounds.

Although the metal chelating tendencies of nitrilotriacetic acid (NTA) have been extensively investigated,<sup>2</sup> little attention has been paid to the corresponding behavior of nitrilotripropionic and the mixed propionicacetic acids. The only propionic acid derivative previously studied is nitrilodiaceticpropionic acid, for which Schwarzenbach, *et al.*,<sup>2a</sup> have reported interactions with alkaline earth ions. An investigation of metal ion equilibria of all the possible combinations resulting from the substitution of acetate and propionate groups on a basic nitrogen atom would make possible a systematic study of the relative stabilities of 5- and 6-rings derived from aliphatic amino acids. In the present paper, the chelating tendencies of nitrilotripropionic acid (NTP), nitrilodipropionicacetic acid (NDPA), and of nitrilodiaceticpropionic acid (NDAP) toward a representative group of metal ions is described. Taken with the work of Schwarzenbach, *et al.*,<sup>2</sup> on nitrilotriacetic acid, the investigation completes the series involving all combinations from the tripropionic to the triacetic acid.

(1) F. C. Bersworth Postdoctoral Fellow, Clark University.

(2) (a) G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949); (b) G. Schwarzenbach and E. Freitag, *ibid.*, **34**, 1492 (1951).

### Experimental

**Apparatus and Procedure.**—The experimental method and conditions employed in this investigation are similar to those described in a previous publication.<sup>3</sup> The amino acids were titrated at 30° with standard 0.1 *M* KOH solution both in the absence of and in the presence of metal ions. Potentiometric measurements of pH were made with a "calibrated" cell consisting of a shielded glass electrode *vs.* a calomel electrode measured by means of a Beckman Model G pH meter. The calibration was carried out with a cell consisting of a number of platinum (hydrogen) electrodes measured against a number of Ag-AgCl electrodes with a Leeds and Northrup type K potentiometer. This calibration was repeated a number of times with actual experimental runs and a correction curve of pH *vs.* pH meter reading was set up for the normal runs made with the glass-calomel cell only. This procedure had the advantage of allowing rapid determinations equivalent to the hydrogen Ag-AgCl measurements within the limits of reading of the pH meter scale. The experimental solution was regulated at an ionic strength of 0.100 by maintaining a large excess of potassium chloride over all other ionic species present. An inert, CO<sub>2</sub>-free atmosphere was employed throughout the titrations. The pH values were converted to hydrogen ion concentration by the assumption that the value of  $\gamma_{\pm} = 0.78$  for 0.1 *M* KCl obtained by Shedlovsky and MacInnes<sup>4</sup> to hold for the experimental solutions. The concentration of amino

(3) S. Chaberek, Jr., and A. E. Martell, *THIS JOURNAL*, **74**, 5052 (1952).

(4) T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).