aqueous layer was extracted with 700 ml. of chloroform and the chloroform extracts were combined and washed with 1350 ml. of water. The chloroform solution was concentrated under reduced pressure to a volume of 450 ml. The mixture was cooled to 0–5°. To the slurry was added slowly 3150 ml. of petroleum ether, the temperature being maintained at 0–5°. After stirring for one hour, the ketol III was collected on a filter, washed with a mixture of petroleum ether and chloroform (4:1), finally with petroleum ether and dried in air at 60°; yield 83.5 g. (90.7%), m.p. 229–231°, $[\alpha]^{25}\text{D}$ 79° (*c* 1, acetone).

Essentially pure material was obtained by stirring the product with a mixture of 210 ml. of isopropyl alcohol and 210 ml. of absolute ether at 20–25° for 30 minutes and then at 0–5° for 30 minutes. The purified ketol was collected and washed with 82 ml. of absolute ether; weight 73.8 g. (recovery 88.4%, over-all, 80%), m.p. 232.5–234.5°, $[\alpha]^{25}\text{D}$ 82.3° (*c* 1, acetone).

Pregnane-17α,21-diol-3,11,21-trione 21-Acetate (III) from IV.—Ten grams (0.025 mole) of the isomeric cyanopregnane[6] IV (m.p. 132–134°) oxidized according to the above procedure, yielded 7 g. (69%) of III, m.p. 232–234°. The ketol was isolated from a mixture of petroleum ether and chloroform with ratio of 3 to 1 instead of 7 to 1, thus the purification step was unnecessary.

Pregnane-3α,17α,21-triol-11,20-dione 3,21-Diacetate (VI) from V.—From 11.1 g. (0.052 mole) of Δ^{17}-20-cyanopregnene-3α,21-diol-11-one diacetate (V)[3] there was obtained 8.43 g. (74.6%) of the corresponding ketol VI; m.p. 237–238°. No melting point depression was observed when mixed with an authentic sample of VI.

Pregnane-3α,17α,21-triol-11,20-dione 21-Acetate (VIII).—Five grams of Δ^{17}-20-cyanopregnene-3α,21-diol-11-one 21-acetate (VII)[1] was treated with potassium permanganate in the manner described previously. The triol 21-acetate VIII was obtained in 75% yield; m.p. 222–226.5°. Inasmuch as the melting point of VIII is not depressed by admixture with III, it was necessary to convert it into the 3,21-diacetate, m.p. 232–235°, by treatment with acetic anhydride in pyridine (93% yield). The structure of the resulting 3,21-diacetate was confirmed by mixed melting point determinations with samples of III and VI. As expected, admixture with III showed depression while the mixture of diacetate with VI showed no depression.

Oxidation of Δ^{17}-20-Cyanopregnene-3α,21-diol-11-one (IX).—Five grams of IX was treated with potassium permanganate in the usual manner. An oil was obtained which was acetylated to give a semi-crystalline product from which no 3α,21-diol diacetate was isolated.

Pregnane-11(β),17(α),21-triol-3,20-dione 21-Acetate (XI).—From 3.12 g. of Δ^{17}-20-cyanopregnene-11(β),21-diol-3-one 21-acetate[7] (X) there was obtained 2.28 g. of crude XI; m.p. 198–205°. Recrystallization of the crude material from acetone–petroleum ether gave 1.24 g. (39%) of XI; m.p. 218–220°—no melting point depression with an authentic sample of XI.

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(7) N. L. Wendler, R. P. Graber, R. E. Jones and M. Tishler, THIS JOURNAL, **74**, 3630 (1952).

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[CONTRIBUTION NO. 1239 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Bolaform Electrolytes. IV. Conductance of α,ω-Bispyridinium Polymethylene Bromides and β,β'-Bisquaternary Substituted Diethyl Ethers in Methanol

BY JAMES C. NICHOL[1] AND RAYMOND M. FUOSS

RECEIVED JULY 26, 1954

The conductances of the following bolaform electrolytes have been measured in methanol at 25°: 1,2-ethane-N,N'-bispyridinium dibromide (I), 1,4-butane-N,N'-bispyridinium dibromide (II), 1,10-decane-N,N'-bispyridinium dibromide (III), diethyl ether bis-β,β'-trimethylammonium diiodide (IV), diethyl ether β-trimethylammonium, β'-methyldiethylammonium diiodide (V), diethyl ether bis-β-methyldiethylammonium diiodide (VI), diethyl ether bis-β-trimethylammonium dimethosulfate (VII) and diethyl ether bis-β-pyridinium dichloride (VIII) over the approximate concentration range 0.05×10^{-3} to 1.5×10^{-3} *N*. The dependence of limiting conductances, reciprocal association constants and intercharge distances between the cationic sites on chain length and structure of end groups is discussed.

The first three papers of this series[2-4] describe conductance studies of 2-1 salts whose cations were made up of a chain of atoms terminated at each end by a trimethylammonium group. In some cases, the chain consisted solely of methylene groups while in others ester or amide linkages were present. Recently, some α,ω-bispyridinium polymethylene salts were described by Dr. J. Hartwell[5] of the National Cancer Institute; these are similar to the salts prepared by Chu but differ in having terminal pyridinium groups rather than alkyl-substituted ammonium groups. Furthermore, Dr. J. Fakstorp[6] of Pharmacia Laboratories (Copenhagen) reported the preparation of a series of salts in which the cations were obtained by substituting various quaternary groups in the terminal β,β'-positions of diethyl ether. These compounds are similar to those of Edelson and Eisenberg, differing in the replacement of ester or amide linkages by an ether linkage in the middle of the cation. Through the kindness of Dr. Hartwell and of Dr. Fakstorp, we received samples of a number of these new salts, which made it possible for us to compare their electrical properties with those of the previously investigated compounds of related structure. This comparison is based on the conductance at 25° of dilute solutions of the salts in absolute methanol.

Experimental

Materials.—The compounds provided by Dr. Hartwell consisted of 1,2-ethane-N,N'-bispyridinium dibromide (I), 1,4-butane-N,N'-bispyridinium dibromide (II) and 1,10-decane-N,N'-bispyridinium dibromide (III). Dr. Fakstorp's compounds included diethyl ether bis-β,β'-trimethylammonium diiodide (IV), diethyl ether β-trimethylammonium, β'-methyldiethylammonium diiodide (V), diethyl ether bis-β-methyldiethylammonium diiodide (VI), diethyl ether bis-β-trimethylammonium dimethosulfate (VII) and diethyl ether bis-β-pyridinium dichloride (VIII). For reference in later discussion, the structural formulas of these compounds, together with code symbols, are given in Table A. The symbol "Py^+" means the group N^+—.

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[1] On leave of absence from Willamette University, Salem, Oregon. Grateful acknowledgment is made to the California Research Corporation for a research fellowship for the academic year 1953–1954.

(2) R. M. Fuoss and D. Edelson, THIS JOURNAL, **73**, 269 (1951).

(3) R. M. Fuoss and V. F. H. Chu, *ibid.*, **73**, 949 (1951).

(4) H. Eisenberg and R. M. Fuoss, *ibid.*, **75**, 2914 (1953).

(5) J. L. Hartwell and M. A. Pogorelskin, *ibid.*, **72**, 2040 (1950).

(6) J. Fakstorp, J. Christiansen and J. G. A. Pedersen, *Acta Chem. Scand.*, **7**, 134 (1953).

TABLE A

STRUCTURES OF ELECTROLYTES

No.	Formula
I	$Br'[Py^+(CH_2)_2Py^+]Br'$
II	$Br'[Py^+(CH_2)_4Py^+]Br'$
III	$Br'[Py^+(CH_2)_{10}Py^+]Br'$
IV	$I'[Me_3N^+CH_2CH_2OCH_2CH_2N^+Me_3]I'$
V	$I'[Me_3N^+CH_2CH_2OCH_2CH_2N^+MeEt_2]I'$
VI	$I'[Et_2MeN^+CH_2CH_2OCH_2CH_2N^+MeEt_2]I'$
VII	$MeSO_4'[Me_3N^+CH_2CH_2OCH_2CH_2N^+Me_3]MeSO_4'$
VIII	$Cl'[Py^+CH_2CH_2OCH_2CH_2Py^+]Cl'$

Conductance determinations were carried out both on the samples as received and after recrystallization from the recommended solvents.[5,6] The conductance changes observed as a result of recrystallization varied from 0.0 to 0.5%. Compound VIII proved difficult to crystallize and the results reported are for the compound as received. All the compounds dissolved without difficulty in methanol except IV, whose solubility did not exceed 3×10^{-3} N.

Methanol was purified as described previously[8], and a specific conductance of less than 5×10^{-8} was readily obtained.

Technique.—All solutions were made up by weight and the density of methanol at 25° (0.7864) was used to compute volume concentrations c in equivalents per liter. For each sample of material, both recrystallized and unrecrystallized, at least one concentration run and one dilution run was carried out (*i.e.*, four runs in all). This is a much more rigorous check on the experimental procedure than that in which either duplicate concentration or dilution runs are made.

The conductance bridge used has been described.[4] The conductance cells were of the type described by Nichol and Fuoss,[7] in which the electrodes (bright platinum) are concentric cylinders with the lead to the outer electrode being a platinum tube which acts as an electrical shield for the lead to the inner electrode. This arrangement eliminates stray electrical paths and reduces frequency dependence solely to polarization at the electrodes. The electrode assemblies were mounted in Teflon plugs turned to a standard taper to fit the electrode vessels, as shown in Fig. 1. Cell constants (0.05742 and 0.03664) were determined by comparison with a cell (k = 2.0146) which was calibrated as described previously.[4]

The design of the electrode vessel permitted rapid and thorough mixing of the liquid in the electrode chamber with the bulk of the solution by swirling. This feature was quite helpful in eliminating errors due to adsorption (which was especially marked with I and absent with VII, the methosulfate). In the dilute range, cell resistance initially increased on standing by as much as 0.1% per minute as the liquid between the electrodes became depleted of electrolyte due to adsorption of ions on the platinum. On swirling (the cell remaining under the thermostat oil, of course), the resistance dropped as fresh solution was pumped into the electrode chamber. Adsorption in concentration runs was distinctly more noticeable than desorption in dilution runs. The excellent agreement between concentration and dilution runs on the same salt is convincing evidence that sorption errors were eliminated, because the errors work in opposite directions in the two methods of changing concentration: neglect of adsorption produces a fictitious maximum in the Λ *vs.* $c^{1/2}$ curve in concentration runs while desorption in dilution runs gives a Λ *vs.* $c^{1/2}$ curve which becomes sharply concave-up in the dilute region.

Initially, polarization errors were eliminated by taking resistance readings, R_{obs}, at frequencies, f, of 5000, 1250 and 550 cycles per second and extrapolating to infinite frequency by assuming the quadratic equation $R_{obs} = R_\infty + af^{-1/2} + bf^{-1}$, where a and b are constants.[7] In the course of the experiments it became apparent that the $af^{-1/2}$ term was insignificantly small ($\leq 0.01\%$ of R_{obs}); hence the resistance-frequency behavior could be represented by the simple relation

$$R_{obs} = R_\infty + bf^{-1}$$

The extrapolation procedure was therefore simplified by observing resistances at frequencies of 5000, 2500 and 1667 cycles per second (chosen so that their reciprocals are in the ratio 1:2:3), taking the average of the increments ($R_{1667} - R_{2500}$) and ($R_{2500} - R_{5000}$), and subtracting this number from R_{5000} in order to obtain R_∞.

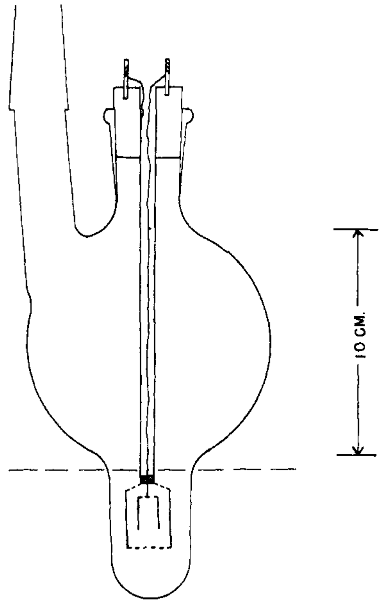

Fig. 1.—Conductance cell; dashed line indicates minimum liquid level.

Results and Discussion

The conductance data are given in Table I where in $1000\kappa/c$, κ is specific conductance corrected for solvent conductance and c is concentration in *equivalents* per liter. The various salts are identified by the code numbers of Table A As mentioned in the introduction, two concentration (c) and two dilution (d) runs were made on each salt, one each for the salt as received and after recrystallization. In order to save space, only the data for the recrystallized salts are included in Table I (except for VIII, where the data refer to the salt as received).

If equivalent conductance is plotted against $c^{1/2}$, curves are obtained which approximate linearity over our working range of concentration. Careful inspection of the curves (see Fig. 2) clearly shows that the linearity is merely the consequence of the presence of an inflection point. It is, however, possible to transform the conductance curve into a linear plot by suitable transformations of the variables.[2,3] As ordinate, we use

$$\Lambda' = F\Lambda$$

where

$$F = \left(\frac{1}{1 + \lambda^0_2/2\Lambda_0}\right)\left(\frac{1}{1 - \delta_{12}\Gamma^{1/2}} + \frac{\lambda^0_2}{2\Lambda}\right)$$

$$\delta_{12} = 3.94 \times 10^6 Q(DT)^{-3/2} + 3(28.98)/\eta\Lambda_0\,(DT)^{1/2}$$

$$Q = q/(1 + q^{1/2}), \text{ and } q = 2/3(1 + \lambda^0_1/\Lambda_0)$$

Then Λ' is plotted against x, where

$$x = cf_B\Lambda'(\Lambda' - \Lambda_0/2)$$

and f_B is obtained from

$$-\log f_B = 1.288 \times 10^6 z_B^2\Gamma^{1/2}(DT)^{-3/2}$$

The linear plot is extrapolated to $x = 0$ to obtain

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(7) J. C. Nichol and R. M. Fuoss, "Symposium on Electrolytes," Division of Physical and Inorganic Chemistry, *J. Phys. Chem.*, **58**, 696 (1954).

TABLE I

CONDUCTANCES IN METHANOL AT 25°

10^4c	Λ	10^4c	Λ
I		III	
0.897	122.31 c	0.638	116.95 c
1.528	117.75 c	0.835	116.11 d
2.902	110.98 c	1.277	114.26 d
3.279	109.74 d	1.829	112.47 d
4.303	106.21 d	2.066	111.88 c
4.311	105.88 d	3.704	107.91 d
6.128	101.15 c	4.852	105.80 c
8.386	96.34 d	6.760	102.81 d
13.995	88.16 d	11.423	97.46 d
II		IV	
0.784	121.63 c	0.805	131.91 c
1.287	118.08 c	1.390	127.46 c
2.388	112.64 c	2.390	121.99 c
3.978	107.22 d	2.936	119.25 d
4.433	105.64 c	3.984	115.64 c
6.086	101.58 d	4.428	113.96 d
6.241	101.19 c	6.486	108.30 d
9.243	95.54 d	9.654	101.92 d
15.215	88.01 d		
V		VII	
0.565	132.09 c	0.938	119.86 c
1.003	128.15 c	1.519	116.05 c
1.842	122.86 c	2.321	111.88 c
2.551	119.30 d	3.483	107.15 c
3.274	116.35 c	3.637	106.69 d
3.605	115.07 d	5.048	102.32 d
5.210	110.12 c	5.105	102.10 c
5.216	109.89 d	7.001	97.50 d
7.698	103.76 d	10.918	90.64 d
VI		VIII	
0.456	129.53 c	0.614	121.49 c
0.823	125.70 c	1.298	117.83 c
1.797	119.80 c	2.781	112.33 c
2.376	116.86 d	3.758	109.76 d
2.949	114.41 c	4.286	108.20 c
3.611	111.82 d	5.807	105.03 d
4.442	109.16 c	6.337	103.94 c
6.418	103.69 d	10.695	97.44 d
9.253	97.91 d		

the value of Λ_0. Since Λ_0, the quantity sought, is one of the unknowns, the calculations involve a process of successive approximations, in which a preliminary value for Λ_0 is obtained by extrapolating the linear part of the Λ *vs.* $c^{1/2}$ curve to $c = 0$. The cationic limiting conductance, λ^0_2, is obtained by subtracting the known anionic limiting conductance, λ^0_1, from the provisional Λ_0. The ionic strength, Γ, is calculated from the relation $\Gamma \approx c(4\Lambda/\Lambda_0 - 1)$. The value of Λ_0 from the first Λ' *vs.* x extrapolation is then used in a second calculation. The process is continued until constant Λ_0 values are obtained. The slopes of the Λ' *vs.* x plots give k_2, the constant describing the association of the first anion to one end of the divalent cation.

For methanol at 25°, $D = 32.63$[8] and $\eta = 0.005445$.[9] In earlier papers of this series, we used $\lambda^0(\mathrm{Br}) = 55.5$; this value has been critically discussed.[3] Since then, a much more reliable value of the single ion conductance λ^0 (Cl) has become available[10,11]; based on this and recent precision conductance work,[12] we have used here the following values of single ion conductances in methanol: $\lambda^0\,(\mathrm{Cl}') = 52.38$, $\lambda^0\,(\mathrm{Br}') = 56.55$ and $\lambda^0\,(\mathrm{I}') = 62.75$. In later discussions where our present results are compared with earlier work, the previous figures have naturally been revised to conform with Gordon's standards. For the methosulfate ion of compound VII, provisional λ^0_1 values used in the course of the extrapolation calculations were obtained by subtracting from the provisional Λ_0 the limiting conductance of the cation as calculated from data on compound IV.

The results for Hartwell's and Fakstorp's compounds are shown in Figs. 2 and 3, respectively, and are summarized in Table II. The number of atoms between the charged nitrogen atoms is given under the heading n. In order to keep the figures from becoming too cluttered, no data are plotted for Compound II in Fig. 2; the curves shown in Fig. 2 are typical of those for all of the compounds. Figure 3 shows the extrapolation plots for Fakstorp's compounds. The intercepts at $x = 0$ give the limiting equivalent conductance, while the slopes determine k_2. It is immediately obvious from the figure that k_2 is about the same for the three iodides and for the methosulfate, while the bispyridinium chloride shows considerably less association than the alkyl compounds. From this, we conclude that the negative charge is fairly uniformly distributed over three oxygen atoms in the $\mathrm{MeOSO_3}'$ ion, so that its effective electrostatic size is about the same as that of the bulky iodide ion. The large value of k_2 for compound VIII suggests that the small chloride ion is solvated, so that the net size of the solvated ion is larger than the iodide ion. (Implicit here is the assumption that the methanol of solvation is retained in the ion pairs.)

TABLE II

PROPERTIES IN METHANOL AT 25°

Cpd.	n	Λ_0	λ^0_2	10^3k_2	10^8R
I	2	132.6	76.1	0.98	6.1
II	4	130.2	73.7	1.16	6.6
III	10	122.1	65.5	3.30	10.8
IV	5	142.1	79.4	0.99	6.4
V	5	139.9	77.2	0.99	6.4
VI	5	135.9	73.2	1.00	6.4
VII	5	130.2	(79.4)	1.02	6.5
VIII	5	127.4	75.0	1.95	..

The quantity R of Table II is the average intercharge distance in the cation calculated from the equation

$$k_2 = (1/2)K \exp(-\epsilon^2/DkTR)$$

as described previously.[4] A value of K, the intrinsic dissociation constant of each of the positively charged sites of the cation is needed for the calcula-

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[8] A. A. Maryott and E. R. Smith, *N. B. S. Circular*, **514**, 5 (1951).

[9] W. N. Maclay and R. M. Fuoss, *J. Polymer Sci.*, **6**, 511 (1951).

[10] J. A. Davies, R. L. Kay and A. R. Gordon, *J. Chem. Phys.*, **19**, 749 (1951).

[11] J. P. Butler, H. I. Schiff and A. R. Gordon, *ibid.*, **19**, 752 (1951).

[12] R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

tion and was estimated for the various compounds as follows: For compound IV, the value $K = 2.9 \times 10^{-2}$, already estimated by Eisenberg and Fuoss[4] for one end of the $Me_3N^+(....)N^+Me_3$ ion was used. Compounds V, VI and VII, all with a chain identical with that in IV, have practically the same value of k_2, and the same value of K as for IV was used. For the bispyridinium salts (compounds I, II and III), K for the single terminal group was set equal to 0.035; this is the average of the value calculated[13] from the conductance of tetramethylammonium bromide[14] and of tetrabutylammonium bromide[15] in methanol.

For compounds I, II and III the cationic conductances decrease and the k_2's increase as chain length increases. This is just what would be expected, since increasing bulk would lower the mobility of the cation, while the increasing distance between charges would tend to diminish the attraction from the unpaired charge on the cation and thereby increase k_2. For the bistrimethylammonium analog of compounds I, II and III, Chu found $k_2 = 0.00104$ for $n = 3$, which is consistent with our results for $n = 2$ and $n = 4$. Compound III can be compared with Edelson's succinic acid salt ($n = 10$) for which $k_2 = 0.00445$ and $R = 15.1$. Our compound III with terminal pyridinium groups on a ten atom chain gives $R = 10.8$; the smaller value for III can be interpreted as the consequence of more coiling of the polymethylene chain of III than of the diester chain of the succinic acid derivative. An equivalent description, of course, is that the diester chain is more extended than the polymethylene chain due to mutual repulsion between the carboxyl dipoles. Compounds IV–VII have a diethyl ether chain ($n = 5$) between the charged nitrogens; the oxygen atom would thus appear to be the equivalent of a methylene group in determining charge separation because our values of k_2 for these compounds agree closely with Chu's result for the pentamethylene salt ($k_2 = 0.00108$). Later consideration of mobility will, however, revise this tentative conclusion.

It will be observed (compounds I, II and III, Table I) that as the chain length decreases the limiting conductance increases by roughly 1.3 units per methylene group. By subtracting this increment from λ^0_2 for compound I we obtain $\lambda^0_2 = 74.8$ for the corresponding bispyridinium salt where $n = 3$. Fuoss and Chu[8] find that $\lambda^0_2 = 78.5$ for the trimethylammonium salt in which $n = 3$, from which we conclude that substitution of pyridinium for trimethylammonium groups decreases the conductance by about 3.7 units. This indirect result agrees fairly well with the difference in conductances of our compounds IV and VIII, from which an increment 4.4 units is obtained.

For compounds IV–VI, the mobility decreases with increasing size of the alkyl groups attached to the quaternary nitrogen, as would be expected. The k_2's, however, are practically identical, which shows that chain length is more effective than size of terminal substituents in determining the extent of ion association. It is interesting that substitution of methosulfate anions VII for iodide IV causes very little change in k_2, while the equivalent conductance for the salt decreases markedly, showing that the methosulfate mobility is lower than that of iodide.

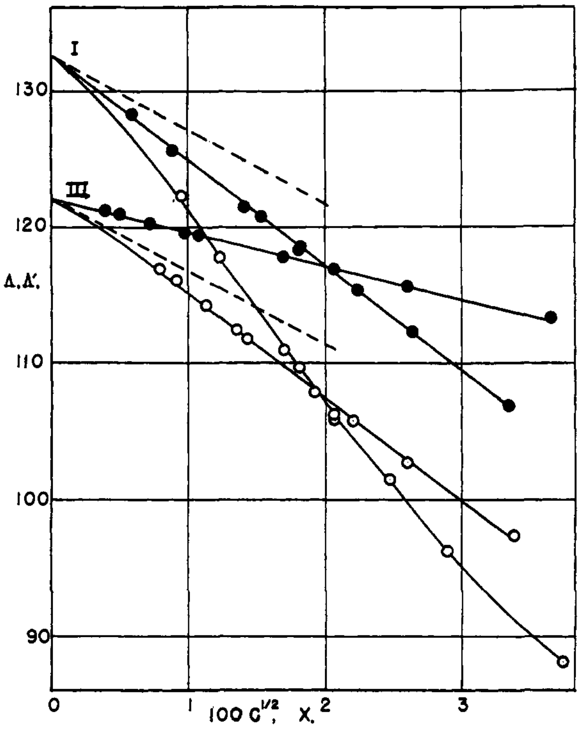

Fig. 2.—Conductance curves (open circles) and extrapolation plots (solid circles) for compounds I (upper set) and III (lower set); Onsager tangents, dotted lines.

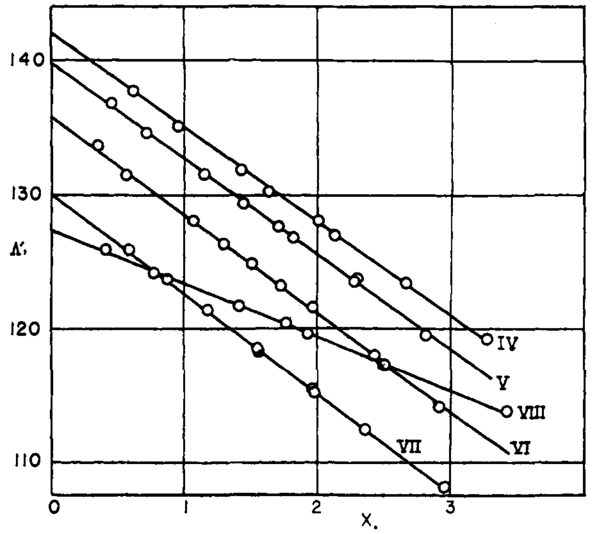

Fig. 3.—Extrapolation plots for compounds IV–VIII.

Substitution of an oxygen atom in place of a methylene group in the chain brings about an increase in the limiting ion conductance. For example, for the hypothetical bispyridinium pentamethylene salt, subtraction of 1.3 from λ^0_2 for compound II yields the estimated value $\lambda^0_2 = 72.4$, as compared to $\lambda^0_2 = 75.00$ for the corresponding ether, compound VIII. Again, for Fuoss and Chu's

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(13) R. C. Miller and R. M. Fuoss, THIS JOURNAL, 75, 3076 (1953).

(14) T. H. Mead, O. L. Hughes and H. Hartley, *J. Chem. Soc.*, 125, 1207 (1923).

(15) H. Sadek and R. M. Fuoss, THIS JOURNAL, 72, 5803 (1950).

1,5-(bistrimethylammonium)-pentamethylene dibromide $\lambda^0_2 = 77.3$ while for compound IV $\lambda^0_2 = 79.4$. Higher mobility for the substituted ethers presumably means a more compact structure. This readily can be obtained if we assume that the ether oxygen is pulled toward one of the cationic nitrogens; molecular models show that there is ample space between methyl groups for near N^+O^- contact. The presence of the negative oxygen near the nitrogen weakens the attraction of the latter for an approaching anion, *i.e.*, acts in the direction of increasing k_2. Increase of R also increases k_2. Hence we conclude that the NC_2OC_2N chain is shorter than the NC_5N chain and that the near equality of the k_2's is the result of compensating effects.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Gluconate Complexes. I. Copper Gluconate Complexes in Strongly Basic Media[1]

BY ROBERT L. PECSOK AND RICHARD S. JUVET, JR.

RECEIVED JUNE 12, 1954

The copper gluconate chelates have been studied polarographically, spectrophotometrically, potentiometrically and amperometrically. From the data obtained the structures of some of the chelates have been postulated and the equilibrium constants at various ionic strengths have been measured. Evidence is given for the existence of at least five species—a 2:4, a 2:2, and a 2:1 copper gluconate species in strongly basic solution and two other different 2:2 complex species in less concentrated basic solutions. The pK for the 2:2 complex in strongly basic solution is 18.2_9, independent of ionic strength, and the pK's for the 2:4 species vary from 20.0_6 to 19.4_3 as ionic strength varies from 3 to 0.45 molar.

The present study is the first of a series of papers dealing with the metal chelates of gluconic acid. Gluconic acid forms very strong complexes with most of the transition elements. These complexes are being investigated polarographically, potentiometrically and spectrophotometrically, where applicable. The polarograph was used in the present investigation for the determination of the dissociation constants of the copper gluconate chelates and for obtaining valuable information concerning their structure.

Traube, Kuhbier and Schröder[2] have prepared solid compounds of barium copper gluconates which analysis showed had empirical formulas close to $(C_6H_8O_7Cu)Ba \cdot 3H_2O$ and $[(C_6H_9O_7)_2Cu]Ba_2 \cdot 9H_2O$. Mehltretter, *et al.*,[3] have compared the sequestering capacity of gluconic acid for copper with several other sugar acids in 3% sodium hydroxide on a gram per gram basis.

Cannan and Kibrick[4] have measured the dissociation constants of the gluconate chelates of several Group II elements using ordinary potentiometric measurements, but found that only weak complexes are formed with these elements. No previous measurements have been reported on the dissociation constants of the transition metal gluconate complexes.

Experimental

Polarograms were recorded according to usual technique[5] with a calibrated Sargent Model XXI automatically recording polarograph. Since the strongly basic solutions used in this work were found to attack agar salt bridges, it was necessary to design a new type of polarographic cell.[6] The resistance was found to be *ca.* 265 ohms when measured through the dropping mercury electrode in a 0.1 M potassium chloride solution. Corrections for IR drop were made where necessary, and corrections were made for residual currents in determining all diffusion current data. The rate of flow, m, was 1.452 mg. sec.$^{-1}$, and the drop time was 5.18 sec. on open circuit and 5.80 sec. at −0.65 v. *vs.* S.C.E. at which most measurements of the diffusion current were made. Temperatures were maintained at 25.0°.

Spectrophotometric investigations were run either on a Cary Model 11PMS automatically recording spectrophotometer (Applied Physics Corp., Pasadena, California) or on a Beckman DU quartz spectrophotometer.

Copper solutions were made from Merck reagent grade copper sulfate and were standardized electrolytically by the method of Kolthoff and Sandell.[7]

Sodium gluconate solutions were prepared from D-glucono-δ-lactone (Matheson, Coleman and Bell) which was recrystallized twice from ethylene glycol monomethyl ether and dried at 110° for 1 hour. The purified lactone was then standardized by titration with standard sodium hydroxide. Care must be taken in this titration since the lactone hydrolyzes rather slowly a few ml. before the equivalence point and the pH slowly decreases as hydrolysis takes place. At the end-point, however, a very definite increase in pH is found. An alternate standardization procedure is to add an excess of standard sodium hydroxide solution followed by a back-titration with standard hydrochloric acid solution. The D-glucono-δ-lactone was found to be 99.7% pure.

Theoretical Discussion

Lingane[8] has pointed out the inherent usefulness of the polarograph for the determination of stability constants and formulas of metal complexes. We have adapted his analysis of the polarographic wave to fit the situation at hand. Two modifications are required: hydroxide ion is involved in the half reaction, and in some cases the concentration of free gluconate is not in large excess.

We may write for the general reaction of the reduction of copper gluconate

$$\text{Complex} + yH_2O + Hg + 2e^- = Cu(Hg) + pGH_4^- + xOH^- \quad (1)$$

where HGH_4 is gluconic acid and GH_4^- is the gluconate ion (H's refer to the secondary hydroxyl hy-

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[1] Presented before the Regional Meeting of the Southern California Section of the American Chemical Society, Los Angeles, May 8, 1954.

[2] W. Traube, F. Kuhbier and W. Schröder, *Ber.*, **69B**, 2655 (1936).

[3] C. L. Mehltretter, B. H. Alexander and C. E. Rist, *Ind. Eng. Chem.*, **45**, 2782 (1953).

[4] R. K. Cannan and A. Kibrick, THIS JOURNAL, **60**, 2314 (1938).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1952.

[6] R. L. Pecsok and R. S. Juvet, *Anal. Chem.*, in press.

[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952, p. 407.

[8] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).