Ion Exchange Equilibrium Studies on Sulfonated Polystyrene Cross-Linked with Pure Divinylbenzenes

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ABSTRACT

Equilibrium isotherms of Na-H, K-H, Rb-H, Cs-H, and Ag-H systems for series of sulfonated polystyrene resins prepared from styrene and m- and p-DVB copolymers (2, 4, 8 mole % DVB) have been studied at 25°C. The difference between the selectivity coefficient (K_H^M) for the 8 mole % m-DVB resin and that for the para isomer resin is relatively large and increases with the natural order of affinity of the cations up to the silver ion. The isotherms of the commercial DVB resin are also different. The variation of K_H^M with the cationic composition (X_R) of the p-DVB resin is larger than that of the m-DVB resin as can be seen in the variation in the slope of plots. These facts are explained in terms of a variation in ion exchange sites which are related to the network structure of the copolymers. This indicates that the exchange sites are more uniformly distributed in the m-DVB resin than in the para isomer resin.

INTRODUCTION

The sulfonated styrene and divinylbenzene (DVB) copolymer is the most widely used and studied cation exchange resin. The DVB used as a cross-linking agent in commercial ion exchange resins is a mixture of several monovinyl and divinyl monomers [1]. As previously described [2], the monomer reactivity ratios of m- and p-DVB with styrene are quite different [r_1 = 1.11, r_2 (m) = 1.00; r_1 = 0.20, r_2 (p) = 1.00]. The different reactivities of these cross-linking agents in copolymerization lead to structural differences in the copolymer network as the precursor of the resin. The complexity and variation of the structure of the copolymer cross-linked by such mixtures may account for difficulties in theoretical studies of ion exchange resins. Most theoretical treatments of ion exchange selectivity assume [3] that all the fixed groups in a given resin behave in an identical manner with respect to their selectivity properties. However, it is clear that any ion exchange resin with a high to moderate degree of cross-linking cannot be considered as homogeneous. Therefore, to explain the resin properties, it has been useful to make the assumption [4-6] that the ion exchange sites in a resin are not all identical.

The swelling ratios [7] of sulfonated polystyrene cross-linked with m- and with p-DVB, and the rate of sulfonation [8, 9] of bead copolymers show differences which can be related to the differences in the cross-linked copolymer structures. We have studied the ion exchange equilibria between sodium, potassium, rubidium, cesium, and silver ions and the hydrogen ion on sulfonated polystyrene resins prepared with 2, 4, and 8 mole % of pure m- and pure p-DVB at 25°C.

The objective of this work was to obtain the equilibrium isotherms of cation exchange resins prepared from copolymers of styrene and pure DVB and to investigate the effect of the resin structure on the selectivity properties. Therefore, it was desired to eliminate as far as possible such complicating factors as ion pairs and complex ion formations. This study was, as a result, confined to the ions of alkali metals. It was also necessary to obtain the resins under nearly identical conditions so that their properties could be carefully compared. Using polyvinyl sulfate suspending agent [10], we were able to prepare high quality (spherical, free from imperfection, and transparent) polystyrene beads cross-linked with DVB in the 125 to 250 μ size. In ion exchange systems involving the hydrogen ion, the effect of reducing the equivalent capacity is always to favor the uptake of the hydrogen ion by the resin at the expense of the other ion [3]. Therefore sulfonations of bead copolymers were run under comparable conditions to obtain resins with the same specific equivalent capacities for all samples.

EXPERIMENTAL

Monomers

Styrene (Baker Chemical Co.) was purified by distillation. Commercial DVB (Dow Chemical Co.) was purified by vacuum distillation. Pure m-DVB (Shell Chemical Co.) was fractionated twice by preparative GC [11] and by vacuum distillation. Pure p-DVB was synthesized by decarboxylation [12] of p-phenylenediacrylic acid and purified by preparative GC [11] and by vacuum distillation. m-DVB and p-DVB were 99.8+% pure by GC analysis.

Bead Copolymerization

Preparation of bead copolymers of polystyrene cross-linked with m-, p-, and commercial DVB using polyvinyl sulfate suspending agent was described in detail in our previous report [10].

Sulfonation

About 8 g of the copolymer beads in the 125 to 250 μ size were preswollen overnight in distilled ethylene dichloride and were added to a flask containing 200 ml of 98% H_2SO_4 at 100°C. After 20 to 24 hr stirring the sulfonated beads were taken out and diluted with decreasing strengths of H_2SO_4 [9]. Specific equivalent capacities as determined by the salt splitting method [13] and water contents by the centrifugation method [14] are given in Table 1. All resins were kept in the potassium ion form and converted to the hydrogen ion form before being used.

Solutions of Exchanging Ion

Sodium chloride (Allied Chemical reagent grade, 99.5%), potassium chloride (Baker analyzed reagent, 99.8%), rubidium chloride (Fisher, purified), cesium chloride (Fisher, certified 99.9%), and silver nitrate (Baker analyzed reagent, 99.8%) were dried overnight at 110°C. Solutions of 1.00 $\underline{M}$ made with these dried materials were kept as stock solutions and were diluted to 0.1000 $\underline{M}$ when required for equilibrium studies.

Determination of Equilibrium Isotherms

Ion exchange isotherms were determined by the progressive-batch method [15] at 25°C. Two grams of dry resin in the hydrogen ion

TABLE 1. Equivalent Capacities and Water Contents of Resins in the
H^+ Form

Cross-link agents	DVB (mole %)	Equiv capacities (meq/g dry resin)	Water contents (g H_2O/g dry resin)
c-DVB	2	5.26 ± 0.005	3.29 ± 0.03
	4	5.36 ± 0.01	1.51 ± 0.02
	8	5.18 ± 0.01	0.84 ± 0.003
m-DVB	2	5.18 ± 0.005	3.56 ± 0.02
	4	5.39 ± 0.005	1.98 ± 0.005
	8	5.24 ± 0.02	1.01 ± 0.002
p-DVB	2	5.26 ± 0.005	3.34 ± 0.01
	4	5.38 ± 0.005	1.74 ± 0.01
	8	5.22 ± 0.015	0.89 ± 0.002

form (10 meq) was added to Y ml (Y = 10 ml) of a solution of exchang-
ing ion M^+ and then diluted to 125 ml with distilled water. The resin
and solution were then stirred in a 25°C water bath until no further
exchange took place (3 to 6 hr). A fraction f (f = 0.8; 100 ml) of the
resulting solution was removed and the number of milliequivalents of
acid liberated was determined by titration with standard 0.1 N NaOH.

bY ml (b = 1.25) of M^+ solution was added to the remaining
solution, and again adjusted to a total volume of 125 ml. After
equilibrium had been reached, an aliquot f was removed and the
number of milliequivalents of the hydrogen ion determined.

For the n-th experiment, $b^{n-1}Y$ ml of M^+ solution was added and
the amount of acid in the n-th aliquot was determined by titration. In
this experiment, values of the constants b and f were assigned for
the reasons given by Cosgrove and Stickland [15] to give a suitable
spacing of points on an isotherm and to keep the total ionic strength
of solution to a minimum, so as to avoid the necessity of making an
activity correction.

From these titration data the molar fraction of each ion on the
resin and in the solution and then the selectivity were calculated.
For convenience, the experimental data for the exchange equilibrium
studies are presented graphically in Figs. 1-9 as a plot of the
selectivity coefficient (K_H^M) vs molar fraction of the cation M^+
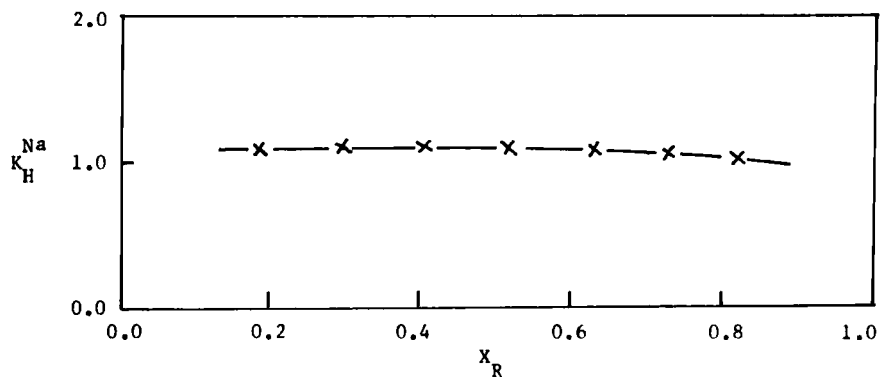of the resin (X_R).

FIG. 1. Na-H exchange on 2 mole % c-, m-, and p-DVB resins.
The points for the three resins coincide within experimental
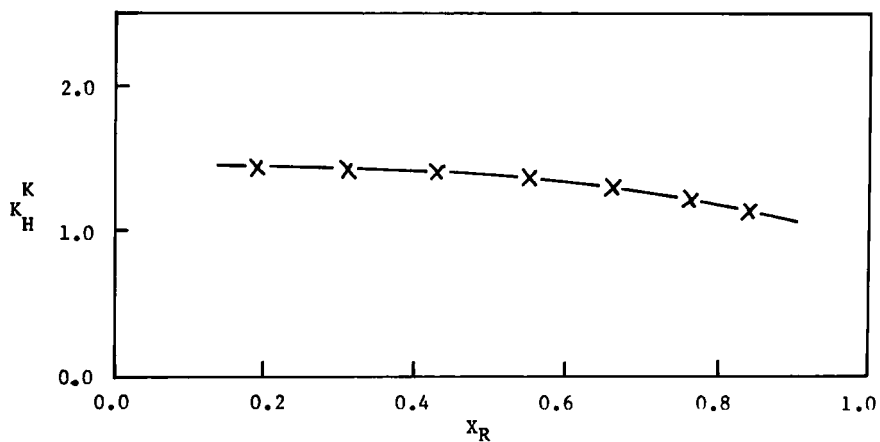limitation at the point given.

FIG. 2. K-H exchange on 2 mole % c-, m-, and p-DVB resins.
The points for the three resins coincide within experimental
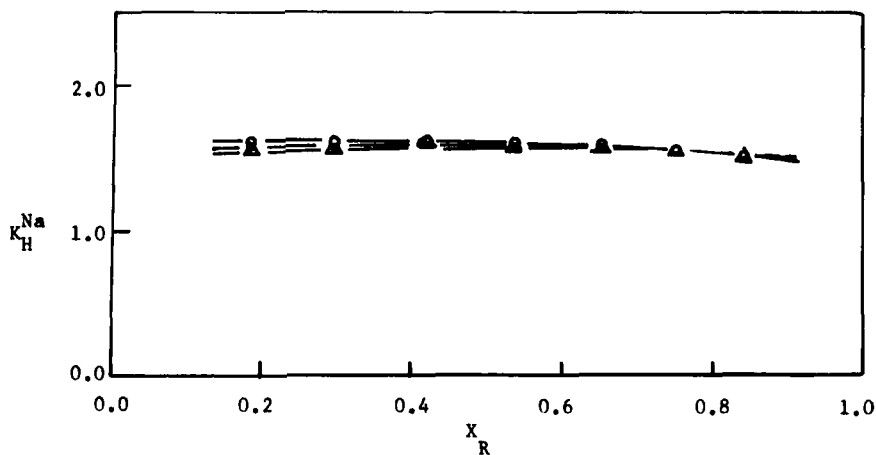limitation at the point given.

FIG. 3. Na-H exchange on 4 mole % DVB resins: ($\circ$) c-DVB; ($\triangle$) m-DVB; ($\bullet$) p-DVB.

Experimental Deviation

It was found that accurate values of $K_H{}^M$ cannot be calculated from the first of the experimental steps ($X_R = 0.1$). At low X_R a small experimental error produces a large relative deviation in $K_H{}^M$. This point ($X_R = 0.1$) is not included in the figures. The overall mean deviation of the duplicate determinations of $K_H{}^M$ is $\pm 0.8\%$ for values of X_R between 0.2 and 0.9.

RESULTS

Figures 1-9 represent the selectivity coefficient ($K_H{}^M$) variation with the counterion composition (X_R) on the resins prepared from styrene and pure m- and p-DVB, as well as from commercial DVB. The following facts will be observed from these data. The isotherms on pure DVB resins show the same qualitative behavior as those on the resins from commercial DVB (Figs. 1-9). The isotherms of the 2% m-DVB resin are identical with those of the 2% p-DVB resin within experimental error (Figs. 1 and 2). However, differences
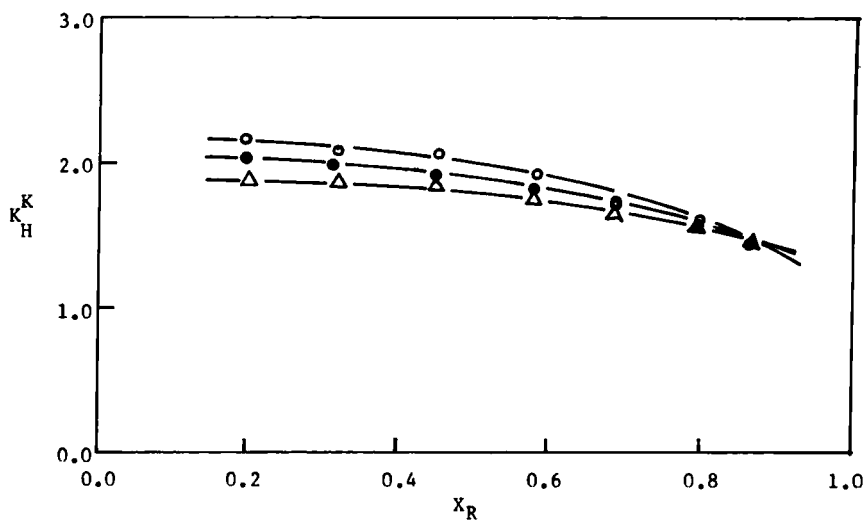
FIG. 4. K-H exchange on 4 mole % DVB resins: (○) c-DVB;
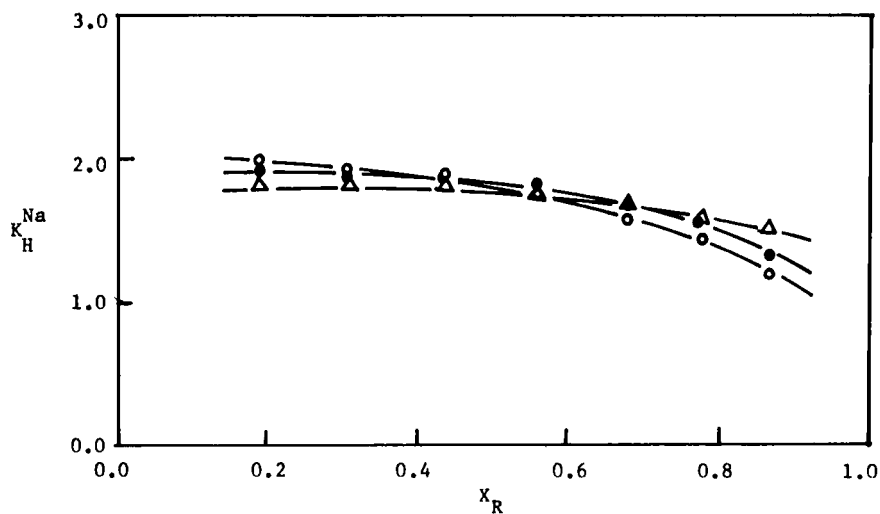(△) m-DVB; (●) p-DVB.

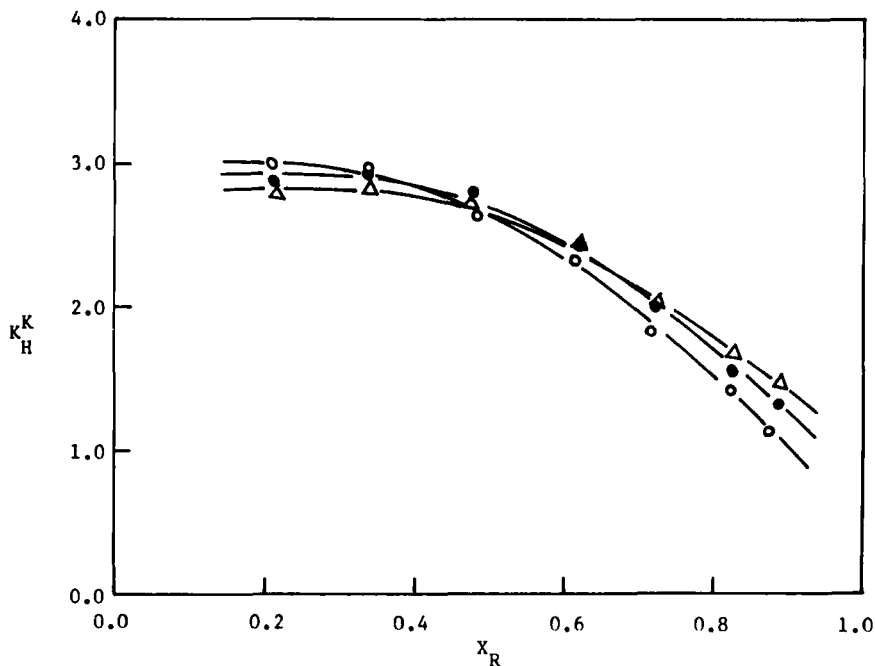FIG. 5. Na-H exchange on 8 mole % DVB resins: (○) c-DVB;
(△) m-DVB; (●) p-DVB.

FIG. 6. K-H exchange on 8 mole % DVB resins: ($\circ$) c-DVB; ($\triangle$) m-DVB; ($\bullet$) p-DVB.

in K_H^M of a given ion pair of the m- and p-DVB resins increase with the degree of cross-linking, i.e., the differences between K_H^{Na} of the p- and m-DVB resins are 0.00, 0.02, and 0.13 at $X_R = 0.2$ for 2, 4, and 8 mole % resins, respectively (Figs. 1, 3, and 5). Figures 5-8 show these large affinity differences between of the 8-mole % m- and p-DVB resins for the Na-H, K-H, and Rb-H, and Cs-H systems. The values of K_H^M of a given ion pair on the 8-mole % p-DVB resin are higher than those on the 8-mole % meta isomer resin when the resins are predominantly in the hydrogen form, but an intersection occurs at $X_R = 0.65$ to 0.8 for all systems. Figure 6, as an example, shows that K_H^K of the 8-mole % para isomer resin is 3.31 at $X_R = 0.2$ and 0.40 for the meta isomer resin at the same X_R, and the intersection point is at $X_R = 0.65$. The intersection points are at $X_R = 0.70$ for Na-H,
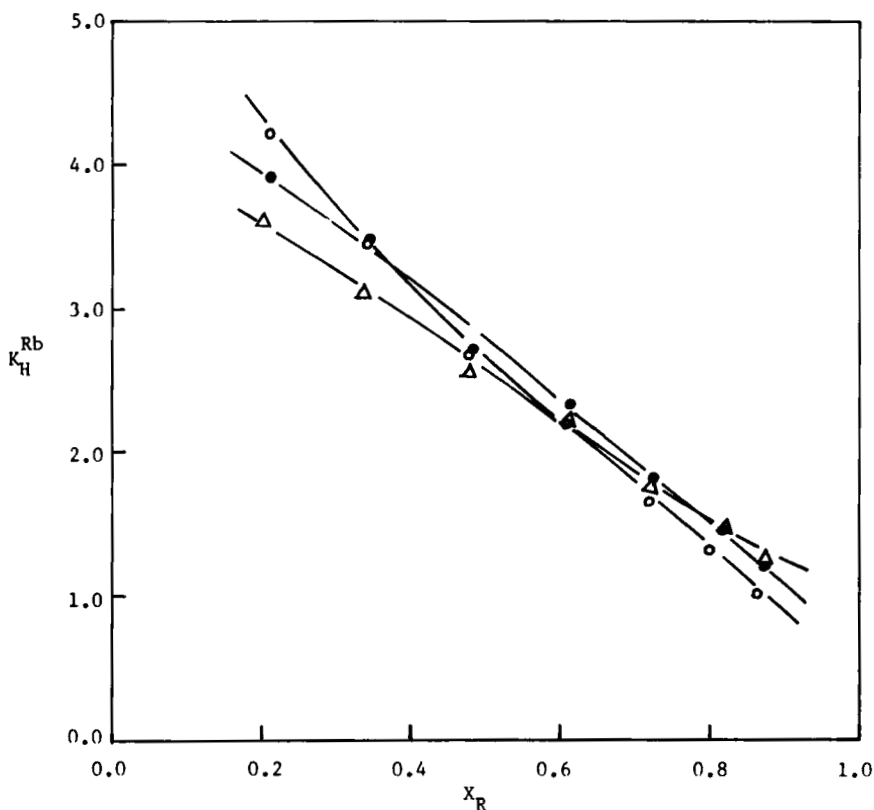
FIG. 7. Rb-H exchange on 8 mole % DVB resins: (○) c-DVB; (△) m-DVB; (●) p-DVB.

0. 80 for Rb-H, and 0.73 for Cs-H system. The differences in K_H^M on the same mole % m- and p-DVB resins increase with the natural order of the affinity of the cation. Figures 5-8 show that differences between K_H^M of 8 mole % p- and m-DVB resins are 0.13 for Na-H, 0.29 for K-H, 0.36 for Rb-H, and 1.59 for Cs-H system at X_R = 0.2. However, these differences vary with the cationic composition of the resin as shown in all the figures. For example, the differences between K_H^{Cs} of the 8-mole % p-DVB resin and that of the 8-mole % meta isomer resin are 1.59 at X_R = 0.20, 0.70
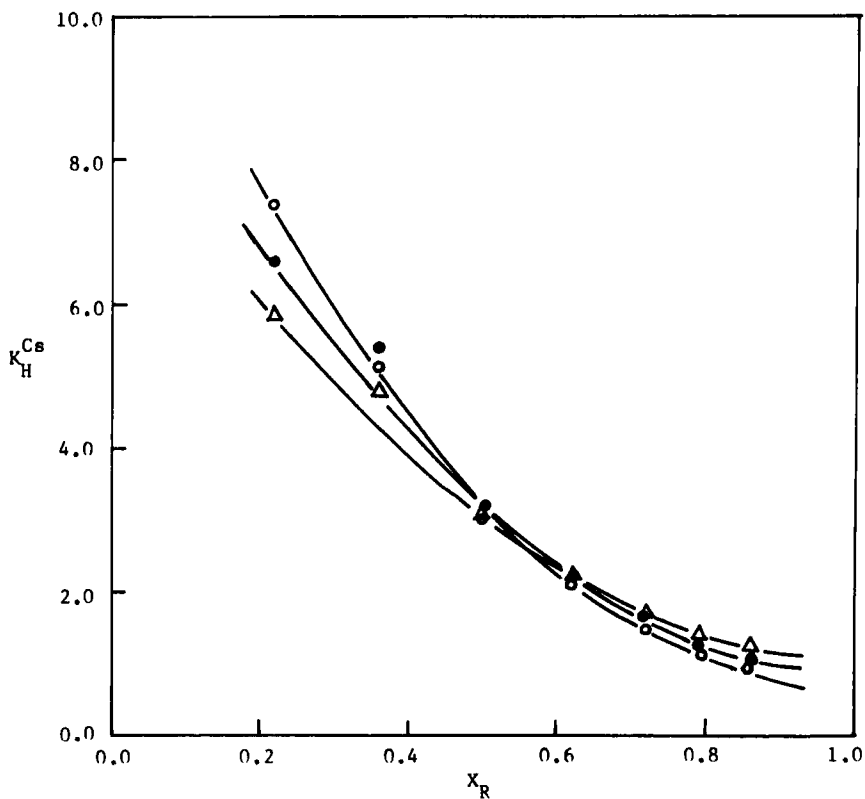
FIG. 8. Cs-H exchange on 8 mole % DVB resins: ($\circ$) c-DVB; ($\triangle$) m-DVB; ($\bullet$) p-DVB.

at 0.35, 0.10 at 0.50, 0.00 at 0.73, and -0.05 at 0.87 (Fig. 8), where a negative value means that K_H^{Cs} of the meta isomer resin is higher than that of the para isomer resin.

These data also show that the variation of K_H^M with the cationic composition of the p-DVB resin is larger than that of the meta isomer resin as can be seen in the slopes, i.e., K_H^M differences of the 8-mole %p-DVB resin between X_R = 0.20 and 0.85 are 0.70, 1.97, 3.04, and 7.17 for Na-H, K-H, Rb-H, and Cs-H systems, respectively. However,
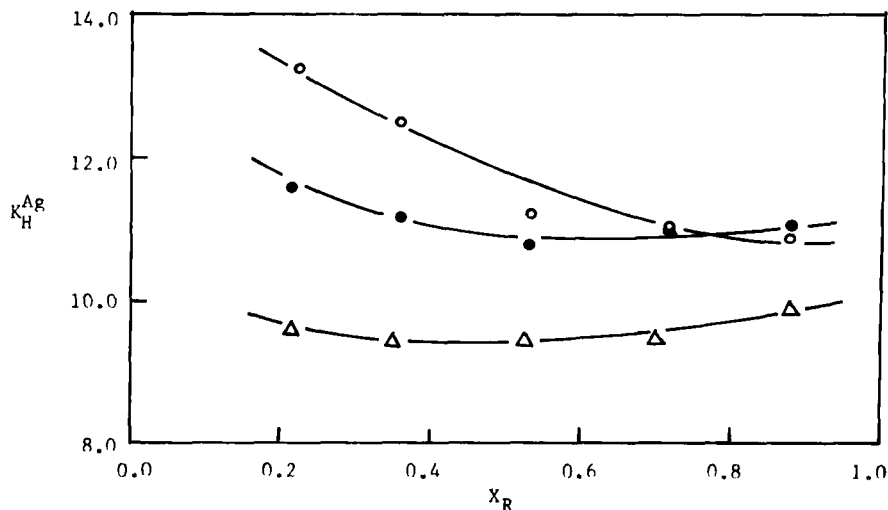
FIG. 9. Ag-H exchange on 8 mole % DVB resins: ($\circ$) c-DVB; ($\triangle$) m-DVB; ($\bullet$) p-DVB.

the differences of the 8-mole % m-DVB resin are 0.47, 1.54, 2.68, and 5.53 for the same ion pair systems, respectively.

The equilibrium isotherms of the Ag-H system on the 8-mole % DVB resins show the most clearly established differences between the meta and para isomer resins (Fig. 9). The difference in K_H^{Ag} of m- and p-DVB resins at $X_R = 0.21$ is 2.13. The differences of K_H^{Ag} between $X_R = 0.21$ and 0.88 are 3.92 and 0.50 for para and meta isomer resins, respectively.

DISCUSSION

In order to explain these phenomena, one has to consider the structural differences between m- and p-DVB resins, which are related to the difference in the amount of cross-linking of the co-polymers (or resins) obtained from the same molar fraction of DVB and the difference in the distribution of the cross-links in the co-polymers. If the selectivity differences on the resins with the same molar fraction of DVB are due to the differences of the amount of cross-linking, the degree of cross-linking in p-DVB resins should be

higher, not lower as observed, than in m-DVB resins [16]. This is not consistent with the result of copolymerization kinetics described in previous report [2]. The result of kinetics shows that p-DVB is incorporated more rapidly into the growing polymer chain than m-DVB during the copolymerization with styrene. This leads the relative bunching of DVB units in the styrene—p-DVB copolymer. From this fact it is expected the reactivity of the unreacted second vinyl group of p-DVB is more reduced than that of m-DVB, perhaps because of lessened freedom of movement of the monomer mixtures. In some cases the pendant vinyl group may be completely shielded from further reaction and may not cross-link at all. It is reasonable that this effect is higher in p-DVB than in m-DVB copolymerization with styrene. From this, the amount of cross-linking does not correlate with the difference in the isotherms on the resins pre-pared from two DVB isomers.

Alternatively, the difference in the distribution of the cross-links (or DVB) in the copolymers has to be considered. The analysis of the previous study [2] shows that the copolymerization of styrene with p-DVB results in a structure with a tightly cross-linked nucleus to which long chains of much more pure polystyrene are attached. In comparison, the styrene and m-DVB copolymer has a structure in which the cross-links are more widely and more uniformly dis-tributed than in the para isomer copolymer. This indicates that the ion exchange sites are more uniformly distributed in the m-DVB resins than in the p-DVB resins. It was noted by Reichenberg and McCauley [4] that such selectivity variations with the resin loading are due to the differing environments of the ion exchange sites. They divided the ion exchange sites into three groups which are located in a low degree, a medium degree, and a very high degree of cross-linking. The first two type sites have low and high selectivities, respectively. However neither type of the fully hydrated ions can approach the third type site.

The isotherms on the 2% m-DVB resin and those on the 2% p-DVB resin show no differences, and variation of K_H^M on these resins with the resin loading is relatively small. This indicates that the environ-ments of the sulfonic acid groups are not significantly different in the 2% DVB resins because of a low degree of cross-linking. However, there are distinctive differences between the isotherms on the higher mole % (8%) m-DVB resins and the para isomer resins as shown in the experimental data. It appears that the large variation of K_H^M with the cationic composition of the p-DVB resin is due to a lack of the homogeneity of cross-links in the copolymer. As one increases the cross-link homogeneity of the copolymer, there is less of a variation in K_H^M with the resin loading as shown in the isotherms of the meta isomer resin.

It is known that in the case of the alkali ions, most cation-exchange resins prefer the smaller solvated ion to the larger one. However, resins with sulfonic acid groups prefer Ag^+ and Tl^+ strongly to alkali ions, though there is little difference in the volumes of the hydrated ions. In spite of its almost identical size, Ag^+ is more strongly attracted because of its great polarizability [16, 17]. The equilibrium isotherms of silver-hydrogen system on the 8% DVB resins show large differences in the values of K_H^{Ag} of m- and p-DVB resins as expected from the high affinity of silver ion (Fig. 9). The differences of K_H^{Ag} between $X_R = 0.21$ and $X_R = 0.88$ are 3.92 and 0.50 for p- and m-DVB resin, respectively. Also, there is less of a variation in K_H^{Ag} of the meta isomer resin.

ACKNOWLEDGMENT

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