carbons are located at the α or β position with respect to the polymer main chain, the observed relations between the mean residue optical rotation [M]D and the optical purity of the polymerization system were nonlinear. Our preliminary studies on the basis of the conformational analyses presented in this paper seems to be quite consistent with these observations. The general conclusions reached in the present treatment regarding the stereochemistry of poly-α-olefins are thus given further support. Full details will be published elsewhere.

Acknowledgment. The author wishes to thank Professor P. J. Flory of Stanford University and Dr. R. Ullman of Ford Motor Company for their valuable discussions. Grateful acknowledgment is also expressed to Mr. M. Ishii of Showa Denko Company for coding and running the computer program.

The Poisoning of Ion-Exchange Resins. Inhibition of Cation Exchange by Cationic Surface-Active Agents

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Abstract: It has been observed that low concentrations of amphiphilic cations, *e.g.*, the cetyldimethylbenzylammonium cation, can markedly reduce the rate of Na^+–Na^+ exchange between the Na^+ form of a styrene-based sulfonic acid type cation exchanger and an aqueous solution of a sodium salt. It is proposed that the amphiphilic ion exerts its effect by forming a lipid-like layer around the resin particle which impedes ion transfer between the aqueous and resin phases. The model bears a resemblance to present-day concepts of the biological membrane and is pertinent to the fouling of ion-exchange resins.

Under appropriate conditions the exchange of small inorganic ions between synthetic ion-exchange resins and aqueous solutions takes place rapidly.[1–3] The exchange reactions which are diffusion controlled can typically have half-times on the order of 1 min. It has been discovered that certain amphiphilic ions, *e.g.*, cationic and anionic surfactants, can intervene in these fast reactions to produce marked inhibitory effects. It is believed that this inhibition is a result of the formation of a lipid-like layer at the resin–solution interface which impedes ion transfer between the aqueous and resin phases. There are aspects of such a model which have qualitative parallels in the Davson and Danielli concept of the biological cell membrane.[4]

Experimental Section

Preparation of Resins. A sample of very uniformly sized resin particles was obtained by screening a quantity of commercial cation-exchange resin, Dowex[5] 50W X8 (20–50 mesh) Na^+ form, and harvesting those beads which stuck in a 30-mesh (U. S.) screen. The uniformly sized resin was labeled with radiosodium by contacting it for 2 hr with an aqueous solution of sodium hydroxide which contained the ^{22}Na radioisotope.

Measurement of Ion-Exchange Rates. A small quantity (about 0.2 g) of the radioactively labeled resin was introduced into a U-shaped tube provided on one arm with a plug of crumpled platinum wire which acted as a retainer for resin when solutions were pumped through the U tube. The tube containing the labeled resin was in turn placed in the well of a γ-scintillation detector which was associated with a rate meter–recorder combination (Figure 1). In this way, an instantaneous record of the resin activity was provided throughout the course of a kinetic experiment. The ion-exchange reaction was effected by pumping through the U tube an appropriate aqueous electrolyte (unlabeled) at such a rate (12 ml/min) that the amount of the exchanging ion supplied to the resin was well in excess of the resin demand. The method thus satisfied the criteria of the "infinite bath technique" of Boyd, *et al.*[1] The rate of removal of sodium ion from the resin, *i.e.*, the rate of exchange, was obtained from the record of the decline of activity of the resin as expressed on the recorder trace. The history of the exchange is expressed graphically as a plot of F *vs.* time (t), where F is the fraction of sodium removed by the aqueous electrolyte.

Surface-Active Agents. The surface-active agents used were obtained as commercial preparations which in some cases contained, in addition to the major component, appreciable quantities of closely related species. The surface-active cationic species studied were cetyldimethylbenzylammonium ($CDMBA^+$),[6a] lauryldimethylbenzylammonium ($LDMBA^+$),[6b] cetylpyridinium (CPy^+),[6c] cetyltrimethylammonium ($CTMA^+$),[6c] and laurylisoquinolinium (LIQ^+).[6d]

Experimental Results and Discussion

Rate of Uninhibited Na^+–Na^+ Exchange. Since it will be a major aim in this paper to demonstrate the inhibitory effect of certain amphiphilic ions on fast exchange reactions, it is instructive to first examine a typical uninhibited reaction. The self-exchange of sodium ions between a resin and solution phase is a typically fast reaction whose mechanism is well understood.[1] Moreover, the reaction is particularly amenable to examination by the radiochemical technique. The sodium form of Dowex 50W X8 (30 mesh) was flushed with 0.1 M NaCl and the fractional exchange determined as a function of time. The results are illustrated in Figure 2. Exchange is essentially complete within a few minutes and the rate may be conveniently expressed as a half-time, *i.e.*, the time taken to attain half-

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[1] G. E. Boyd, A. W. Adamson, and L. S. Myers, *J. Am. Chem. Soc.*, **69**, 2836 (1947).

[2] D. Reichenberg, *ibid.*, **75**, 589 (1953).

[3] F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 250 ff.

[4] H. Davson and J. F. Danielli, "Permeability of Natural Membranes," 2nd ed, Cambridge University Press, London, 1952.

[5] Dowex is a registered trademark of The Dow Chemical Co.

[6] (a) "Cetol," Fine Organics, Inc.; (b) "Culversan 60LC," Culver Chemical Co.; (c) Fine Organics, Inc.; (d) "Isothan Q-15" Onyx Chemicals.

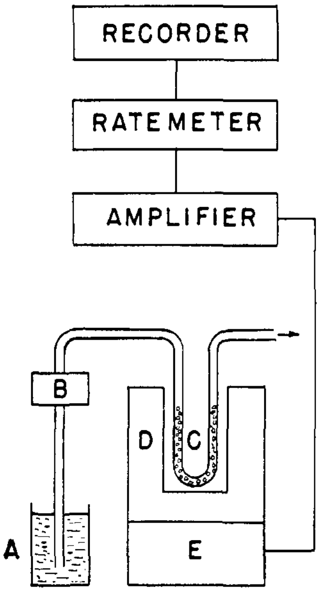

Figure 1. Experimental arrangement: (A) aqueous solution, (B) peristaltic pump, (C) ^{22}Na-labeled Dowex 50, (D) well-type γ-scintillation crystal, (E) photomultiplier.

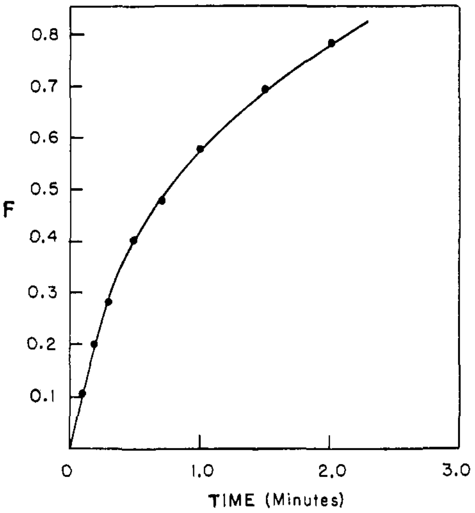

Figure 2. The exchange of Na$^+$ between Na$^+$ resin (Dowex 50W X8; 30 mesh) and 0.1 M NaCl.

exchange. The half-times determined for 0.2 and 0.05 M NaCl were 0.65 and 1.2 min, respectively, indicating some control being exerted by the diffusional resistance in the bounding Nernst layer. Most of the subsequent data will be related to the exchange with 0.1 M NaCl ($t_{1/2}$ = 0.75 min) which will occasionally be referred to as "the control."

Effect of CDMBA$^+$ on Na$^+$–Na$^+$ Exchange. The effect of a relatively low concentration of a quaternary surfactant on the exchange of sodium ions between the resin and aqueous phase is illustrated in Figure 3. The sodium-22 labeled resin was contacted with an aqueous solution, which as well as containing Na$^+$ (0.1 M), also contained the cetyldimethylbenzylammonium cation (CDMBA$^+$) at the much lower level of 0.001 M. The progress of exchange in this reaction is illustrated by curve B while curve A refers to the control. Initially there was rapid removal of sodium from the resin which in speed paralleled the control, but, when approximately

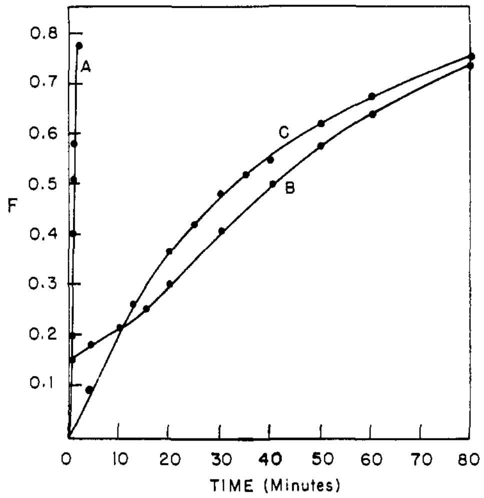

Figure 3. The exchange of Na$^+$ between Na$^+$ resin and (A) 0.1 M NaCl, (B) 0.1 M NaCl + 0.001 M CDMBA$^+$Cl$^-$, (C) 0.1 M NaCl + 0.001 M CDMBA$^+$Cl$^-$ after pretreatment of resin with 0.001 M CDMBA$^+$Cl$^-$.

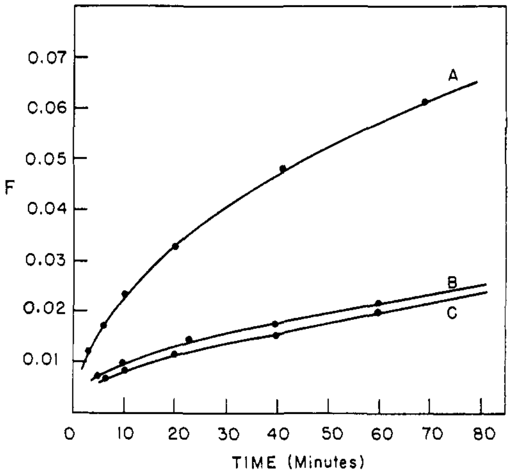

Figure 4. The kinetics of the exchange reaction Na$^+$ resin + Q$^+$(soln) $\rightarrow$ Q$^+$ resin + Na$^+$(soln): (A) Q$^+$ = CTMA$^+$, (B) Q$^+$ = LIQ$^+$, (C) Q$^+$ = CDMBA$^+$.

15% exchange was reached, an abrupt retardation in the exchange rate was observed. Whereas the control required only 0.75 min to reach half-equilibrium, this retarded reaction took 40 min. It is convenient at this point to introduce what is believed to be the explanation for this marked reduction in rate. When resin is contacted with an aqueous phase containing Na$^+$ and an amphiphilic cation Q$^+$, *e.g.*, CDMBA$^+$, two exchange reactions are initiated and take place concurrently, *viz.* displacement of Na$^+$ on the resin by (1) Na$^+$ in solution, and (2) Q$^+$ in solution. Previous work[7] and work in this laboratory (Figure 4) has established that the ion exchange of Na$^+$ by a species as large as CDMBA$^+$ is extremely slow. It is a reasonable assumption therefore that the exchange represented by Figure 3B is predominantly due to Na$^+$–Na$^+$ exchange with a minor amount attributable to CDMBA$^+$–Na$^+$ exchange. Nevertheless, this minor amount of CDMBA$^+$ absorbed by the resin has a profound effect on the concurrent Na$^+$–Na$^+$ exchange. How might

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[7] (a) D. K. Hale, D. I. Packham, and K. W. Pepper, *J. Chem. Soc.*, 844 (1953); (b) T. R. E. Kressman, *J. Phys. Chem.*, **56**, 118 (1952).

this come about? Although the bulk resin phase is relatively inaccessible to the CDMBA$^+$ species, its surface is not so limited and can rapidly adjust to its equilibrium counterion requirements. It is proposed that the surface of the resin, on contact with Na$^+$ and CDMBA$^+$, rapidly reaches an equilibrium condition wherein many, if not a majority, of the surface sites will be associated with CDMBA$^+$ species. It is further assumed that this exchanged CDMBA$^+$ can adsorb more CDMBA$^+$ in excess of the surface ion-exchange capacity and lead to a highly organized interfacial structure as illustrated in Figure 5. Such an organization of amphiphilic species at the resin interface thereby interposes a lipid-like membrane between the aqueous and resin phases which could constitute a barrier to the transfer of sodium ions and lead to a marked reduction in exchange rate. The assumption of back-to-back adsorption of excess CDMBA$^+$ finds support in two other observations. (1) At a concentration of 10^{-3} *M*, CDMBA$^+$Cl$^-$ is well above its critical micelle concentration (4.2×10^{-5} *M*)[8] Since the formation of micelles is a manifestation of the tendency for the nonpolar regions of the surfactant ion to aggregate, it is to be expected that the localized high surface density of exchanged CDMBA$^+$ should be conducive to added association of CDMBA$^+$ in excess of the exchange capacity. (2) Tamamushi and Tamaki[9] have shown in a study of the exchange of long-chain electrolytes onto cation exchangers that in certain cases adsorption in excess of the cation-exchange capacity can be observed.

As well as being involved in this surface exchange, CDMBA$^+$ will also slowly exchange into sublayers of the resin forming a relatively more massive lipophilic region which, although probably lacking the order of the surface layer, would also be expected to impede Na$^+$ transport. Thus, if sites in the sublayer are predominantly occupied by large sluggish Q$^+$ ions, then inhibition of small ion transport across the sublayer can be expected for at least two reasons: (1) a sparsity of mobile carriers, or in other words, few "unpoisoned" sites; and (2) the hydrophobic character of this layer resulting from the oleophilic character of the predominant counterion species Q$^+$.

It is especially noteworthy that inhibition occurred within a very short time (~0.2 min) after initiation of the exchange reaction. Since only a very small amount of Q$^+$ could be absorbed during this period, the rapid onset of poisoning attests to the remarkable efficacy of the Q$^+$ layer in inhibiting Na$^+$–Na$^+$ exchange. Estimates of the thickness of the Q$^+$ layer obtained by extrapolation of the data of Figure 4 to short times must necessarily be uncertain. However, it is possible to place an upper limit on the amount of Q$^+$ picked up by the resin at the onset of inhibition since it cannot exceed that amount of Q$^+$ supplied to the resin in 0.2 min. This may be calculated simply from the concentration of Q$^+$ and the flow rate of the aqueous phase past the resin sample. Such a calculation leads to the conclusion that the thickness of the Q$^+$ layer on a 30-mesh (600-μ diameter) resin at the onset of inhibition does not exceed 0.75 μ.

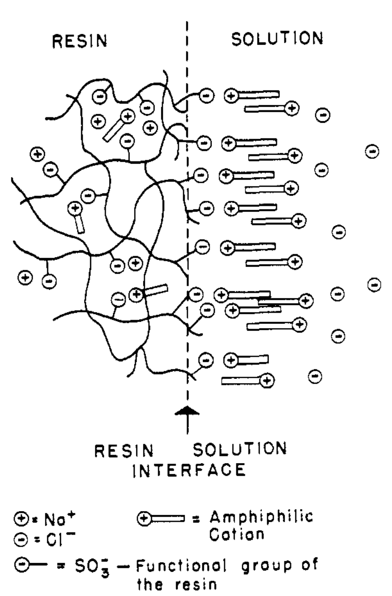

Figure 5. Model of the lipid-like layer at the resin–solution interface.

Returning to Figure 3, it is proposed that the initial surge of exchange (curve B) corresponds to Na$^+$–Na$^+$ exchange which can take place during the short (about 0.2 min) but finite time necessary to establish the interfacial barrier. This initial surge can be eliminated if, just prior to the main exchange reaction, the resin is given a brief (1 min) treatment with 0.001 *M* CDMBA$^+$ (curve C). What remains unexplained is the fact that this reaction was observed to proceed more rapidly ($t_{1/2}$ = 34 min) than that which involved no pretreatment with CDMBA$^+$.

Effect of Other Cationic Surfactants on Na$^+$–Na$^+$ Exchange. The effect of a number of other cationic surfactants on Na$^+$–Na$^+$ exchange was examined by pretreating the ^{22}Na-labeled resin with a 0.001 *M* solution of the surfactant followed immediately by reaction of the resin with a solution which was 0.1 *M* NaCl and 0.001 *M* surfactant. The inhibitory effects may be gauged from a comparison of the half-times of Na$^+$–Na$^+$ exchange recorded in Table I. The range of inhibitory effects is large, with the laurylisoquinolinium species being outstanding in its ability to retard exchange. The inhibition by LIQ$^+$ was explored in more detail (Figure 6) by varying the concentration of LIQ$^+$ at a fixed level of NaCl (0.1 *M*) and eliminating the LIQ$^+$ preconditioning step. The kinetic curves all display the same behavior, namely an initial rapid exchange and an abrupt transition to the retarded region. Moreover, the amount of exchange that takes place

Table I. Inhibition of Na$^+$–Na$^+$ Exchange on Dowex 50 by Various Amphiphilic Cations (Q$^+$)

Q$^+$	$t_{1/2}$, min
Control (no Q$^+$)	0.75
Cetyltrimethylammonium (CTMA$^+$)	6.5
Cetylpyridinium (CPy$^+$)	16.0
Lauryldimethylbenzylammonium (LDMBA$^+$)	25.0
Cetyldimethylbenzylammonium (CDMBA$^+$)	34.0
Laurylisoquinolinium (LIQ$^+$)	520

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(8) P. H. Cardwell, *J. Coll. Interface Sci.* **22**, 430 (1966).
(9) B. Tamamushi and K. Tamaki, *Trans. Faraday Soc.*, **55**, 1013 (1959).

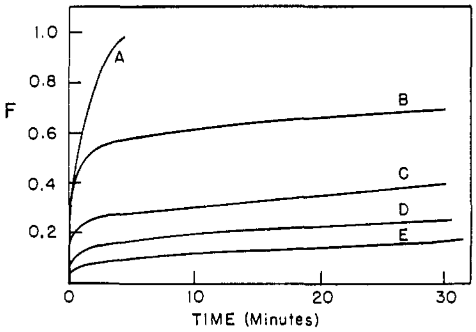

Figure 6. The effect of LIQ^+ concentration on the exchange of Na^+ between Na^+ resin and 0.1 M NaCl + xM LIQ^+Cl: (A) $x = 0$, (B) $x = 2 \times 10^{-4}$, (C) $x = 5 \times 10^{-4}$, (D) $x = 10^{-3}$, (E) $x = 2 \times 10^{-3}$.

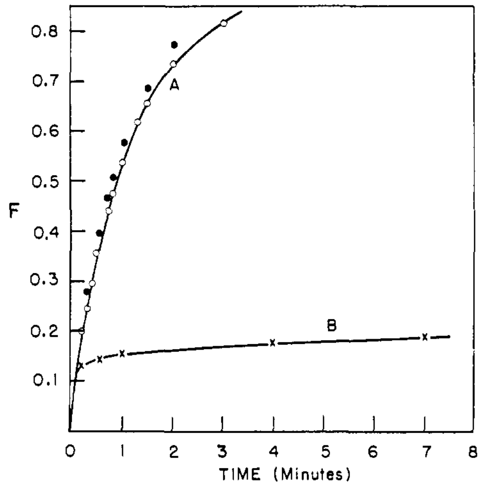

Figure 7. Effect of pretreatment of Na^+ resin with polyvinylbenzyltrimethylammonium ($PVBTMA^+$) chloride on Na^+ exchange between Na^+ resin and 0.1 M NaCl + 0.001 M $CDMBA^+Cl^-$: (×) no pretreatment with $PVBTMA^+$, (⊙) pretreatment with $PVBTMA^+$, (●) control.

before the inhibition depends on the concentration of LIQ^+. If, as discussed earlier, the rapid exchange corresponds to that time during which the interfacial barrier is being established, then one obvious explanation of the effect of LIQ^+ concentration emerges. Since one would expect the rate of growth of the interfacial barrier to depend on the rate of transmission of LIQ^+ to the interface, the growth rate would naturally depend on the concentration of LIQ^+ in the aqueous phase. As the LIQ^+ concentration is lowered, barrier formation is delayed and the uninhibited Na^+–Na^+ exchange is concomitantly prolonged. It is noteworthy that, when retardation has been established, the subsequent rate of exchange is practically independent of the LIQ^+ concentration as adjudged by the slopes of the curves in the retarded region.

In attempting to explain the range of inhibition displayed by the various amphiphilic cations (Q^+), the ion exchange competition between Na^+ and Q^+ for surface sites must necessarily be considered. A high proportion of resin sites occupied by Q^+ may be expected to favor a compact impermeable layer, whereas the reverse would lead to a layer made "leaky" through infiltration by sodium ions. The degree of saturation of sites by Q^+ will depend on a number of factors including (1) the relative concentrations of Na^+ and Q^+ and (2) the relative affinities of Na^+ and Q^+ for the sulfonate functional group of the resin. It is well known that aromatic substituents in organic ions increase their affinity for styrene-based resins.[10] Consequently from the order of effectiveness in Table I, one could derive a correlation between the affinity of Q^+ for the $-SO_3^-$ sites and its ability to form a more or less "leak-free" barrier on the resin surface. It is worthy of note that the laurylisoquinolinium species seems particularly successful in this competition for surface sites. At a level of 2×10^{-4} M, LIQ^+ was capable of exerting an inhibitory effect despite the fact that the sodium ion concentration was 500-fold greater (Figure 6, curve B).

Effect of Polyelectrolyte Pretreatment of the Resin on Its Tendency to Poison. In developing the model of the barrier layer, distinction was made between Q^+ adsorbed at the resin solution interface and that adsorbed into the more massive layer beneath. Such a distinction is justified on the grounds that Q^+ could conceivably form a highly organized lipid-like layer in the relatively unrestricted environment at the interface. It was further argued that the inhibition might be attributable in large part to such a highly organized layer. The very abrupt onset of inhibition suggested that this might be the case, but, to obtain possible substantiation of this idea, the following experiment was devised. A sample of ^{22}Na-labeled Na-form resin was briefly treated with a dilute solution (0.001 M) of a cationic polyelectrolyte, polyvinylbenzyltrimethylammonium chloride. When this treated resin was flushed with 0.1 M NaCl + 0.001 M $CDMBA^+$, an exchange reaction as described by curve A in Figure 7 was observed. This may be compared with the control (solid points) and the reaction with 0.01 M NaCl + 0.001 M $CDMBA^+$ (curve B) obtained without prior treatment with the polyelectrolyte. It was assumed, and subsequently verified experimentally, that the polyelectrolyte, by virtue of its size, would exchange only onto the surface sites of the resin. It was anticipated therefore that its presence there could interfere with and perhaps prevent the formation of the $CDMBA^+$ surface layer. It was further assumed that the presence of polyelectrolyte at the interface would not interfere with adsorption of Q^+ into the more massive layer beneath the interface. Consequently, if the Q^+ surface layer was the dominant barrier, then immunity to poisoning of polyelectrolyte-treated resin was a predictable outcome. The fact that resin pretreated with polyelectrolyte reacted almost as fast as the control gives some credibility to the above argument, namely that the initial surface layer formed is the major barrier to transfer of small hydrophilic ions such as sodium. However, observations on the influence of resin cross-linking on its tendency to poison can be reconciled with a model which deemphasizes the dominance of the surface layer.

Effect of Resin Cross-Linkage on Its Tendency to Poison. Samples of Dowex 50W X4, Dowex 50W X8, and Dowex 50W X12, cation-exchange resins suitably screened (30 mesh) and labeled with ^{22}Na, were contacted with 0.1 M NaCl + 0.001 M $LDMBA^+Cl^-$. No polyelectrolyte pretreatment was involved. The results of this series of experiments are illustrated in Figure 8.

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

It is evident that the lower the degree of cross-linking the more prone the resin is to poisoning as adjudged by the slope of the F *vs.* t plot in the retarded region. Since a lower degree of cross-linking will lead to more rapid invasion of the resin by Q^+ with a concomitantly more rapid growth of the barrier layer, the above observations are consistent with attributing the inhibition to the massive Q^+ layer rather than the surface layer. The immunity to poisoning conferred by polyelectrolyte pretreatment would then invite the conclusion that the polyelectrolyte at the resin surface impedes transfer of Q^+ into the bulk resin phase as well as interfering with the Q^+ surface layer.

The Co-Ion Effect. In the simple uninhibited case of Na^+–Na^+ exchange, the co-ion which accompanies the Na^+ in solution has little effect on the rate of exchange.[11] However, in a system inhibited by an amphiphilic cation, the nature of the co-ion affects the rate of exchange quite considerably. This co-ion effect may be seen in the data of Table II which summarize the half-times of exchange reactions involving Na-form resin and solutions 0.1 M NaX + 0.001 M CDMBA^+.

Table II. Effect of Co-Ion (X^-) on the Exchange Reaction Na Resin *vs.* 0.1 M NaX + 0.001 M CDMBA^+

X^-	$t_{1/2}$, min
I^-	5.9
$\mathrm{NO_3}^-$	16.9
Cl^-	34.0
$\mathrm{CH_3COO}^-$	148.0

It has not been possible at this stage to develop an unambiguous explanation of the co-ion effect, but it is interesting to note that the order of effectiveness parallels the order of anion-exchange affinities.[12] If it is assumed that the displacement of a surfactant species, Q^+, from the resin surface depends not only on the sodium ions but rather on the concerted action of sodium and its co-ion X^-, then co-ions with the highest affinity for quaternary ammonium would offer the most assistance in this respect and lead to the most "leaky" barriers. On this basis the co-ions of Table II follow their expected order of efficacy.

Effect of Organic Solvents in an Inhibited System. When relatively small amounts of certain organic solvents were added to an inhibited system, an increase in rate was observed. Thus, whereas the reaction of Na resin with 0.1 M NaCl + 0.001M LIQ^+ took several hours to reach half-equilibrium when pure water was the solvent, the half-time was reduced to 30 min when the solvent was 96% $\mathrm{H_2O}$–4% *n*-butyl alcohol (v/v). It is believed that the *n*-BuOH is extracted into the lipid-like surfactant layer, thereby increasing its polarity and promoting the transfer of the very polar sodium ion. Such an effect has parallels in the work of Rosano,[13] wherein he found that the transfer of water through thick nonpolar oil layers was facilitated by the presence of polar organic additives in the aqueous phase.

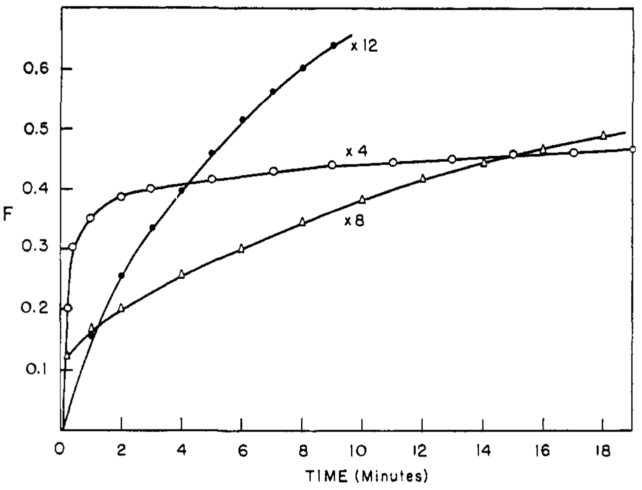

Figure 8. Effect of resin cross-linking on Na^+ exchange between Na^+ resin and 0.1 M NaCl + 0.001 M $\mathrm{LDMBA}^+\mathrm{Cl}^-$.

Donnan Membrane Effects. The influence of Donnan or double-layer potentials is a necessary consideration in any treatment of diffusion of charged species across charged interfaces. In the case of cation exchange with an uninhibited resin, transfer of sodium ions across the resin solution interface is promoted by the Donnan potential at the interface. However, on examination of the model depicted by Figure 5, it is evident that the Na^+ in solution sees a surface which, as far as charge is concerned, is just the opposite of that in the uninhibited system. The double layer comprising the adsorbed cationic surfactant and its associated diffuse layer of negative counterions is more characteristic of an anion-exchange resin, and one would therefore expect Na^+ in the solution phase to be excluded from this region. This invites the conclusion that it is this exclusion effect that is the origin of the slow rates of Na^+–Na^+ exchange in an inhibited system. However, some approximate calculations of the exchange rate which would be expected, if this were the sole rate-controlling effect, give values that are much higher than those observed. It is therefore concluded that, whereas the Donnan potential can undoubtedly contribute to the retardation, the major effect derives from the low diffusion rate of ionic species across the lipid-like region of the interface.

Inhibition of Anion-Exchange Reactions. An obvious extension of this work was to examine the effect of anionic amphiphilic ions on simple reactions involving anion-exchange resins. A few experiments were performed which demonstrated that similar inhibitions are found in such systems; for example, an alkyl benzenesulfonate species markedly retards Cl^-–$\mathrm{NO_3}^-$ exchange on Dowex 1X8, a typical quaternary ammonium anion-exchange resin.

Implications in Resin Fouling. Dissolved organic constituents such as humic and fulvic acids which occur in natural waters pose problems in deionization systems. The problem manifests itself as a marked reduction in the system's ability to produce high-quality (low conductivity) water. The drop in efficiency is attributable to the limited capacity available to such large organic contaminants in conventional anion exchangers. This leads to an early breakthrough of the contaminants which being ionic lead to an unacceptably high con-

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(11) See ref 3, p 251.

(12) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1951).

(13) H. L. Rosano, *J. Coll. Interface Sci.*, **23**, 73 (1967).

ductivity of the effluent water. It is pointed out, however,[14] that the accumulation of the contaminant on the resin does not interfere with the removal of inorganic substituents. In light of the present work, it may be concluded that in these instances the layer of contaminant which accumulates on the outside of the resin is not sufficiently thick or lipid-like to impede the desirable function of the resin, namely its ability to remove small inorganic ions. The work described in this contribution does indicate, however, that if the organic contaminant has the appropriate size and constitution, *e.g.*, an amphiphilic ion, then the resin's ability to remove small inorganic ions can also be impaired.

Implications in Biological Membrane Behavior. Mass transfer across lipid-like monolayers is of interest to biologists because of its obvious relevance to cell permeability. The influence of monolayers on gas transmission across the air–water interface is quite amenable to study, and considerable success has been realized in manipulating and studying this particular interface.[15] However, the construction of significant areas of stable lipid layers between contiguous aqueous phases is experimentally a much more demanding task. Resin solution systems afford a very convenient source of two aqueous phases capable of stable coexistence when in contact and possessing a well-defined interfacial area of considerable magnitude. Were it possible to interpose lipid layers between these phases, then this resin–lipid layer–solution system might afford a very convenient experimental means of studying lipid membrane transport. The model that has been proposed in this contribution to explain the inhibitory effects observed places a special emphasis on the lipid-like character of the interfacial region. If this is a legitimate representation of the mechanism, then this work demonstrates that ion-exchange resin systems may provide a useful additional tool in the study of transfer across lipid membranes.

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[14] R. Kunin, "Amber-Hi-Lites," No. 88, 1965, Rohm & Haas Co., Philadelphia, Pa.

[15] V. K. La Mer, Ed., "Retardation of Evaporation by Monolayers," Academic Press Inc., New York, N. Y., 1962.

Reactions of He^3H^+ Ions with Gaseous Hydrocarbons. III. Cyclopropane, Propane, Isobutane, and *n*-Butane

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Abstract: The reactions of the He^3H^+ ions, formed from the decay of molecular tritium, with *c*-C_3H_6, C_3H_8, *n*-C_4H_{10}, and *i*-C_4H_{10} were investigated at the pressures of 20 and 760 torr, under conditions excluding the interference of radiolytic processes. The nature and the yields of the tritiated reaction products, determined by radio gas chromatography, are consistent with the hypothesis that the He^3H^+ ions attack the gaseous hydrocarbons, giving excited protonated species, which dissociate into neutral fragments and simpler ions along energetically allowed pathways. The formation of the observed labeled products can be rationalized taking into account the various fragmentation processes and the consecutive reactions of the fragment ions with the inactive hydrocarbon. The reaction of He^3H^+ ion with *c*-C_3H_6 yields labeled C_3H_6 hydrocarbons, whose formation requires the stabilization of a fraction of the protonated ions. Furthermore, the high yield of tritiated *c*-C_3H_6 suggests a cyclic structure for the protonated ion and provides direct evidence for the existence of the cyclopropanium ion often postulated in different fields of chemistry. In the case of C_3H_8 and *n*-C_4H_{10}, on the other hand, the results can be interpreted without requiring the intervention of the stabilized protonated ions.

In the first paper of this series,[1] the β decay of molecular tritium was shown to provide a simple and convenient means to introduce an extremely reactive protonating agent, the He^3H^+ ion, into gaseous systems at atmospheric pressure, and to study its reactions by tracer techniques. The method was applied, under conditions excluding any interference from radiolytic processes, to the study of the ionic processes involved in the protonation of toluene,[1] and of methane and ethane,[2] by the He^3H^+ ions.

The present paper deals with the protonation of cyclopropane, propane, and the butanes with the same reagent.

The study of the reactions of the He^3H^+ ions with cyclopropane is of special interest, since the analysis of the tritiated reaction products provides some hope of establishing the cyclic structure of the protonated cyclopropane ion, which obviously cannot be demonstrated by mass spectrometric techniques. Such experimental evidence would represent a direct support for the existence of this cyclic $C_3H_7^+$ ion, often postulated to account for certain anomalies in the mass spectra of the alkanes,[3–5] and as intermediate in a variety of reactions occurring in solution.[6–8]

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[1] F. Cacace and S. Caronna, *J. Am. Chem. Soc.*, **89**, 6848 (1967).

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