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Author

Bucher, J.

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ANION EXCHANGE RESIN SELECTIVITY AS A FUNCTION OF RESIN COMPOSITION, REVISITED*

J. Bucher and R. M. Diamond

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

B. Chu

State University of New York
Stony Brook, New York 11790

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Abstract

It is found that in contradiction to previous work, the $\text{ClO}_4^- - \text{Cl}^-$ and $\text{Cl}_3\text{CO}_2^- - \text{Cl}^-$ (and presumably $\text{SCN}^- - \text{Cl}^-$) anion-exchange resin systems show no change or a moderate increase in $K_{\text{B/Cl}}$ with increasing resin chloride mole fraction, and not a marked decrease. Thus, these systems show the same behavior as other univalent anion exchange systems, and there is no need to involve a special ion-pair cluster mechanism.

Introduction

It has long been known that the selectivity coefficient or equilibrium quotient

$$K_{B/A} = \frac{[\bar{B}][A]}{[\bar{A}][B]} \quad (1)$$

for the (univalent) ion exchange reaction,

(where the superscript bar denotes the resin phase) generally depends upon the resin composition. The data available are mostly for cation exchange, and they show that with moderate to high cross-linked resins the value of $K_{B/A}$ usually remains constant or decreases slightly as $\bar{X}_B$, the mole fraction of B in the resin phase, increases.¹⁻⁵ The decrease usually is more marked, the higher the cross linking.

There are a number of exceptions to this general behavior, one of the most dramatic sets being three univalent anion-exchange systems studied by Gregor et al.⁶ using a strong-base resin, Dowex 2-X8. With perchlorate, thiocyanate, and trichloroacetate ions vs. chloride, they found a steep increase in $K_{B/Cl}$ with $\bar{X}_B$, of the order of a factor of 10^2 . Other anions, such as I^- , Br^- , NO_3^- , IO_3^- , $CH_3CO_2^-$, and F^- showed the usual pattern of a slight decrease. To explain the behavior of ClO_4^- , SCN^- , and $Cl_3CO_2^-$, the authors postulated that 1) selectivity was due to ion-pair formation between the resin group and the counter ion, and 2) these particular anions caused an enhancement of the likelihood of another ion pair occurring in the vicinity of one already formed, a clustering of the ion pairs. Since we did not think

that electrostatic ion pairing occurs to any significant extent between the large trimethylbenzylammonium cations of the resin and the ClO_4^- , SCN^- , and Cl_3CO_2^- counter ions,⁷ and since if it did occur, we might expect the resulting decrease in local charge density to cause the opposite effect, namely a hindrance to nearby ion pairing, we decided to repeat these measurements.

Experimental

The $\text{CCl}_3\text{CO}_2^- - \text{Cl}^-$ system was studied by batch equilibrations of ~ 0.8 g samples of Dowex 1-X8 resin shaken overnight with 25 ml of various mixtures of 0.10M NaCl and $\text{CCl}_3\text{CO}_2\text{Na}$ solutions. After equilibration, the aqueous Cl^- was determined with AgNO_3 using dichlorofluorescein as indicator, and the total concentration ($\text{CCl}_3\text{CO}_2^- + \text{Cl}^-$) of the aqueous solutions was checked by titration with HClO_4 in glacial acetic acid. Knowing the capacity of the resin (3.13 meq/g dry Cl^- -form resin), the value of $K_{\text{CCl}_3\text{CO}_2/\text{Cl}}$ can be calculated for each equilibrium value of $\bar{X}_{\text{Cl}}$. As a check, the $\text{CH}_3\text{CO}_2^- - \text{Cl}^-$ system was studied in a similar way, although the resin used was Dowex 1-X10 (capacity = 2.69 meq/g dry Cl^- -form resin), and the external solution ionic strength varied from 0.020M to 1.0M in the different runs.

The analytical difficulties are somewhat greater in investigating the $\text{ClO}_4^- - \text{Cl}^-$ system (but see Ref. 8), so the very similar system $\text{ReO}_4^- - \text{Cl}^-$ was studied instead, as a convenient radiotracer, $^{186}\text{ReO}_4^-$, could be used. Two resin samples were employed, a Dowex 1-X2 and a Dowex 1-X10, with equivalent capacities of 4.38 and 3.04 meq/g dry Cl^- -form resin, respectively, and the procedure used was as follows. A resin sample of known weight (~ 0.5 g) was placed in a small sintered-glass filter fitted with a centrifuge cone as a receiver. A definite volume of a 0.024M KReO_4 solution containing a known amount of radioactive ReO_4^- tracer was poured repeatedly through the resin. After equilibrium, the filter was centrifuged and the amount of ReO_4^- in the filtrate was determined radiometrically. The Cl^- was determined by the Volhard method. Since the resin capacity is known, a value for $K_{\text{ReO}_4/\text{Cl}}$ at that particular $\bar{X}_{\text{Cl}}$ is determined. The resin sample is then equilibrated with a new perrhenate solution, and the process repeated to obtain a new value of $K_{\text{ReO}_4/\text{Cl}}$ at a lower $\bar{X}_{\text{Cl}}$.

Results and Discussion

In Figure 1 are plotted the values of $K_{B/Cl}$ vs. $\bar{X}_{Cl}$ found in the present study for $ReO_4^- - Cl^-$, $Cl_3CO_2^- - Cl^-$, and $CH_3CO_2^- - Cl^-$ exchanges. In all three systems the values of $K_{B/Cl}$ remain constant or increase slightly with $\bar{X}_{Cl}$. This agrees with what was found for the $CH_3CO_2^- - Cl^-$ system in Ref. 6, but disagrees completely with the 100-fold decrease for ClO_4^- and $Cl_3CO_2^-$ found there. We do not know the reason for the disagreement. But our $ReO_4^- - Cl^-$ data are in agreement with a detailed study of the similar $ClO_4^- - Cl^-$ system published by Freeman.⁸ We believe these results are correct, and so interpretable without recourse to a new type of clustered ion pairing.

Indeed, there have been a number of explanations for the usual type of behavior;^{1,5,9-12} most have in common the idea that some form of resin heterogeneity is the ultimate origin. That is, micro-regions in the resin phase differ from each other for one or more of a number of physical or chemical reasons.^{13,14} For example, in the original polymerization of the styrene-divinylbenzene mixture, it is likely that micro-regions in the resulting beads differ in their cross linking and pore-size distribution, as well as the degree of entanglement of the matrix. The reactions used to create the ionic exchange groups can further alter the micro-structure in a non-uniform way by the addition of methylene bridges and by the number and placement of the resin-ion sites on the polymer matrix. As a result, the charge density and water content may vary in the resin on a micro-scale. So there are a variety of ways in which micro-regions in the resin may differ, and there is evidence of varying degrees of confidence that all these ways do occur. As a result, the different micro-regions may have differing selectivities for ions (this does not require ion pairing in the resin, but is more likely related

to the availability of water in these regions to hydrate the ions and to reduce the electrostatic free energy of the charged resin matrix). Naturally, those sites that most favor the favored ion, say B, will be occupied first by it, and only as $\bar{X}_B$ increases will the other less favorable sites be exchanged. Thus, the value of $K_{B/A}$ will gradually fall to an average over all sites as $\bar{X}_B \rightarrow 1$.

More specific explanations are possible, and we would like to mention one which is compatible with the idea of resin heterogeneity. Since we believe selectivity is determined mostly by the differences in hydration of the two ions in the two phases,⁷ we must consider how the availability of water for ion hydration changes with a change in resin composition. As the resin equivalent fraction of the ion least in need of hydration increases, the amount of water in the resin phase decreases, but the availability of water for hydrating ions increases. As a result, the resin phase becomes slightly more favorable to that ion most in need of hydration, and so the latter ion's distribution into the resin may increase, causing $K_{B/A}$ to fall with increasing $\bar{X}_B$.

Footnotes and References

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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Figure Caption

Fig. 1. Plot of the equilibrium quotient, $K_{B/Cl}$, vs. resin mole fraction, $\bar{X}_{Cl}$, for 1) Dowex 1-X10 $ReO_4^- - Cl^-$; 2) Dowex 1-X8 $Cl_3CO_2^- - Cl$, 3) Dowex 1-X10 $CH_3CO_2^- - Cl$ systems.

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Fig. 1

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