COMMUNICATIONS TO THE EDITOR

CHAIN ELECTROLYTES[1]

Sir:

We are studying polyelectrolytes in which chain atoms carry ionic charges. Typical is the polyelectrolyte (I) formed by the addition of methyl bromide to the polyester obtained from methyldiethanolamine and succinic anhydride

(I) $HO[CO(CH_2)_2COO(CH_2)_2N^+Me_2(CH_2)_2O]_nH—nBr'$

Theoretical bromide for *n* infinite is 26.99%; two different preparations gave 22.73 and 23.38%, indicating incomplete addition of methyl bromide. End-group titrations gave molecular weights of 3515 and 2720. The salt hydrolyzes in water but is stable in methanol.

At 1.2 g./100 cc. in methanol, (I) has a reduced viscosity of 0.091. For comparison, polyvinylpyridine with molecular weight 80,000 has an intrinsic viscosity of only 0.15. High viscosities thus seem to be characteristic of polyelectrolytes[2] regardless of the location of the charges.

Conductance curves in methanol are shown in Fig. 1, where concentration is stoichiometric normality of bromide. The marked curvature indicates a high degree of association of counter ions to the polycations. Ordinary electrolytes, such as the addition product (II) of methyl bromide to methyldiethanolamine, are only slightly associated in solvents with high dielectric constant, as shown by the approach to the Onsager limiting slope. In our polysalts, ten positive charges are constrained to remain near each other, regardless of dilution. A bromide ion has a potential energy large compared to kT in the resulting field and therefore at finite concentrations, a certain fraction of bromide ions accompany the polycations. The polycations thus act like droplets of concentrated solution within the liquid, regardless of total dilution. The polycation configuration will, however, depend on dilution: with decreasing total concentration, probability of escape of bromide ions from the field of the polycation will increase, and intramolecular mutual repulsion between unpaired charges on chain nitrogens will then cause the chain to uncoil.

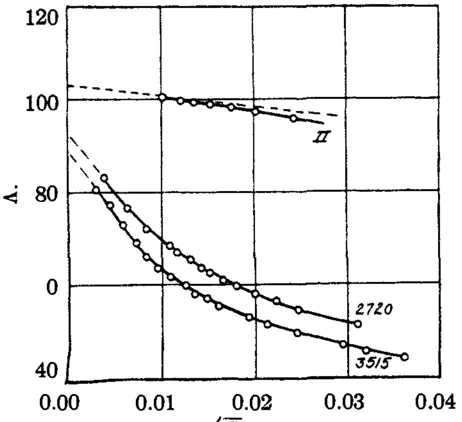

Fig. 1.—Conductance of salts I and II in methanol.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT
DAVID EDELSON
RAYMOND M. FUOSS

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[1] Office of Naval Research. ProjectNR054-002.

[2] R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, **246** (**1948**).

ULTRAVIOLET ABSORPTION BANDS OF IODINE IN AROMATIC HYDROCARBONS

Sir:

In the course of an investigation of the nature of the solvent–solute interaction in solutions of iodine now in progress, new evidence has been found for the presence of addition compounds of iodine and the solvent molecule. We find that the absorption spectrum of the violet-red solution of iodine in benzene shows in addition to the well known absorption maximum at 5000 Å. with a molar extinction coefficient of 1010, an absorption maximum in the ultraviolet region at 2970 Å. having a molar extinction coefficient (based on the iodine concentration) of 9600. This new absorption peak does not appear in solutions of iodine in hexane and carbon tetrachloride which are a pure violet with absorption peaks at 5200 Å. in the visible region. The evidence therefore points to the presence of an iodine–benzene complex. Preliminary measurements show that the height of the absorption peak at 2970 Å. is directly proportional to both the iodine concentration and the benzene concentration, indicating that the addition compound consists of one molecule of iodine bound to one molecule of benzene.

A possible explanation for the presence of such a complex appears to lie in an acid–base interaction in the electron donor–acceptor sense such as we see in the union of I^-, the base, with I_2, the acid, to form I_3^-. Evidence of basic character in benzene is its union with boron trifluoride, boron trichloride and with concentrated sulfuric acid. Additional evidence in support of this hypothesis is to be found in the recent work of Fairbrother,[1] who reports that iodine has an abnormally high dielectric polarization in such solvents as benzene, *p*-xylene, dioxane and di-isobutylene. If this basic character of benzene is also responsible for its union with iodine, then the substitution of methyl groups should increase basic strength and ability to interact with iodine. This is borne

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[1] F. Fairbrother, *Nature*, **160**, 87 (1947).