TRIALKYLSILYL SULFATES

Sir:

Treatment of a concentrated sulfuric acid solution of a hexa-alkyldisiloxane with ammonium chloride or fluoride gives the trialkylchlorosilane or the corresponding fluoro compound.[1] During a study of the mechanism of this reaction we have obtained two trialkylsilyl sulfates, the first examples of sulfuric acid esters of silanols.

The trialkylsilyl sulfates are obtained by the action of fuming sulfuric acid on hexa-alkyldisiloxanes. Concentrated sulfuric acid

$$R_3SiOSiR_3 \xrightarrow{SO_3} (R_3Si)_2SO_4$$

gives a much lower yield.

Hexamethyldisiloxane, 100 g., 0.62 mole, was added slowly with cooling and vigorous agitation to 85 g. of fuming sulfuric acid containing 20% SO_3. The cold solution was extracted with six 100-cc. portions of dry pentane. After removal of the solvent under reduced pressure, the liquid residue changed on cooling to a mass of white crystals. Treatment of the sulfuric acid layer with water gave a recovery of 26% of the disiloxane used. The filtered sulfate, m. p. 56–58°, weighed 76 g., 69% yield based on unrecovered disiloxane. The sulfate must be handled in a dry atmosphere as it fumes vigorously in ordinary air. Treatment with water gave hexamethyldisiloxane. Titration of the sulfate with standard alkali gave a neutral equivalent of 117; calcd. 121. Carbon was determined by wet combustion with dichromate, sulfuric acid and silver chromate.

Anal. Calcd. for $C_6H_{18}Si_2SO_4$: Si, 23.1; SO_4, 39.6; C, 29.6. Found: Si, 22.7; SO_4, 40.4; C, 29.7.

Triethylsilyl sulfate, b. p. 170° at 12 mm., $n^{20}\text{D}$ 1.4442, was prepared similarly. With water it gave the original disiloxane and sulfuric acid.

Anal. Calcd. for $C_{12}H_{30}Si_2SO_4$: Si, 17.2; SO_4, 29.4; neut. equiv., 163. Found: Si, 17.2; SO_4, 29.5; neut. equiv., 166.

We thank R. N. Walter of this Laboratory for the analyses reported in this Communication.

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[1] *Cf.* Flood, THIS JOURNAL, **55**, 1735 (1933).

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DETERMINATION OF THE ACTIVITIES OF SEVERAL COEXISTING IONS BY THE GIBBS-DONNAN EQUILIBRIUM WITHOUT THE USE OF SPECIFIC ELECTRODES

Sir:

The electrometric determination of the activities of ions for which specific electrodes do not exist has recently become possible in solutions of single electrolytes by the use of "membrane electrodes."[1,2] Heretofore, however, the activities of several coexisting species of ions of the same sign in solution could be determined unequivocally only if specific electrodes, which are lacking for many common ions, could be used. Attempts to overcome this difficulty indirectly have been only indifferently successful.

I should like to point out that the Gibbs–Donnan membrane equilibrium principle permits a solution of this problem in a general manner by consideration of the ion distribution *ann* of the membrane potential.

Membranes of extreme ionic selectivity[1,2,3] make the new method widely applicable, permitting the measurement of membrane equilibria under particularly favorable conditions with speed and accuracy.[2,4,5] It is however not exclusively restricted to these simple conditions.

A solution I contains the anions R^- and NO_3^-, and the cations K^+, Na^+ and NH_4^+, the activities of which $(a_{K^+})_I$, $(a_{Na^+})_I$ and $(a_{NH_4^+})_I$ have to be determined. A "permselective" membrane permeable to all cations and impermeable to all anions[1,2,3,5] separates solution I from a KCl solution II of known concentration. Solution II is isoösmotic with I, or is made isoösmotic by the addition of non-diffusible non-electrolyte.[6] The volume of I is made infinitely larger than that of II so that the composition of I is not changed significantly after equilibration with II.

After the system is equilibrated the membrane potential E is measured and solution II analyzed. The final state of the system is

$$\overset{\text{I}}{[K^+]_I[Na^+]_I[NH_4^+]_I[R^-]_I[NO_3^-]_I} \Big\| \overset{\text{II}}{[K^+]_{II}[Na^+]_{II}[NH_4^+]_{II}[Cl^-]_{II}}$$

The activities of the cations in II $(a_{K^+})_{II}$, $(a_{Na^+})_{II}$ and $(a_{NH_4^+})_{II}$ are calculated from the known analytical concentrations according to the Debye–Hückel theory.

The Gibbs–Donnan theorem postulates for the ion distribution

$$\frac{(a_{K^+})_I}{(a_{K^+})_{II}} = \frac{(a_{Na^+})_I}{(a_{Na^+})_{II}} = \frac{(a_{NH_4^+})_I}{(a_{NH_4^+})_{II}} \qquad (1)$$

and for the membrane potential

$$E = \frac{RT}{F}\ln\frac{(a_{K^+})_I}{(a_{K^+})_{II}} = \frac{RT}{F}\ln\frac{(a_{Na^+})_I}{(a_{Na^+})_{II}} = \\ = \frac{RT}{F}\ln\frac{(a_{NH_4^+})_I}{(a_{NH_4^+})_{II}} \qquad (2)$$

The unknown activities of the cations in solution I $(a_{K^+})_I$, $(a_{Na^+})_I$ and $(a_{NH_4^+})_I$ can be evaluated from equation (2).

The new method should be of particular interest in colloid chemistry and physiology.

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[1] K. Sollner, THIS JOURNAL, **65**, 2260 (1943).

[2] H. Gregor, Ph.D. Thesis, Minneapolis, 1945.

[3] K. Sollner, *J. Phys. Chem.*, **49**, 47, 171 (1945).

[4] K. Sollner, *ibid.*, **40**, 265 (1945).

[5] K. Sollner and H. Gregor, THIS JOURNAL, **67**, 346 (1945).

[6] This precaution is actually unnecessary; cation exchange equilibrium is reached without significant osmotic water movement.[2]