is that $C_4H_3^+$ undergoes electron-transfer reaction 6 to

$$C_4H_3^+ + C_6H_6 \longrightarrow C_6H_6^+ + C_4H_3 \quad (6)$$

give $C_6H_6^+$. Although $C_4H_3^+$ is a potential proton-transfer agent, the electron-transfer reaction is apparently faster.

Discussion

Calculations on the $C_6H_6^+$ ion indicate that its ground state has a uniform charge density on all six carbons,[11] and this gives the ion a very low energy (ΔH_f = 233 kcal/mole).[10] Forming a chemical bond with the ion at the expense of the uniform charge distribution gives no decrease in energy, at least in the case of $C_6H_7^+$ (ΔH_f = 235 kcal/mole).[12]

Besides being of low energy, $C_6H_6^+$ ion is very stable. Our work with benzene–Kr^+ or the appearance potential data show that about 5 ev more than the minimum ionization energy is needed to begin fragmentation of the ion. Although something is known about the stability of the ions formed from various benzene energy levels,[7] we do not know whether our destructive electron-transfer process is making benzene ions in repulsive states or too high vibrational levels of bonding states.

Our findings that $C_6H_6^+$ is unreactive and rapidly formed by electron transfer to benzene fragment ions are useful in interpreting the results of benzene radiolysis. Since little ionic chemistry will occur, free radicals will have to produce the observed products, and experimental results conform with this view. The over-all reaction observed in benzene radiolysis can be largely explained by the reactions of H atoms and phenyl radicals.[13]

The use of electron transfer to rare gas ions as a technique for producing new fragmentation patterns of additive molecules under chemical ionization conditions has been illustrated here. Because of the high pressure in the ion source, the rare gas ions should be near thermal energy, a situation unattainable in beam experiments. The high total pressure also permits the cascading of ionization (*e.g.*, the Xe–benzene–toluene experiment), and the study of reactions of resulting hydrocarbon ions with the parent molecule or additives is in principle possible. Thus some new chemical ionization techniques have been demonstrated in studying the reactions of benzene ions.

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[11] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 481.

[12] F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, 1, 96 (1961).

[13] T. Gauman, *Helv. Chim. Acta*, 46, 2873 (1963).

The Binding of Quaternary Ammonium Ions by Polystyrenesulfonic Acid Type Cation Exchangers[1]

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Abstract: A thermodynamic study was made of the binding of quaternary *n*-alkylammonium ions by cross-linked polystyrenesulfonic acid type cation exchangers. Calorimetric measurements of the exchange reactions with sodium ion at 25° showed that the enthalpy and entropy changes were negative for the preferential binding of tetramethyl- and tetraethylammonium ions by lightly cross-linked sodium-form exchanger, but, with tetra-*n*-propyl- and tetra-*n*-butylammonium ions, heat was absorbed and the entropy increased markedly. The increase in the preferential uptake with the size of the tetra-*n*-alkylammonium ion therefore was determined by the entropy increase in the exchange reaction (*i.e.*, hydrophobic bonding). The selective uptake of Me_4N^+ ion decreased with increasing exchanger cross-linking, and with nominal 8% DVB exchanger the Na^+ ion was preferred for all compositions. The heat of exchange became progressively less negative, and with the most highly cross-linked preparation heat was absorbed when Me_4N^+ replaced the Na^+ ion, but the entropy change remained constant. The decrease in the binding of Me_4N^+ ion with increased cross-linking was attributed to the increase in enthalpy of the molecular network of the ion exchanger when it expanded to accommodate the large organic cation. A comparison of the enthalpy with the free energy of swelling showed that the entropy also increased, which is contradictory to the hypothesis that ion exchangers are rubber-like gels. The more highly cross-linked polystyrenesulfonate exchangers behaved as if they were in a glass-like state (*i.e.*, a rubber below its gel point).

The ion-exchange reactions of quaternary *n*-alkylammonium ions, R_4N^+, in aqueous solution with singly charged cations on polyelectrolytes appear to be unusual in a number of respects.[2–8] In reactions with alkali metal ions on lightly cross-linked polystyrenesulfonic acid (PSSA) exchangers the binding of R_4N^+ increases with ion size,[3] but with lightly cross-linked polymethacrylic acid (PMA) a *decrease* with increasing size is observed.[7] However, with both strong-acid and

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, 1208 (1949).

[3] H. P. Gregor and J. I. Bregman, *J. Colloid Sci.*, 6, 323 (1951).

[4] K. D. Hale, D. I. Packham, and K. W. Pepper, *J. Chem. Soc.*, 844 (1953).

[5] J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *ibid.*, 2740 (1964).

[6] A. Schwartz and G. E. Boyd, *J. Phys. Chem.*, **69**, 4268 (1965).

[7] I. F. Miller, F. Bernstein, and H. P. Gregor, *J. Chem. Phys.*, **43**, 1783 (1965).

[8] D. G. Smith, *J. Chem. Soc., Sect. A.*, 936 (1966).

weak-acid exchangers a decrease in the uptake of R_4N^+ ions occurs as their equivalent fraction, $x_{R_4N^+}$, on the exchanger increases. Further, with both types of exchangers a marked decrease in absorption is observed as the cross-linking of the polyelectrolyte is increased. This latter behavior contrasts with that found in the reactions of the alkali-metal cations with each other and with H^+ ion where the uptake of the preferred ion increases with cross-linking.

Apparently mutually exclusive interpretations have been proposed to account for the atypical ion-exchange reactions of the quaternary *n*-alkylammonium ions. For example, the decrease in the relative affinity in PSSA exchangers with increasing $x_{R_4N^+}$ has been attributed, *ad hoc*, to heterogeneity in cross-linking;[8] selectivity coefficient values for small $x_{R_4N^+}$ represent exchange in lightly cross-linked regions, and, for large $x_{R_4N^+}$, exchange in highly cross-linked regions of the exchanger. On the other hand, thermodynamic calculations[6] on the tetramethylammonium sodium ion-exchange reaction have indicated that an important factor causing the decrease in relative affinity for tetramethylammonium ion with increasing $x_{Me_4N^+}$ or cross-linking was the increase in configurational free energy of the molecular network of the exchanger when the relatively large Me_4N^+ ion (radius = 3.5 A) was taken up. An additional contributing factor was the interaction of Na^+ ion with the sulfonate groups in the ion exchanger which increased with $x_{Me_4N^+}$ and with cross-linking relatively more rapidly than did the interaction of Me_4N^+ ion.

There has been speculation as to the causes for the increase in binding with the size of the quaternary ammonium ion observed with strong-acid exchangers. Several authors[2,3] have argued that van der Waals forces are determining and that Coulomb forces, which are predominant for inorganic cations, play but a minor role. More recently, however, it has been suggested[9] that large, singly charged ions which do not coordinate neighboring water molecules into an hydration shell are preferentially forced out of solution into the less structured (less hydrogen-bonded) exchanger phase. This latter hypothesis, unfortunately, cannot account for the relative affinity *decrease* with increasing R_4N^+ ion size in reactions with alkali metal cation on PMA exchangers noted above. Likewise, calculations[7] based on polyelectrolyte theory which predict a lowering in binding with increasing R_4N^+ ion size cannot explain the increase with size found with strong-acid exchangers.

The calorimetric and equilibrium ion distribution measurements described in this paper were undertaken to determine if information on the enthalpy and entropy changes in the reactions of several of the quaternary *n*-alkylammonium ions with sodium ion on PSSA exchangers would facilitate a choice among the foregoing hypotheses. For example, an evolution of heat accompanying the binding of R_4N^+ ions might be expected if their selective uptake were "water-structure induced." If van der Waals absorption were a dominant factor, an enthalpy decrease which increased with ion size might be expected. If work to expand the molecular network of the cation exchanger to accommodate the R_4N^+ ion were important, the entropy change should become increasingly negative with increasing cross-linking if ion exchangers are rubber-like gels.

Experimental Section

The PSSA-type cation exchangers employed in our earlier investigation[6] were used in this research. The quaternary ammonium chlorides were obtained from Eastman Organic Chemicals, Rochester, N. Y. The tetraethyl- and tetra-*n*-propylammonium chloride preparations were those employed in an earlier research[10] where details on their purification are given.

The calorimeter has been described in other reports from this laboratory;[11] its operation was checked by measurements of the heat of solution of THAM.[12,13] Approximately 2–3 mequiv of exchanger initially in the sodium or quaternary ammonium form was used in the reactions with *ca.* 500 ml of 0.1 *M* aqueous solutions of NaCl or R_4NCl. The exchanger was recovered quantitatively after each heat of exchange measurement and the sodium plus quaternary ammonium ions it contained were eluted with 20 ml of 1.0 *M* HNO_3 solution. The total mequivalents of exchanger was determined by titration of the H^+ ion displaced by elution subsequently with 2.0 *M* NaCl solution. Aliquots of the final calorimeter solution and the HNO_3 eluent from the exchanger were analyzed for Na^+ ion by flame spectrophotometric methods and for quaternary ammonium ion by amperometric titration with standardized aqueous solutions of sodium tetraphenylborate.[14] The mequivalents of exchange reaction in the calorimeter were estimated from the known initial composition (*i.e.*, either NaR or R_4NR) of the exchanger and its final composition as determined by analysis. The calorimeter sensitivity was *ca.* 0.005 cal, and the amount of reaction was known to ±0.01 mequiv. Observed heats of exchange were corrected for the heat of pipet opening (*i.e.*, 0.010 cal evolved). The reaction temperature was 25.2°, and the results are given in defined calories (1 cal = 4.1840 absolute joules).

Preliminary measurements were made with the most lightly cross-linked exchanger (*i.e.*, nominal 0.5% DVB content) to determine if a heat effect was produced when 1.11 mequiv of the sodium form of the polyelectrolyte in equilibrium with pure water was immersed in 0.1 *M* NaCl solution. In this reaction a significant deswelling of the exchanger occurred, and the gel was invaded by external electrolyte solution (*i.e.*, "Donnan invasion"). An almost negligible heat absorption was observed (*i.e.*, *ca.* 25 cal equiv^{-1}) suggesting that either the heat of deswelling (heat absorbed) and the heat of electrolyte invasion were of opposite sign and approximately equal or, more probably, that both were quite small. Measurements of the dependence of the heat of ion exchange on the ionic strength of the external electrolyte also were performed with the results presented below.

A column technique was employed to measure equilibrium selectivity coefficients for the preferred uptake of tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium ions in their exchange reactions with sodium ion on the 0.5% DVB cation exchanger. Approximately 2 mequiv of exchanger was brought to equilibrium with mixed quaternary ammonium and sodium chloride solutions at a constant ionic strength of 0.01 or 0.1 *m* by passing a *ca.* 200-ml volume of electrolyte through the bed four to five times. The bed was drained and suction was applied to complete the removal of interstitial and surface-occluded solutions. The ions in the exchanger were eluted with 20 ml of 1 *N* HNO_3, and the bed was rinsed with 80 ml of pure water to give 100 ml of total eluate made exactly to volume. The mequivalents of exchanger in the bed were determined by acidimetric titration. Aliquots of the influent and eluent solutions were analyzed for Na^+ and for R_4N^+ ion with the methods described above. The mequivalents of R_4N^+ plus Na^+ ions in the equilibrium exchanger were in agreement with the total mequivalents of exchanger employed; the sum of the concentrations of these same ions in the equilibrium mixed electrolyte solution was in agreement with the chloride ion concentration (*ca.* 0.01 *M*) determined by microargentiometric titration. The precision of the

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(9) B. Chu, D. C. Whitney, and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **24**, 1405 (1962).

(10) S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, **69**, 2374 (1965).

(11) G. E. Boyd, F. Vaslow, and S. Lindenbaum, *ibid.*, **71**, 2214 (1967).

(12) R. J. Irving and I. Wadso, *Acta Chem. Scand.*, **18**, 195 (1964).

(13) S. Gunn, *J. Phys. Chem.*, **69**, 2902 (1965).

(14) E. Smith, L. F. Worrell, and J. S. Sinsheimer, *Anal. Chem.*, **35**, 58 (1963).

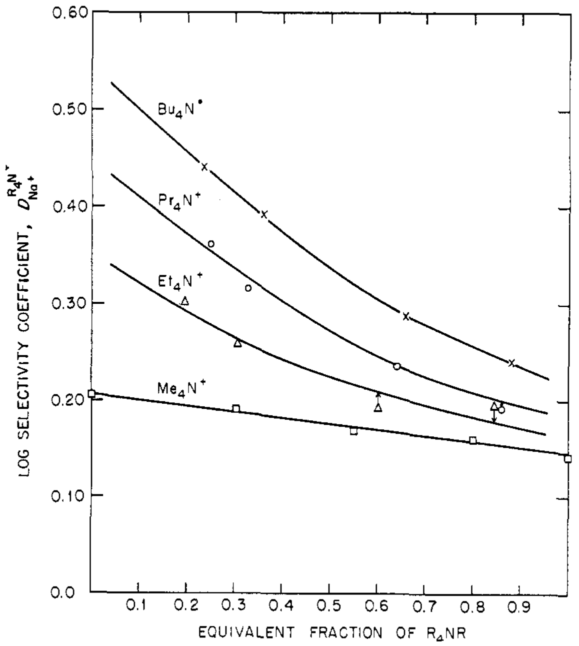

Figure 1. Equilibrium selectivity coefficients at 25° for exchange of tetra-*n*-alkylammonium with sodium ions on nominal 0.5% DVB cross-linked polystyrenesulfonate.

computed equilibrium concentration product ratios (*i.e.*, selectivity coefficients) was *ca.* ±3%, as estimated from the precision of the analyses for R_4N^+ and Na^+ ions and the propagation of errors in the mass law expression.

Results and Discussion

The heats of partial exchange, Q, measured with tetramethyl-, tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium ions against Na^+ ion on nominal 0.5% DVB cross-linked exchanger are summarized in Table I. Except with n-Bu_4N^+ ion, Q was relatively small. Interestingly, the heat evolved in the binding of Et_4N^+ ion was less than with Me_4N^+ ion, and with n-Pr_4N^+ and n-Bu_4N^+ ions heat was absorbed. With Me_4N^+ and Et_4N^+ ions Q appeared to be independent of the ion equivalent fraction in the exchanger, $x_{R_4N^+}$, within experimental error. With n-Pr_4N^+ and n-Bu_4N^+ ions, however, the exchange reaction became more endothermic as $x_{R_4N^+}$ increased. The data of Table I also reveal that the Me_4N^+–Na^+ exchange reaction became more exothermic as the ionic strength of the external mixed electrolyte decreased.

The data of Figure 1 show that the binding of quaternary ammonium ions by the 0.5% DVB exchanger increased with ion size and decreased with $x_{R_4N^+}$. The decrease of the selectivity coefficient with $x_{R_4N^+}$ cannot be attributed to heterogeneity in this exchanger as its molecular network is quite open and all its ion-exchange sites are available to even the largest quaternary ammonium ions. It seems more probable that the decreased binding of the R_4N^+ cations may be attributed to their interactions with one another when they constitute a majority of the total counterions and/or to an increased binding of the minority Na^+ counterions because of the less efficient screening of the electrostatic charges on the polyelectrolyte chains by the large quaternary ammonium ions.

The dependence of Q for the exchange of tetramethylammonium with sodium ion on exchanger cross-linking and on $x_{Me_4N^+}$ may be inferred from the data in Table II.

Table I. Heats of Partial Exchange at 25° for the Ion Exchange of Quaternary *n*-Alkylammonium Ions with Sodium Ion on Lightly Cross-Linked PSSA (0.5% DVB)

Ionic strength, μ	Initial compn, $x_{R_4N^+}$	Final compn, $x_{R_4N^+}$	Exchange, mequiv	Heat of partial exchange, cal equiv^{-1}
		Me_4N^+–Na^+		
0.1	0.00	0.98	1.18	−435
0.1	0.00	0.97	1.17	−430
0.1	0.00	0.96	1.60	−422
0.1	0.00	0.94	2.72	−437
0.1	0.00	0.95	2.56	−435
0.1	1.00	0.054	1.61	415
0.1	1.00	0.055	1.75	(450)
0.1	1.00	0.012	2.73	430
0.01	0.00	0.82	1.18	−570
0.01	1.00	0.30	1.05	496
		Et_4N^+–Na^+		
0.1	0.00	0.93	2.62	−402
0.1	1.00	0.13	2.21	396
		n-Pr_4N^+–Na^+		
0.1	0.00	0.94	2.62	542
0.1	1.00	0.13	2.16	−692
		n-Bu_4N^+–Na^+		
0.1	0.00	0.94	2.37	1980
0.1	1.00	0.17	1.90	−2640

Heat was evolved in the selective uptake of Me_4N^+ ion by the nominal 0.5 and 2% DVB cross-linked exchangers, but with the 8% DVB preparation heat was absorbed when $x_{Me_4N^+} < 0.7$. The increasing exothermicity of the exchange reactions as the fraction of Me_4N^+ ion increased in all of the exchangers was unexpected. This behavior, moreover, is the reverse of that predicted if there were heterogeneity in the cross-linking of the nominal 2, 4, and 8% DVB exchangers.

Table II. Heats of Partial Exchange at 25° for the Ion Exchange of Tetramethylammonium with Sodium Ion on Cross-Linked PSSA Exchangers[a]

Exchanger cross-linking (nominal % DVB)	Initial compn, $x_{Me_4N^+}$	Final compn, $x_{Me_4N^+}$	Exchange, mequiv	Heat of partial exchange, cal equiv^{-1}
0.5	0.00	0.95	2.56	−435
	1.00	0.012	2.73	430
2.0	0.00	0.74	8.92	−195
	1.00	0.17	9.04	270
4.0	0.00	0.62	10.04	43
	1.00	0.184	11.48	131
8.0	0.00	0.52	9.91	347
	1.00	0.22	13.83	−70

[a] Reactions at $\mu = 0.1$.

Standard free energies, $\Delta G°$, and enthalpies of exchange, $\Delta H°$, were estimated for the (hypothetical) reaction

$$\begin{aligned} &\text{NaR } (a = 1, \text{ equil. with } 0.1\ N\ \text{NaCl}) + \text{R}_4\text{NCl (aq, } a = 1) \rightleftharpoons \\ &\quad \text{R}_4\text{NR } (a = 1, \text{ equil. with } 0.1\ N\ \text{R}_4\text{NCl}) + \\ &\quad\quad \text{NaCl (aq, } a = 1) + n\text{H}_2\text{O } (a_w = 1) \end{aligned}$$

where the reactants and products are in their respective standard states. The free-energy change was computed with the relation

$$\Delta G^\circ = -2.3RT\int_0^1 \log D_0 \, dx_{R_4N^+}$$

The required D_0 values were found by correcting the observed selectivity coefficients (Figure 1) by the thermodynamic activity coefficient ratio, $\gamma_\pm^2(\mathrm{NaCl})/\gamma_\pm^2(\mathrm{R_4NCl})$, which was evaluated for aqueous 0.01 or 0.1 *m* mixtures by the method of Robinson and Stokes.[15] Necessary values for the activity coefficients of the quaternary ammonium chlorides were taken from an earlier research.[16]

The standard enthalpy change was obtained with the relation

$$\Delta H^\circ = \Delta H + \Delta\phi_L$$

where ΔH is the integral heat of cation exchange and $\Delta\phi_L$ is the relative apparent molal heat content difference, $\phi_L(\mathrm{R_4NCl}) - \phi_L(\mathrm{NaCl})$. Values of ΔH were found by graphical integrations of the differential heats of exchange, $\Delta\bar{H} = dQ/dx$, using the definition, $\Delta H = \int_0^1 \Delta\bar{H} dx_{R_4N^+}$. The required $\Delta\phi_L$'s were derived using[17] $\phi_L(\mathrm{NaCl}) = 87$ cal mole^{-1} and the values of $\phi_L(\mathrm{R_4NCl})$ at $m = 0.1$ reported in another investigation from this laboratory.[18]

Standard thermodynamic quantities for the exchange of the tetra-*n*-alkylammonium ions with sodium ion on lightly cross-linked polystyrenesulfonate are presented in Table III, and standard enthalpies, free energies, and entropies for the exchange of tetramethylammonium with sodium ion in more highly cross-linked exchangers are given in Table IV.

Table III. Standard Heats, Free Energies, and Entropies of Exchange at 298.2°K of the Tetra-*n*-alkylammonium Ions with Sodium Ion on Nominal 0.5% DVB Cross-Linked Polystyrenesulfonate (μ = 0.1)

Cation	ΔH, kcal mole^{-1}	$\Delta\phi_L$, kcal mole^{-1}	ΔH°, kcal mole^{-1}	ΔG°, kcal mole^{-1}	ΔS°, eu
Me_4N^+	−0.54[a]	−0.01	−0.55	−0.26	−1.0
	−0.44	−0.12	−0.56	−0.28	−1.0
Et_4N^+	−0.40	−0.095	−0.50	−0.33	−0.2
n-Pr_4N^+	0.62	−0.06	0.56	−0.37	3.1
n-Bu_4N^+	2.31	0.10	2.21	−0.46	9.0

[a] Reaction at ionic strength of 0.01 *m*.

Table IV. Thermodynamic Quantities at 298.2°K for the Exchange of Tetramethylammonium with Sodium Ion in Cross-Linked Polystyrenesulfonate Exchangers[a]

Cross-linking % DVB	$-\Delta H$, kcal mole^{-1}	$-\Delta H^\circ$, kcal mole^{-1}	$-\Delta G^\circ$, kcal mole^{-1}	$-\Delta S^\circ$, eu
0.5	0.44	0.56	0.28	1.0
2.0	0.24	0.36	0.095	0.9
4.0	0.07	0.19	−0.06	0.9
8.0	−0.16	−0.04	−0.27	0.8

[a] ΔG° values computed from equilibrium distribution data in ref 6.

The role of quaternary ammonium ion size is shown by the data of Table III. As the size increases the binding increases (*i.e.*, $-\Delta G^\circ$ increases); however, the exchange reaction becomes less exothermic and with the *n*-Bu_4N^+ ion there was a relatively large standard enthalpy increase. These counter-variations are reflected by the entropy change which was negative and small for Me_4N^+ and Et_4N^+ but positive and large for the *n*-Pr_4N^+ and *n*-Bu_4N^+ ions. In view of the fact that the swelling of the lightly cross-linked exchanger increases significantly when the ionic strength of the external electrolyte decreases from 0.1 to 0.01 *m* (*i.e.*, its water content increases from 2050 to *ca.* 4100 g equiv^{-1}), it is of interest to note (Table III) that ΔH° was virtually independent of μ. This result suggests that the Me_4N^+ and Na^+ counterions on the exchanger were present in an effectively high localized concentration near the polyelectrolyte chains which is not altered by changes in the distention of the molecular network caused by changes in the concentration of external electrolyte.

Observations on dilute aqueous solutions of the quaternary *n*-alkylammonium salts have suggested that the larger cations in this series interact with water so as to stabilize its hydrogen-bond structure appreciably.[19,20] In particular, recent measurements of the electric conductivity[21] and viscosity *B* coefficients[22] of the tetra-*n*-alkylammonium salts and of their effect, as determined in this laboratory, on the near-infrared absorption band at 0.97 μ in water[23] and determinations of heats of mixing[24] have confirmed the view that in aqueous solutions Pr_4N^+ and Bu_4N^+ are efficient water "structure-promotors," whereas Me_4N^+ appears to be a "structure-breaker." With the Et_4N^+ ion, which is of intermediate size, structure-forming and structure-breaking effects appear to cancel.

In the light of the foregoing discussion it may be inferred that the sign and magnitude of ΔS° for the exchange reactions of R_4N^+ with Na^+ ions on lightly cross-linked polystyrenesulfonate (Table III) give a reliable indication of the structure-altering properties of the quaternary *n*-alkylammonium ions. Thus, the removal of the structure-breaking Me_4N^+ ion from solution is accompanied by a negative ΔS° and an increase in structural order in the aqueous phase, the extraction of Et_4N^+ gives an almost zero standard entropy change, but the removal of the large *n*-Pr_4N^+ and *n*-Bu_4N^+ ions produces a large decrease in order because of the collapse of the "ice-like" regions in the aqueous phase. This collapse is signaled by a large increase in ΔS°. The assumption here is made that the entropy of transfer of Na^+ ion from the exchanger (where it exists as a fully hydrated "counterion" in an electric double layer) to the bulk solution phase gives only a very small, possibly negative contribution to the net observed ΔS° of the exchange reaction.[25] The

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(15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth & Co., Ltd., London, 1955, p 440.

(16) S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, **68**, 911 (1964).

(17) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards, Washington, D. C., 1965, NSRDS-NBS2.

(18) S. Lindenbaum, *J. Phys. Chem.*, **70**, 814 (1966).

(19) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(20) H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(21) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966).

(22) R. L. Kay, T. Vituccio, C. Zawoyski, and D. F. Evans, *ibid.*, **70**, 2336 (1966).

(23) K. W. Bunzl, *ibid.*, **71**, 1358 (1967).

(24) R. H. Wood and H. L. Anderson, *ibid.*, **71**, 1871 (1967).

(25) Interpretations of the evidence for the water-structure perturbing action of Na^+ ion vary. Entropy of solution data have been taken to indicate it to be a net structure-breaker while the viscosity *B* coefficient value suggests it is a structure-former; *cf.* J. L. Kavanau, "Water and

configuration of the polyelectrolyte chains in the lightly cross-linked ion exchanger also will change when Na^+ ions are replaced by R_4N^+ ions, but this contribution to $\Delta S°$ should be negligibly small. The R_4N^+ counterions bound to the polyelectrolyte probably exert either structure-promoting or structure-breaking effects on the water near them. The spacing of the structurally bound sulfonate ions on the polyelectrolyte chains is such, however, that some overlap of the "hydration cospheres" of the quaternary ammonium cations may occur.

The variation in $\Delta H°$ with R_4N^+ ion size at 25° shown in Table III indicates, in accordance with the equation

$$\mathrm{d} \ln K_a/\mathrm{d}T = \Delta H°/RT^2 \qquad \text{(A)}$$

where K_a is the thermodynamic equilibrium constant for the ion-exchange reaction, that as the temperature increases above room temperature the difference in binding, $n\text{-Bu}_4N^+ > n\text{-Pr}_4N^+ > Et_4N^+ > Me_4N^+$, will increase rapidly. However, at some temperature below 25° the sequence must invert and Me_4N^+ should become the most strongly bound quaternary ammonium ion. This forecast, of course, assumes that $\Delta H°$ does not vary with temperature which is probably incorrect as undoubtedly a large $\Delta C_p°$ exists. Therefore, at this time it must suffice to say that the sequence $n\text{-Bu}_4N^+ > n\text{-Pr}_4N^+ > Et_4N^+ > Me_4N^+$ holds at 25° but not necessarily at lower temperatures.

The "hydrophobic interaction" of the larger quaternary *n*-alkylammonium cations with water appears to be the cause for their preferred binding by PSSA exchangers, as thereby the extent of their contact with neighboring water molecules can be reduced. This binding is favored, however, only because of an entropy effect as an enthalpy increase ($\Delta H° > 0$) occurs when $n\text{-Pr}_4N^+$ and $n\text{-Bu}_4N^+$ ions are removed from dilute aqueous solutions. A closely analogous behavior is shown by nonpolar molecules in water, and the effect, perhaps inappropriately referred to as "hydrophobic bonding," is known to be important with proteins whose polypeptide chain configurations are sometimes determined by the tendency of their nonpolar side chains to escape from aqueous phases.[26–28]

The effect of increased PSSA exchanger cross-linking on the heat of exchange is noteworthy. The data of Table IV show that the preferential uptake of Me_4N^+ ion by the sodium forms of nominal 0.5 and 2% DVB exchanger was caused by the enthalpy decrease in the reaction. However, $\Delta H°$ for the 2% DVB preparation was smaller than for the lightly cross-linked exchanger; further, the reaction became endothermic in the 4 and 8% DVB exchangers. Interestingly, the replacement of Na^+ by Me_4N^+ ion took place in all four exchangers with an almost identical $\Delta S°$, so that the decrease in quaternary ammonium ion binding and the selectivity coefficient reversal with increased cross-linking can be attributed to the increase in $\Delta H°$. The enthalpy change required to increase the volume of the molecular network of the 8% DVB exchanger to accommodate the Me_4N^+ ion may be estimated as 0.54 kcal mole^{-1} from the difference in $\Delta H°$ (Table III) for the 8 and 0.5% DVB exchangers, respectively. The increase in the free energy of the 8% DVB exchanger when it is transformed from the sodium to the tetramethylammonium salt form may be estimated with the relation

$$\Delta G°(\text{network}) = \int_{V_i}^{V_f} \pi \, \mathrm{d}V_e \qquad \text{(B)}$$

where $V_i = 315$ and $V_f = 382$ ml mole^{-1} are the initial (Na form) and final (Me_4N form) magnitudes of the equivalent volume, V_e, respectively, and π is the strain in the network (*i.e.*, dimensions of pressure). An "equation of state" relating π and V_e at constant temperature may be derived from the results from another investigation;[6] for the 8% DVB preparation, $\pi = 1.05V_e - 239$ and $\Delta G°(\text{network}) = 0.21$ kcal mole^{-1}. Combining $\Delta G°$ and $\Delta H°$ the result, $\Delta S°(\text{network}) = 1.1$ eu, is obtained.

This finding that the entropy of the polyelectrolyte molecular network *increases* with swelling is completely contradictory to the idea that ion exchangers are rubber-like gels. The entropy of network swelling for a statistical network with chain lengths equal to those in an 8% DVB cross-linked ion exchanger may be estimated approximately with the Flory–Rehner theory to be *negative* and no greater than one- or two-tenths of a unit. Moreover, with rubber the enthalpy increase on extension is small compared with the entropy decrease which occurs because of the reduction in the number of configurations available to the molecular chain segments in its structure.[29,30] The result above indicates that cross-linked PSSA exchangers behave as if they were in a crystalline or more probably in a glass-like state where an entropy increase with expansion would be expected. This hypothesis is supported by the results from an investigation conducted some time ago[31] wherein Young's moduli of elasticity of the order of 10^8–10^9 dynes cm^{-2} were found with cross-linked PSSA exchangers. These moduli are one to two orders of magnitude larger than those for rubber.

Measurements of the elastic behavior of a sulfonated phenol–formaldehyde-type cation exchanger have supplied additional support for the view that cross-linked ion exchangers are comparable to the glassy state of rubber below its gel temperature.[32] The retractile force exerted on stretching thin strips of exchanger immersed in aqueous electrolyte solution was found to *decrease* with increasing temperature, and the entropy change, $T(\mathrm{d}S/\mathrm{d}l)_{P,T}$ was found to be positive and slightly smaller than the enthalpy variation, $(\mathrm{d}H/\mathrm{d}l)_{P,T}$.

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Solute-Water Interactions," Holden-Day Inc., San Francisco, Calif., 1964, p 55 ff.

(26) W. Kauzman, *Advan. Protein Chem.*, **14**, 1 (1959).

(27) G. Némethy and H. A. Sheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962).

(28) G. Nemethy, *Angew. Chem. Intern. Ed. Engl.*, [3] **6**, 195 (1967).

(29) L. R. G. Treloar, "The Physics of Rubber," Oxford University Press, London, 1949.

(30) P. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(31) G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

(32) D. Koschel and R. Schlögl, *Z. Physik. Chem.* (Frankfurt), **11**, 137 (1957).