up and a white precipitate formed. When addition was complete, the green mixture was poured onto ice and the product was collected and washed with water. The product was soluble in 10% sodium hydroxide and in 10% sodium bicarbonate. Recrystallization from acetone–water yielded 0.145 g. (51%) of colorless III, m.p. 301–305° dec.

(uncor.); infrared spectrum: C=O, 5.72(s), 5.92(s); C=C, 6.20(s) μ.

Anal. Calcd. for $C_{10}H_4Cl_2O_4$: C, 46.4; H, 1.6; Cl, 27.4. Found: C, 46.7; H, 1.6; Cl, 27.1.

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COMMUNICATIONS TO THE EDITOR

THE FUOSS–ONSAGER CONDUCTANCE EQUATION AT HIGH CONCENTRATIONS

Sir:

Fuoss and Onsager,[1,2] in presenting their theory of the conductance of free ions, were careful to point out that it is applicable to dilute solutions below a concentration where the value of κa is less than 0.2. They have demonstrated the validity of the theory below this concentration but, at this writing, the behavior of their conductance equation has not been investigated at higher concentrations. Mercier and Kraus[3] have measured the conductance of dilute solutions of tetramethylammonium picrate up to about $3 \times 10^{-3} N$ in dioxane–water mixtures from pure water up to 70% dioxane. An analysis by Fuoss and Kraus[4] indicates that this electrolyte is completely dissociated over this entire range of mixtures. Accascina, prior to the advent of the Fuoss–Onsager theory, measured the conductance of Me_4NPi in a 55% dioxane–water mixture to a concentration of 0.226 N. Subsequently, Kay analyzed the data using an IBM computer[5] and obtained 33.39 and 6.14 $\times 10^{-8}$ for Λ_0 and a, respectively. The results are shown graphically in Fig. 1.
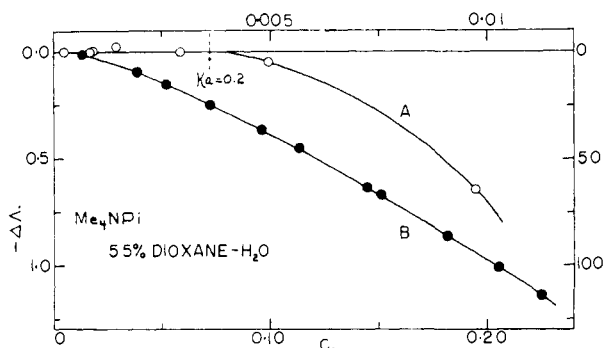

Fig. 1.—Deviation between observed and calculated equivalent conductances· A, dilute range, coördinates left and above; B, entire range, coördinates right and below.

In plot A of this figure are shown values of $\Delta\Lambda = \Lambda_{obs} - \Lambda_{calc}$ plotted as functions of C for concentrations up to 0.01 N. It will be noted that the calculated values of Λ closely approximate

(1) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

(2) R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).

(3) P. L. Mercier and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **41**, 1033 (1955).

(4) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

(5) Program No. 004 at the Brown Computing Center

those observed at concentrations below 3×10^{-3} N. The average deviation between the terms is 0.015 Λ-unit or 0.05%. At concentrations above 4×10^{-3} N, calculated values begin to diverge from the experimental ones. The concentration at which $\kappa a = 0.2$ is 3.6×10^{-3} N. Thus, deviations are within experimental error below this concentration but increase markedly at concentrations much beyond this limit. Plot B of Fig. 1 covers the entire concentration range up to 0.226 N. It can be seen that up to about 0.01 N the differences are not large enough to show on the plot. At higher concentrations, the difference increases, reaching very large values at high concentration. At the highest concentration, the calculated conductance is almost seven times the measured value.

The results of this analysis show rather convincingly that the theory reproduces the experimental values closely over the concentration range in which the approximations made in deriving the theory are justified, but, as expected, at higher concentrations the deviations become steadily greater than the experimental error. The experimental data will be presented elsewhere in due course.

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RELATIVE ARYL RADICAL AFFINITIES OF MONOMERS

Sir:

Evidence[1,2,3] has been presented that the mechanism of the Meerwein reaction involves addition of an aryl radical to a monomer followed by rapid halogen transfer from cupric chloride or from a higher chloro-complex. Thus, competitive Meerwein reactions might provide the means for measuring relative rate constants for the addition of aryl radicals to olefins. This possibility has now been realized.

Acrylonitrile (A) and methacrylonitrile (MA) were selected as reference monomers. In a typical experiment 0.4 mole of both methyl acrylate and acrylonitrile were allowed to compete for the phenyl

(1) S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); THIS JOURNAL, **80**, 1904 (1958).

(2) S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1070 (1957).

(3) J. K. Kochi, THIS JOURNAL, **79**, 2942 (1957).