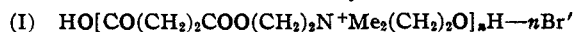


## COMMUNICATIONS TO THE EDITOR

CHAIN ELECTROLYTES<sup>1</sup>

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



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<sup>2</sup> 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 indi-

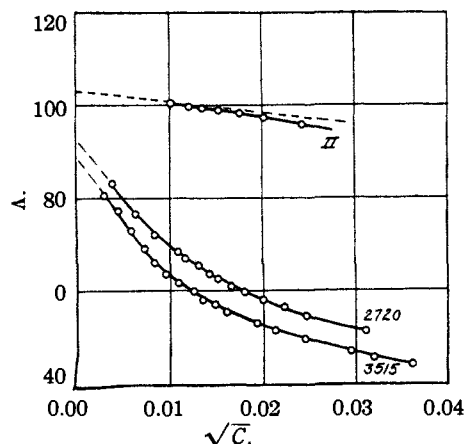


Fig. 1.—Conductance of salts I and II in methanol.

icates 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 concen-

trated 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.

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DAVID EDELSON  
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RECEIVED JULY 19, 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  $\text{I}^-$ , the base, with  $\text{I}_2$ , the acid, to form  $\text{I}_3^-$ . 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,<sup>1</sup> 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

(1) Office of Naval Research, Project NR054-002.

(2) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **8**, 246 (1948).

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

out by the fact that a simple visual examination of iodine solutions of equal concentration in benzene, toluene, *o*-xylene, mesitylene and  $\alpha$ -methylnaphthalene shows that the color shifts stepwise in that order ending with a brown solution. Preliminary measurements of the absorption spectra of these iodine solutions show an absorption band in the ultraviolet region similar to that of benzene.

This work is being continued and a complete report of the results will be given in a paper soon to be submitted for publication.

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HANS A. BENESI  
JOEL H. HILDEBRAND

RECEIVED JULY 15, 1948

### $\beta$ -PELTATIN, A NEW COMPONENT OF PODOPHYLLIN

Sir:

The fractionation of the drug podophyllin by chromatographic adsorption on alumina has yielded, beside podophyllotoxin and  $\alpha$ -peltatin,<sup>1</sup> a new crystalline substance in about 4% yield for which the name  $\beta$ -peltatin is proposed. The new compound possesses about the same high necrotizing activity<sup>2</sup> for mouse sarcoma 37 as  $\alpha$ -peltatin.

$\beta$ -Peltatin crystallizes from alcohol in colorless, transparent prisms, m. p. 231.1–238.0° (shrinks at 225.5°) cor.;  $[\alpha]^{26}_D - 115^\circ$  ( $c$ , 1.009, absolute alcohol). *Anal.*<sup>3</sup> Calcd. for  $C_{22}H_{22}O_8$ : C, 63.75; H, 5.35. Found: C, 64.0; H, 5.6. Calcd. for three methoxyl groups: 22.5; found, 22.2. Molecular weight values (Rast) for derivatives of both  $\alpha$ - and  $\beta$ -peltatin agree with the formula  $C_{22}H_{22}O_8$  and indicate that the peltatins are thus isomeric with podophyllotoxin.<sup>4</sup>  $\alpha$ -Peltatin has one less methoxyl group than  $\beta$ -peltatin and podophyllotoxin.

Beside the methoxyl content,  $\alpha$ - and  $\beta$ -peltatin differ in their color reactions with sulfuric acid and in the properties of their derivatives. With concentrated sulfuric acid, both peltatins give an immediate yellow color, rapidly turning reddish brown with  $\alpha$ -peltatin and green with  $\beta$ -peltatin; the final color with both peltatins is red. A series of derivatives of the peltatins has been prepared and will be reported at a later date.

Structural and biological studies with  $\beta$ -peltatin are in progress.

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NATIONAL INSTITUTE OF HEALTH  
U. S. PUBLIC HEALTH SERVICE JONATHAN L. HARTWELL  
BETHESDA, MARYLAND WENDELL E. DETTY

RECEIVED JULY 22, 1948

(1) J. L. Hartwell, *THIS JOURNAL*, **69**, 2918 (1947).

(2) Unpublished results of Joseph Leiter and Faith Jouvenal.

(3) By Mrs. M. M. Ledyard and Mrs. Evelyn Peake National Institute of Health.

(4) W. Borsche and J. Niemann, *Ber.*, **66**, 1633 (1932); E. Späth, F. Wessely and E. Nadler, *ibid.*, **66**, 125 (1933).

### THE CRYSTALLINE TRIHYDROCHLORIDES OF STREPTOMYCIN AND MANNOSIDOSTREPTOMYCIN

Sir:

The preparation of the crystalline reineckate, sulfate,<sup>1</sup> helianthate,<sup>2</sup> and the calcium chloride double salt<sup>2</sup> of streptomycin and the reineckate of mannosidostreptomycin<sup>3</sup> has been reported. To date, there has been no published information on the crystallization of a simple mineral acid salt of either of these antibiotics. We now wish to report that, starting with relatively pure material, we have obtained the trihydrochlorides of streptomycin and mannosidostreptomycin in the crystalline state from methanol solution.

The streptomycin trihydrochloride crystallizes with two molecules of water of crystallization as monoclinic prisms showing birefringence. The crystalline material was shown to be a single substance by a modification of the Craig counter-current distribution technique<sup>4</sup> and thus to be free of mannosidostreptomycin. On heating on the hot-stage, the dihydrate decomposes gradually without melting. When the trihydrochloride was dried at 55° *in vacuo*, it had the following analytical composition: C, 34.86; H, 6.36; Cl, 14.25 (Calcd. for  $C_{21}H_{39}N_7O_{12} \cdot 3HCl \cdot 2H_2O$ : C, 34.54; H, 6.36; Cl, 14.57). After drying at 100° *in vacuo*, the anhydrous material showed  $[\alpha]^{26}_D - 86.1^\circ$  (1.0% in water) and the following analytical data were obtained: C, 36.27; H, 6.14; N, 14.29; Cl, 15.69 (Calcd. for  $C_{21}H_{39}N_7O_{12} \cdot 3HCl$ : C, 36.50; H, 6.13; N, 14.19; Cl, 15.40).

When assayed with *K. pneumoniae* in a broth-dilution test,<sup>5</sup> the trihydrochloride dihydrate had a potency of 820 units/mg. and on this basis the anhydrous material would have an activity of 891 units/mg.<sup>6</sup>

The trihydrochloride of mannosidostreptomycin crystallizes in the form of hexagonal plates which are isotropic. By means of the counter-current distribution method,<sup>4</sup> this material was also shown to be a single entity and to be free of streptomycin.

After drying at 55° *in vacuo*, the trihydrochloride was found to have the following analysis: C, 36.45; H, 6.26; Cl, 12.14 (Calcd. for  $C_{27}H_{49}N_7O_{17} \cdot 3HCl \cdot 2H_2O$ : C, 36.47; H, 6.35; Cl, 11.96). When dried at 100° *in vacuo*, the anhydrous material showed  $[\alpha]^{26}_D - 54.1^\circ$  (1.0% in water)

(1) J. Fried and O. Wintersteiner, *Science*, **104**, 273 (1946).

(2) R. L. Peck, N. G. Brink, F. A. Kuehl, Jr., E. H. Flynn, A. Walti and K. Folkers, *THIS JOURNAL*, **67**, 1866 (1945).

(3) J. Fried and E. Titus, *J. Biol. Chem.*, **168**, 391 (1947).

(4) A modification of the counter-current distribution described by Titus and Fried (*J. Biol. Chem.*, **174**, 57 (1948)) has been developed by our colleagues Drs. Plaut and McCormack which eliminates the appearance of the tautomers of the two streptomycins in the Craig diagram.

(5) R. Donovan, D. Hamre, F. Kavanagh and G. Rake, *J. Bact.*, **50**, 623 (1945).

(6) Based on the F. D. A. working standard. Spectrophotometric assays based on a maltol method, similar to that published by G. F. Mueller (*THIS JOURNAL*, **69**, 195 (1947)), have confirmed these microbiological results.