0.7 ml. of 2 *N* base was added beyond the point of neutralization with phenolphthalein as the indicator.

The copolymer, sample IX, 185 ml. was added dropwise in benzene solution to alcoholic sodium ethoxide from 120 mg. sodium, water was added, followed by one pellet of sodium hydroxide, and the organic solvents distilled off. After adding 1 ml. of 5 *N* hydrochloric acid the solution was diluted to 25 ml. (solution P-3).

A small part of this solution was used for studies with urease. The remainder of this solution was kept in a closed volumetric flask and gelled after seven days. The gel had a sauce-like consistency after shaking. Addition of one pellet of sodium hydroxide and heating for two hours in boiling water did not cause solution (*p*H 11). After two days standing, ten drops of thioglycolic acid and two pellets of sodium hydroxide were added and solution occurred almost immediately in the cold.

A similar solution was prepared using 189 mg. of copolymer IX, 70 mg. of sodium and 13 drops of 5 *N* hydrochloric acid (solution P-4, 25 ml., *p*H 9–10).

Sixteen drops (0.4 g.) of this solution were diluted and oxidized with 25 drops (*ca.* 1.45 g.) of 0.00874 *N* iodine, of which the first sixteen caused no precipitation, the next three a slight turbidity, and the next three a definite turbidity. The last two drops caused a precipitate and a blue starch–iodine color.

A similar solution was prepared from 292 mg. of copolymer IX and 69 mg. of sodium (solution P-5, 25.5 ml.).

Two milliliters of this solution was oxidized with 5.2 ml. of 0.00874 *N* iodine solution in the presence of bicarbonate. The precipitate formed did not dissolve when boiled for one hour with 28 drops of *ca.* 0.7 *N* sodium thioglycolate and the filtrate gave no precipitate on acidification. A portion of the suspension dissolved on adding six pellets of sodium hydroxide and refluxing.

**Reaction of Deactivated Urease with Polymers.**—Jack Bean urease employed was obtained in powder form (Type II, Sigma Chem. Corp., St. Louis, Missouri).

The colorimetric method developed by Van Slyke and Archibald[13] was employed with minor modifications. Two 40-ml. vials, one containing a urea phosphate buffer at *p*H 6.7 and the other containing a phosphate buffer at *p*H 7.7, were suspended in a constant temperature bath at 29.8 ± 0.2°, one drop of a mixed indicator (16 mg. brom thymol blue, 17 mg. of phenol red and two drops of 2 *N* base diluted with water to *ca.* 30 ml.) were added followed by a known amount of urease solution (or suspension in the case of urease reactivated by the copolymer), the time necessary for the urea buffer to match the color of the control was determined, and from this and the concentration of the urease the activity in Sumner units (S.U.) per mg. urease were calculated according to equation 1

$$A = \frac{1800}{tU} \qquad (1)$$

where $A$ is activity in S.U. per mg., $t$ the time in seconds and $U$ the urease added in mg. This equation is a modification of the equation given in the original article. The factor 1800 is a combination of the factors 0.6 (correction for temperature) 60 (conversion from minutes to seconds) and 50 (arising from the buffer composition and the definition of the Sumner unit).

The procedure was to prepare a *ca.* 10% urease solution, determine its activity, deactivate the enzyme by adding 0.00874 *N* iodine and determine the activity after reactivation by the addition of neutralized cysteine, sodium thioglycolate, or polymer and redetermine the activity. The solution was then allowed to stand with the reactivating agent overnight and the activity again determined. The results are summarized in Table I.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

# Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VII. Derivatives of 1,X-Diamino-alkanes[1]

BY GEORGE B. BUTLER AND RUDOLPH J. ANGELO

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As an approach to a study of the effect of distance between active centers in strongly basic ion-exchange polymers on the exchange properties, a number of unsaturated quaternary ammonium salts have been prepared, characterized and polymerized. As intermediates the 1,X-bis-(diallylamino)-alkanes from ethane through decane were prepared. Quaternary ammonium salts studied included the methyl bromide and allyl bromide derivatives of each of the amines.

Polymerization of pure unsaturated quaternary ammonium salts[2] offers an excellent means of producing strongly basic ion-exchange polymers free of other reactive functional groups. It has been shown that the rate of ion-exchange processes is a function of a diffusion factor,[3] and that diffusion rates depend upon the degree of cross-linking of the polymer network. The degree of swelling of an ion-exchange material, also a function of the degree of cross-linking, has an effect on this rate of diffusion of the ions to the exchange centers. Ion-exchange materials having a low degree of swelling, from a practical standpoint, are limited in the fraction of the theoretical capacity of the polymer which can be attained under conditions of practical usage due to this diffusion rate. For example, it has been shown[4] that for a polymer having a coefficient of swelling of 5.08, 88.8% of the theoretical capacity can be attained, while under similar conditions, for a polymer having a coefficient of swelling of 1.17, only 39.4% of the theoretical capacity was attained.

The degree of cross-linking of the polymer network has also been shown to be a factor in the exchange capacity[5] and this capacity decreases as the size of the ion to be exchanged attains a threshold value. This threshold value decreases with increasing degrees of cross-linking, thus supporting the idea that ion-exchange materials are not capable of exchanging ions having an effective diameter larger than the diameter of the opening which permits diffusion to the internal structure of the particle.

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[1] This paper was presented before the Ion Exchange Conference, Gordon Research Conferences, AAAS, New Hampton, N. H., June, 1955, and before the Ion Exchange Symposium, Southeastern Regional Meeting, ACS, Columbia, S. C., November, 1955.

[2] The most recent paper of this series appeared in THIS JOURNAL, **76**, 2418 (1954).

[3] G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

[4] G. B. Butler and R. L. Goette, *ibid.*, **74**, 1939 (1952).

[5] R. Kunin, *Anal. Chem.*, **21**, 87 (1949).

TABLE I

UNSATURATED TERTIARY DIAMINES

| Derivative of $(C_3H_5)_2N(CH_2)_nN(C_3H_5)_2$ | | B.p. | | | Anal. N, % | | |
|---|---|---|---|---|---|---|---|
| $n^a$ | Formula | °C. | Mm. | $n^{25}D$ | Calcd. | Found | Yield, % |
| 3 | $C_{15}H_{26}N_2$ | 88–89 | 0.5 | 1.4711$^b$ | 11.95 | 11.57 | 80.5$^{l,m}$ |
| 6 | $C_{18}H_{32}N_2$ | 124 | .8 | 1.4708$^c$ | 10.13 | 10.21 | 21.7$^{l,n}$ |
| 7$^d$ | $C_{19}H_{34}N_2$ | 124–126 | .1 | 1.4719 | 9.65$^e$ | 9.51$^f$ | 87.5$^l$ |
| 8$^g$ | $C_{20}H_{36}N_2$ | 134–138 | .1 | 1.4651$^{23}$ | 9.20$^h$ | 9.15$^i$ | 75.5$^l$ |
| 9 | $C_{21}H_{38}N_2$ | 146–148 | .07 | 1.4723 | 79.3$^j$ | 79.8$^j$ | 94.5$^{l,m}$ |
| | | | | | 11.93$^k$ | 12.01$^k$ | |
| 10 | $C_{22}H_{40}N_2$ | 152–158 | .07 | 1.4725 | 8.43 | 8.27 | 70.5$^{l,m}$ |

[a] $n = 1$[1]; $n = 2$[5]; $n = 4,5$[6]. [b] $d^{25}_4$ 0.8415. [c] $d^{25}_4$ 0.8465. [d] Dihydrobromide, m.p. 129–130°; *Anal.* Calcd.: Br, 35.33. Found: Br, 35.50. [e] C, 78.6; H, 11.8. [f] C, 78.5; H, 11.5. [g] Dihydrobromide, m.p. 137–138°. *Anal.* Calcd.: Br, 34.26. Found: Br, 34.26. [h] C, 78.9; H = 11.8. [i] C, 78.8. H, 11.7. [j] C. [k] H. [l] Method I. [m] II. [n] IV.

Since quaternary ammonium polymer formation by polymerization of a monomer containing the desired functional group permits a greater degree of homogeneity in the resulting polymer than the technique which requires introduction of the desired functional group into an existing polymer network, "tailor-making" a polymer for a desired purpose becomes more easily accomplished. Furthermore, since the monomer itself constitutes its own cross-linking agent, it is possible to readily change the effective pore size of the polymer by altering the distance between exchange units without changing the degree of cross-linking per exchange center, thus keeping the coefficient of swelling relatively constant.

This paper includes details of syntheses of the bis-(methyldiallylammonium)-alkane dibromides and the bis-(triallylammonium)-alkane dibromides in which the quaternary ammonium centers are separated by from two to ten methylene groups, polymerization of these monomers and determination of the capacities and swelling coefficients of the resulting polymers. Details of the study of the effect of distance between exchange centers on the exchange properties will be reported later.

## Experimental

**Preparation of Amines.**—1,2-Bis-(diallylamino)-ethane has been reported[6] and was prepared for this work by the procedure (I) described. For those amines for which appropriate starting materials were not available for use in procedure (I) or in which (I) failed to give the desired compound,[7] the method of Laakso[8] and Reynolds (II) was used. If (II) failed to give the desired product[7] reduction of the bis-(diallylamide) of the appropriate dibasic acid by use of lithium aluminum hydride (III) was employed. Since hexamethylenediamine was readily available, 1,6-bis-(diallylamino)-hexane was prepared by reaction of the diamine with allyl bromide in presence of sodium carbonate (IV), as well as by the more satisfactory (I).

As intermediates for preparation of 1,9-bis-(diallylamino)-nonane and 1,10-bis-(diallylamino)-decane by (II), the following compounds were prepared[8] and characterized: 1,9-di-(*p*-toluenesulfonoxy)-nonane, m.p. 77°, yield 85.5% theor. *Anal.* Calcd. for $C_{23}H_{32}O_6S_2$: C, 58.49; H, 6.77. Found: C, 58.87; H, 6.89. 1,10-Di-(benzenesulfonoxy)-decane, m.p. 46°, yield 85.8% theor. *Anal.* Calcd. for $C_{22}H_{30}O_6S_2$: C, 58.14; H, 6.66. Found: C, 57.67; H, 6.79.

Since neither heptamethylene glycol, octamethylene glycol, nor the corresponding bromo derivatives could be obtained through commercial sources, 1,7-dibromoheptane was synthesized by the following reaction sequence: (1) 1,5-dibromopentane was converted to pimelonitrile (73%) by the procedure for glutaronitrile,[9] diethyl pimelate (73%) was prepared by the procedure for ethyl *n*-valerate,[10] heptamethylene glycol (93%) was prepared by lithium aluminum hydride reduction[11] and 1,7-dibromoheptane (50%) was obtained by the procedure for bromides.[12] 1,8-Dibromooctane (63%) was obtained by a similar sequence from 1,6-dibromohexane, suberonitrile (87%), diethyl suberate (73%) and octamethylene glycol (97%).

The physical properties, yields, analyses and methods of preparation used for the new amines synthesized and characterized are recorded in Table I.

**Determination of Base Strengths of Amines.**—Using a Beckman *p*H meter, the amines were titrated with 1.000 *N* HCl. A 50% by volume water–ethanol mixture was used as solvent. The following example will illustrate the procedure; 0.4280 g. of 1,2-bis-(diallylamino)-ethane was dissolved in 50 ml. of the solvent. Titration with standard acid was carried out, *p*H recordings being made for each ml. of acid added. From the plot and the relationship $pK_b = p\text{OH} - \log \text{salt/base}$, $pK_b$ values were calculated from at least two *p*H values on each side of the mid-point of the curve. Values reported are average values; however, maximum deviation from the average value was ±0.05. A plot of $pK_b$ values is shown in Fig. 2.

**Preparation of Quaternary Ammonium Salts.**—The procedure for preparation of these compounds utilized as solvents dry ketones, usually acetone, methyl ethyl ketone or acetophenone. The appropriate diamine was dissolved in three times its weight of solvent. This solution, contained in a suitable flask equipped with stirrer, condenser, thermometer and inlet tube, was cooled in an ice-bath while the appropriate bromide was added. Methyl bromide was condensed in a Dry Ice–acetone bath, and allowed to vaporize into the reaction vessel at the desired rate. Since many of the compounds produced were hygroscopic, the reaction was protected from moisture by use of a drying tube. After addition was complete the reaction was stirred overnight, the crystalline product isolated by filtration, washed with dry acetone and dry ether, and placed in a vacuum desiccator. No heating was required during the reaction period in order to obtain satisfactory yields of the methyl bromide derivatives. For the allyl bromide derivatives, gentle heating on a steam-bath for one or two hours after addition was employed. The products were analyzed for bromide content by titration. The physical properties, yields and analyses of these compounds are recorded in Table II.

**Polymerization of Quaternary Ammonium Bromides.**—Two methods of polymerization were investigated: (1) solution polymerization and (II) suspension polymerization. The solution polymerization procedure employed was essentially the same as that previously described.[1] The approximate ratio of 0.45 g. of water and 0.024 g. of 60% *t*-butyl hydroperoxide per gram of quaternary ammonium salt was used.

The suspension polymerization procedure involved addition of 37.5 g. of a 67% aqueous solution of the monomer to 200 ml. of a 25% solution of ethylbenzene in mineral oil.

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(7) G. B. Butler and R. J. Angelo, *ibid.*, **77**, 1767 (1955).

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(9) H. Gilman, *et al.*, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., 1951, p. 536.

(10) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 163.

(11) Adams, *et al.*, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

(12) Blatt, ref. 9, Vol. II, 1943, p. 246.

TABLE II

QUATERNARY AMMONIUM SALTS

| $n^a$ | Derivatives of $(C_3H_5)_2\underset{R}{\overset{+\,Br^-}{N}}(CH_2)_n\underset{R}{\overset{+\,Br^-}{N}}(C_3H_5)_2$ R | Code | Formula | M.p., °C. | Anal. Br, % Calcd. | Found | Yield, % |
|---|---|---|---|---|---|---|---|
| 2 | $CH_3$ | A | $C_{16}H_{30}N_2Br_2$ | 191–192 dec. | 38.97 | 38.86 | 96.2 |
| 3 | $CH_3$ | C | $C_{17}H_{32}N_2Br_2$ | 109–111 | 37.67 | 37.78 | 89.6 |
| 3 | $C_3H_5$ | D | $C_{21}H_{36}N_2Br_2$ | 185–187 | 33.55 | 33.34 | Quant. |
| 4 | $CH_3$ | E | $C_{18}H_{34}N_2Br_2$ | 163–165 dec. | 36.41 | 36.47 | 85.0 |
| 4 | $C_3H_5$ | F | $C_{21}H_{38}N_2Br_2$ | 168–170 | 32.59 | 31.74 | 91.7 |
| 5 | $CH_3$ | G | $C_{19}H_{36}N_2Br_2$ | 133–135 | 35.34 | 35.32 | 87.3 |
| 5 | $C_3H_5$ | H | $C_{23}H_{40}N_2Br_2$ | 153–155 | 31.69 | 31.70 | 92.2 |
| 6 | $CH_3$ | I | $C_{20}H_{38}N_2Br_2$ | 202–203 dec. | 34.28 | 34.28 | Quant. |
| 6 | $C_3H_5$ | J | $C_{24}H_{42}N_2Br_2$ | 179–180 dec. | 30.83 | 30.77 | 91.5 |
| 7 | $CH_3$ | K | $C_{21}H_{40}N_2Br_2$ | 193–194 dec. | 33.27 | 33.34 | 86.2 |
| 7 | $C_3H_5$ | L | $C_{25}H_{44}N_2Br_2$ | 192–193 dec. | 30.02 | 29.95 | 77.8 |
| 8 | $CH_3$ | M | $C_{22}H_{42}N_2Br_2$ | 178–180 | 32.33 | 32.38 | 58.7 |
| 8 | $C_3H_5$ | N | $C_{26}H_{46}N_2Br_2$ | 195–197 dec. | 29.24 | 28.58 | 50.0 |
| 9 | $CH_3$ | O | $C_{23}H_{44}N_2Br_2$ | 187–189 dec. | 31.45 | 31.23 | 80.0 |
| 9 | $C_3H_5$ | P | $C_{27}H_{48}N_2Br_2$ | 201–202 dec. | 28.26 | 28.41 | 84.0 |
| 10 | $CH_3$ | Q | $C_{24}H_{46}N_2Br_2$ | 163–165 dec. | 30.59 | 30.51 | 85.0 |
| 10 | $C_3H_5$ | R | $C_{28}H_{50}N_2Br_2$ | 200 dec. | 27.82 | 27.76 | 83.0 |

[a] $n = 1$, R = $C_3H_5$[1]; $n = 2$, R = $C_3H_5$[5], (B).

Stirring was adjusted to the desired rate, and the temperature adjusted at 50°; 0.42 g. of 60% *t*-butyl hydroperoxide was added, and stirring continued for 48 hours without interruption. The product was removed, washed with acetone and water, and dried. Yields by this technique ranged from 90–99%.

**Determination of Properties of Polymers.**—Those polymers prepared by the solution polymerization method were ground and the 20–40 mesh fraction was used for further tests. Those polymers prepared by the suspension polymerization method were screened and the 20–40 mesh fraction was employed. The theoretical capacities of the polymers were calculated from the empirical formulas of the bromides. The swelling coefficients were determined by methods previously described.[13] The capacities were determined on resin samples conditioned as previously described,[13] by titration. A weighed quantity of resin sample, after conditioning, was placed in a 250-ml. beaker with 75 ml. of distilled water. To this mixture was added 50 ml. of 0.20 *N* potassium bromide solution. After standing for five minutes, the mixture was titrated with 0.0195 *N* hydrobromic acid solution by using a Beckman Model K automatic titrator. The endpoint was set at *p*H 7 by adjustment with a standard buffer solution, and the anticipation rate was set at *p*H 7. Titration was allowed to proceed for a total time of one hour. The properties of the polymers are recorded in Table III. A plot of the fraction of theoretical capacity obtained *vs.* the number of carbon atoms in the methylene chain is shown in Fig. 1.

TABLE III

PROPERTIES OF POLYMERS OF QUATERNARY AMMONIUM SALTS

| Polymer of | Theor. capacity, meq./g. | One-hour capacity Meq./g. | Meq./ml. | Swelling coefficient |
|---|---|---|---|---|
| A | 4.88 | 2.50 | 1.34 | 1.48 |
| B | 4.33 | 2.88 | 1.22 | 1.45 |
| C | 4.72 | 2.72 | 0.82 | 1.67 |
| D | 4.20 | 3.14 | 1.14 | 1.52 |
| E | 4.57 | 2.89 | 1.13 | 1.44 |
| F | 4.08 | 3.46 | 0.86 | 2.97 |
| G | 4.43 | 3.20 | 1.00 | 2.11 |
| H | 3.97 | 3.66 | 1.22 | 1.88 |
| I | 4.29 | 2.58 | 0.69 | 2.21 |
| J | 3.86 | 3.35 | 1.14 | 1.69 |
| K | 4.17 | 2.57 | 0.86 | 1.83 |
| L | 3.76 | 3.16 | 1.17 | 1.64 |
| M | 4.05 | 2.66 | 0.96 | 1.69 |
| N | 3.66 | 2.12 | .56 | 2.33 |
| O | 3.94 | 2.53 | .86 | 1.80 |
| P | 3.57 | 2.16 | .75 | 1.76 |
| Q | 3.83 | 2.27 | .92 | 1.50 |
| R | 3.48 | 2.10 | .90 | 1.43 |

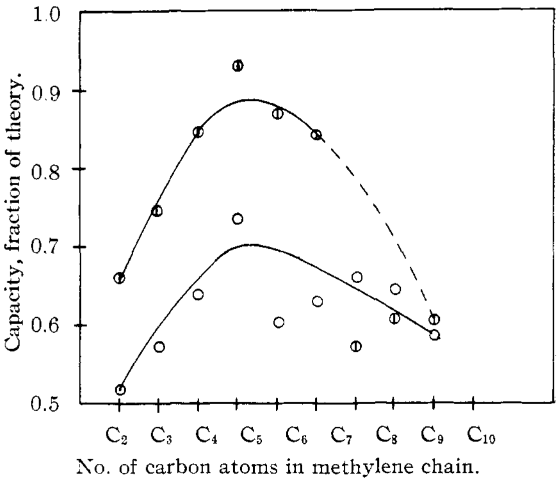

Fig. 1.—Titration of polymers with Beckman Model K automatic titrator over a one-hour period: O, dimethyltetraallyl series; ⦶, hexaallyl series.

## Discussion of Results

The procedure used for determination of capacities of polymers in this work can only be considered as a means of determining the available capacity of a given polymer under practical conditions. Only in a few instances did the actual capacity as determined by this method approach the theoretical capacity. The results in Table III and Fig. 1 regarding the fraction of the theoretical

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(13) G. B. Butler, R. L. Bunch and F. L. Ingley, THIS JOURNAL, **74**, 2543 (1952).

capacity obtained for each polymer can only be significant in terms of rate of ion exchange. As pointed out above,[3] rate of ion exchange is a function of a diffusion factor, and can be dependent upon degree of cross-linking, and coefficient of swelling, as well as upon the size of the ion to be exchanged.[5] Evidence to support the statement regarding significance of these values was obtained when a sample was allowed to titrate for longer periods. Additional evidence has been obtained by Husa[14] who employed an equilibrium method of determining capacities of polymers described in this paper. This method was based on the method of Mattson[15] and the results have shown that 96–100% of the theoretical capacities of these polymers can be attained if given enough time. Results of these experiments will be published at a later date.

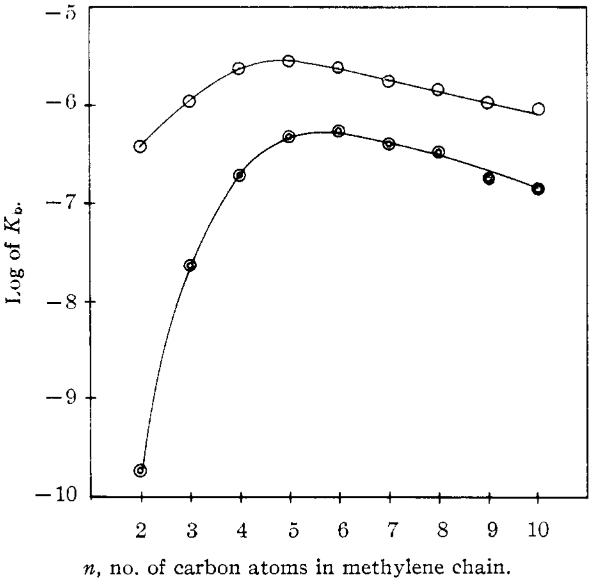

Fig. 2.—Plot of $pK_b$ values for tetraallyl $n$-methylenediamines: O, $pK_{b1}$; ◎, $pK_{b2}$.

Figure 1 shows that a maximum occurs in the rate of exchange at $n = 5$ for both the methyldiallyl series and the triallyl series of polymers. Also, the rate for the triallyl series is greater than that for the methyldiallyl series. On the assumption that a higher degree of cross-linking occurs in the triallyl series, the ion-exchange rate would be expected to be less in this series than in the less cross-linked methyldiallyl series. However, it is unlikely that all allyl groups present are involved in polymerization reactions because of steric effects. A comparison has been made[16] between regeneration rates of a copolymer containing a residual double bond and a copolymer containing no residual double bond. The half-time for regeneration in the former was considerably less than that for the latter. The reverse exchange was also found to be faster in the former copolymer.

The maxima occurring at $n = 5$ were unexpected. On the basis of a model of the polymers under consideration, it is to be expected that exchange could occur more readily at $n = 10$ than at $n = 2$, and that the fastest rate should occur at $n = 10$. A possible explanation lies in the relative electron deficiencies of the quaternary ammonium centers. This can be a function of the basicity of the amines from which the polymers were derived. In order to check this possibility, the ionization constants of the amines were determined. These values are plotted in Fig. 2, and it will be observed that a maximum occurs at $n = 5$ for $pK_{b_1}$ and at $n = 6$ for $pK_{b_2}$. A possible explanation for the proximity and regularity of $pK_{b_1}$, and $pK_{b_2}$ at higher values of $n$, has been offered by Gero[17] who studied the polymethylenediamines from $n = 2$ through $n = 5$. Although the basic strengths of the amines may account for the maxima at $n = 5$ for the polymers, no explanation appears obvious for the more rapid decrease in rate of exchange with increasing values of $n$ beyond 5 in the polymers than is the case with ionization constants of the parent amines.

A unique relationship exists between the distance between quaternary ammonium centers in the monomers and the exchange behavior of the resulting polymers. Since polymerization would result in formation of new pentamethylene bridges between the quaternary ammonium centers, polymers derived from the monomers in which $n = 5$ would be highly symmetrical with respect to distances between quaternary ammonium centers. Polymers derived from monomers in which $n<5$ would possess "holes" of a certain size and smaller while those derived from monomers in which $n>5$ would possess "holes" of this certain size and larger. It is possible that the symmetrical nature of those polymers derived from monomers in which $n = 5$ has some effect on the exchange rate.

Another possible cause[18] for the unexpected maxima observed in Fig. 1 is the possibility of molecular entanglement. As the number of carbon atoms in the methylene chain between the ionic centers increases there could be greater opportunity for "looping" and hence for a kind of cross-linking resulting from van der Waals attraction. This effect might be expected to cause a rather abrupt change in the rate of increase of swelling coefficient beyond $n = 5$; however, no such change was observed.

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[17] A. Gero, *ibid.*, **76**, 5159 (1954).

[18] This possibility was suggested by one of the referees.