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Selectivity of M^+–H^+ Ion-Exchange Absorption on Sulfonic Resins in Ternary Solutions

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ABSTRACT

The selectivity of M^+–H^+ ion-exchange absorption ($M^+ = Na^+$ or K^+) on sulfonated acrylonitrile–butadiene–styrene copolymer previously crosslinked with resol has been investigated in ternary MCl–HCOOH–H_2O solutions at 298 K. Hypotheses are put forward concerning the factors determining the selectivity of the cation-exchange resins in solutions of weak organic acids.

INTRODUCTION

The use of mixed or nonaqueous solvents in ion-exchange reactions is of considerable interest in connection with the growing use of the ion-exchange method for the purification and isolation of various organic substances, in particular weak organic acids. A large amount of work on enhanced selectivity of ion exchangers in uni-univalent exchange in a variety of mixed solvent as well as in nonaqueous media have been developed (1–11) and experimentally verified (12–14). This paper describes a study of the selectivity of M^+–H^+ ion-exchange absorption on synthesized sulfonated acrylonitrile–butadiene–styrene copolymer previously crosslinked with various amounts of resol (5, 10, 15, and 20% wt/wt) in ternary MCl–HCOOH–H_2O solutions. The selectivity coefficient (K_H^M) of the general ion-exchange reaction

$$M_W^+ + H_R \rightleftharpoons M_R + H_W^+ \qquad (1)$$

where the subscripts W and R refer to the ions ($M^+ = Na^+$ or K^+) in

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the ternary solutions and resinous exchanger, respectively, is given by

$$K_{\mathrm{H}}^{\mathrm{M}} = \frac{X_{\mathrm{MR}}}{X_{\mathrm{HR}}} \frac{C_{\mathrm{HW^+}}}{C_{\mathrm{MW^+}}} \qquad (2)$$

where X_{MR} and X_{HR} are the equivalent ionic fractions of the ions in the resin phase, and $C_{\mathrm{HW^+}}$ and $C_{\mathrm{MW^+}}$ are the concentrations of the ions in ternary solutions.

EXPERIMENTAL

Chemicals

Sodium and potassium chloride (BDH) were used. All other chemicals and formic acid were of analar grade. Sulfonated acrylonitrile–butadiene–styrene copolymer crosslinked with various amounts of resol (5, 10, 15, and 20% wt/wt) were synthesized as reported in an earlier investigation (15). It was conditioned and sieved to 420–250 μm and made free from fine particles, since the resin was subjected to sodium–hydrogen cycles and air dried to constant weight (16, 17). The exchange capacities of the exchangers were 3.40, 2.81, 2.21, and 1.83 meq·g^{-1} of dry H$^+$-form resin, respectively.

Equilibrium Procedure

All equilibrium studies were carried out by using 0.5 g of the exchanger in ternary $MCl–HCOOH–H_2O$ solutions (50 mL) in glass-stoppered flasks at constant temperature (298 K). The reaction flasks were shaken intermittently during the interval time of equilibrium (about 6 hours) under thermostatic conditions controlled within ±0.1°C. In each series of experiments the concentration of the metal chloride was varied and its maximum value did not exceed 0.5 M, while the formic acid concentration was kept constant: 0.1, 1.0, and 3.0 M. For comparison, analogous exchange processes were investigated in the cation exchanger of the $MCl–HCl–H_2O$ system. The solution phase was analyzed for equilibrium exchange by atomic absorption (Perkin-Elmer Model 2380).

RESULTS AND DISCUSSION

The experimental data show that the selectivity in relation to alkali metal ions in media containing formic acid is higher than with hydrochloric acid solutions and to a greater extent the higher the concentration of carboxylic acid in the liquid phase (Fig. 1). In terms of the pH and ionic strength, the reference solutions are close to the formic acid solutions

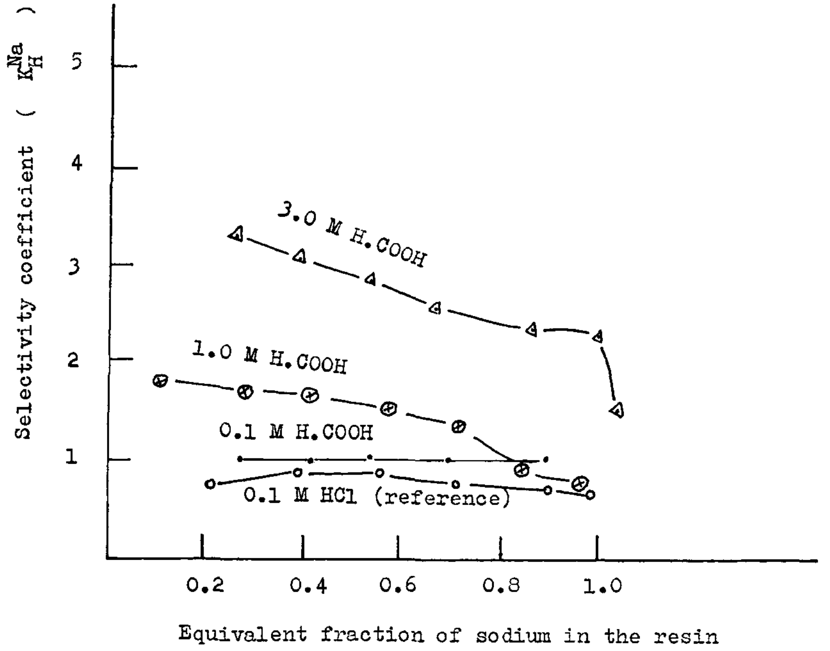

FIG. 1 The Na$^+$-H$^+$ exchange on the sulfonic acid acrylonitrile–butadiene–styrene copolymer (10% resol) in ternary solutions.

investigated. On this basis it was assumed that the increase of selectivity is a result of the effect of the organic component—the formic acid. The intensification of the dependence of K_H^M on the composition, most clearly manifested by an increase of the acid concentration, and the sharp decrease of K_H^M at high degrees of saturation of the resin by metal ions (X_{NaR} > 0.8–0.9) (Fig. 1), are characteristic of ion-exchange absorption from solutions of a weak organic acid. The familiar selectivity series ($K^+ > Na^+ > H^+$) holds for formic acid solutions. One of the factors determining selectivity is dehydration of the ion-exchange resin which, in the given instance, is due not only to the absorption of alkali metal cations but also to the molecular sorption of formic acid. Account must be taken of the different characteristics of interphase distribution of the components of the solvents, which was regarded as a binary water–formic acid mixture. While the amount of water diminishes in the course of ion-exchange absorption, the concentration of carboxylic acid in the ion-exchange increases (Fig. 2). These phenomena become more pronounced for ion-exchange absorption involving ions of a metal having a higher atomic number, because the molecular sorption of carboxylic acid on the sulfonic

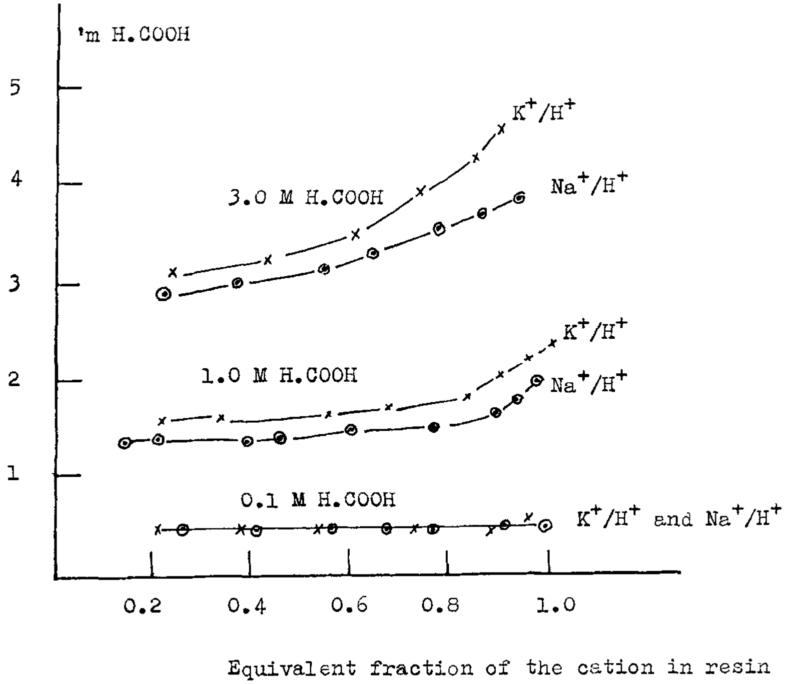

FIG. 2 Variation of the molarity of formic acid in the cationic sulfonic acid resin with the equivalent fraction of Na^+ or K^+ in the resin (10% resol) at various concentrations of formic acid.

acid cation-exchange resin increases in the sequence $H^+ < Na^+ < K^+$. The decrease in content of the more polar solvent component (water) during the exchange process and the accumulation of the less polar component (formic acid) with its low dielectric constant value tend to diminish the effective dielectric constant of the resin phase. Ultimately, the M^+–SO_3 ion pair interaction is facilitated by absorption from media containing a weak organic acid.

The sequence of relative affinities of the uni-univalent exchange on sulfonated resins is evidently normal, i.e., it corresponds to an increase in selectivity with a decrease in the size of the hydrated ion. This order is consistent with the increase in hydration of the divalent cations as well as the increase of the percentage of the crosslinking matrix (1, 10, 18, 19) (Table 1). According to the complete Donnan theory, the selectivity coefficient, K_H^M, is given by

$$\ln K_H^M = \ln(\gamma'_M/\gamma'_H) - \ln(\gamma_M/\gamma_H) + \pi(V'_H - V'_M)/RT \qquad (3)$$

TABLE 1
Exchange Capacities and Absorption of MCl–$HCOOH$–H_2O Contents for the Univalent Cation on Variously Crosslinkled Sulfonated Resins

Resol content, % (wt/wt)	Capacity, $meq \cdot g^{-1}$ resin	Ternary solution absorption, $g \cdot g^{-1}$ resin			
		HR[a]	LiR	NaR	KR
5	3.40	0.34	0.33	0.29	0.27
10	2.81	0.30	0.26	0.22	0.19
15	2.21	0.28	0.23	0.20	0.17
20	1.83	0.27	0.22	0.18	0.15

[a] R = resin.

where γ_M and γ_H denote the activity coefficients of alkali metal ions and hydrogen ions in solution, respectively, γ'_M and γ'_H denote the activity coefficients of alkali metal ions and hydrogen ions in the resin phase, respectively, π denotes the internal swelling pressure, and V'_M and V'_H denote the partial molar volume of alkali metal ions and hydrogen ions in

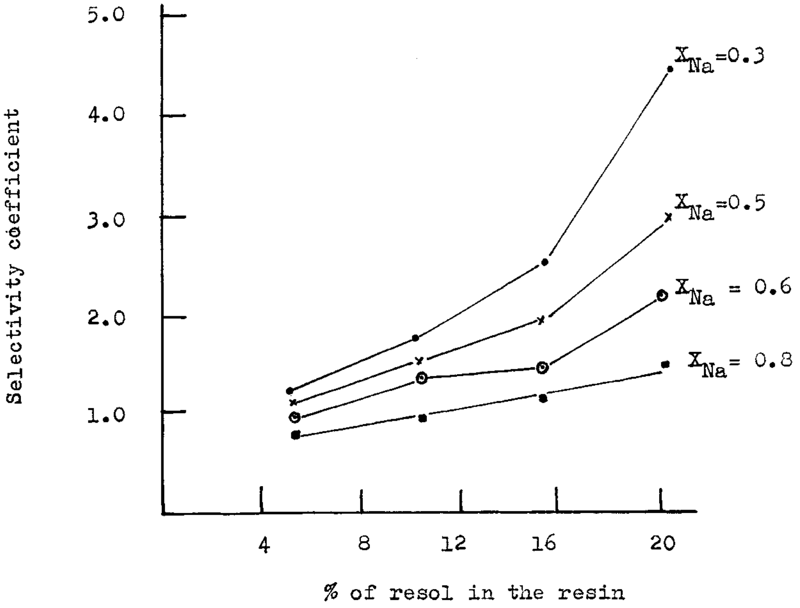

FIG. 3 Variation of the selectivity coefficient with variously crosslinked cationic resins for Na^+–H^+ exchange in 1.0 M formic acid solution.

the resin, respectively. The change in the selectivity coefficient should therefore be considered to be due to the change in one or more of the three terms in Eq. (3). The variations of the selectivity coefficient with the percentage of resol in the cationic resins at constant X_{NaR} are shown in Fig. 3. These variations in selectivity coefficients with the percentage of resol content at constant X_{MR}, due to changes in the second and third terms of Eq. (3), are characteristic. The same behavior is shown for K^+–H^+ exchange. In nearly all cases, $K_{\mathrm{H}}^{\mathrm{M}}$ decreases with increasing X_{MR}, i.e., the affinity of the resin for a given ion decreases with an increase in the amount of ion on the resin. The order of decreasing ionic mobilities is $K^+ > Na^+ > H^+$, and of numerous other physicochemical properties, all of which depend on the size of the hydrated cation.

These results confirm the view of some workers (21) that ion-exchange affinity is determined primarily by the size of the hydrated ion, with ions of small hydrated volume being preferred to large ions. It is also accepted that the hydrated hydrogen ion is larger than that of the sodium and potassium ions.

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