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SELECTIVITY IN HETEROVALENT ANION EXCHANGE;
ION PAIRING vs. ION HYDRATION*

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Abstract

The values of the selectivity coefficients, $K_{B/A}$, for heterovalent exchange with a strong-base resin and radiotracer ReO_4^- , CrO_4^{2-} , and WO_4^{2-} vs. macro Cl^- , and radiotracer $\text{Cr}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_6^{4-}$ vs. macro CN^- have been determined. These results show that in such systems, contrary to early ideas on the nature of resin selectivity, the direction of the exchange is determined by the superior hydration of the ions in the dilute external aqueous phase over that in the resin phase, and not by ion pairing in the latter phase.

Introduction

For the ion-exchange reaction



where the superscript bar indicates the resin phase, it has become customary to write the equilibrium constant

$$\mathcal{K}_{B/A} = \frac{(\bar{B})(A)}{(\bar{A})(B)} = \frac{[\bar{B}][A]\bar{\gamma}_B\gamma_A}{[\bar{A}][B]\bar{\gamma}_A\gamma_B} = K_{B/A} \frac{\bar{\gamma}_B\gamma_A}{\bar{\gamma}_A\gamma_B} \quad (2)$$

and to assume the same standard state for both phases. Then

$$\mathcal{K}_{B/A} = 1 = K_{B/A} \frac{\bar{\gamma}_B\gamma_A}{\bar{\gamma}_A\gamma_B} \quad (3)$$

If, as is usually the case, the standard state chosen is the hypothetical state of unit activity with the properties of the infinitely dilute solution, the ratio γ_A/γ_B of the external-phase activity coefficients can be made as close to unity as is desired by decreasing the concentration of that phase.

Thus eq. 3 becomes

$$K_{B/A} = 1 = K_{B/A} \frac{\bar{\gamma}_B}{\bar{\gamma}_A} \quad (4)$$

$$\text{or } K_{B/A} = \frac{\bar{\gamma}_A}{\bar{\gamma}_B}$$

The equilibrium quotient or selectivity constant, $K_{B/A}$, depends only upon the resin-phase activity coefficients. Partly as a result of this type of derivation, early researchers often formulated ion-exchange resin selectivity as a function mainly of resin properties.¹⁻⁷

But we are free to choose the standard states in whatever manner we desire. If we choose the standard state to be the pure salt resin, then, although the ratio $\bar{\gamma}_B/\bar{\gamma}_A$ is not unity, the greatest part of the variation in $K_{B/A}$ comes from γ_A/γ_B , the aqueous-phase ratio. Now the source of resin selectivity would appear to come mainly from the external solution phase.

In fact, of course, the origin of resin selectivity comes from a difference of differences; the differences in the interactions of the two ions in the two different phases. However, the properties and characteristics of one phase may actually dominate the exchange. A number of types of studies can indicate the relative importance of the various interactions. One such type is a study of heterovalent exchange, in particular the direction of selectivity for ions of different charge. Several ion-exchange models⁵⁻⁷ postulate the dominant importance of Coulomb forces in the resin phase, that is, of ion pairing between the counter ion and the resin-fixed ion. As a natural consequence of such models, ion selectivity can be predicted to go up, the higher the charge on the ion, and indeed such a general rule has been given by a number of authors.

But the opposite behavior, a decrease in resin affinity with increasing ionic charge would be the rule if, as has also been proposed,^{8,9} ion-water interactions (hydration) in the dilute external solution, rather than ion-resin ion contacts (ion pairing), were the most important factors in exchanges

involving strongly basic or strongly acidic resins. The higher-charged ion has a greater need for hydration, a larger hydration energy, than the lower-charged one. And since the best hydration is obtained in the dilute external phase rather than in the concentrated resin phase, the higher-charged ion goes into the aqueous solution preferentially, forcing the other ion into the less desirable resin phase.

The present paper presents some experimental evidence for choosing between these points of view; the data come from the heterovalent ion exchange of some large complex ions. Obviously it would be best to compare ions of similar size and structure, though differing in charge, so as to minimize all effects other than that of the charge on the selectivity. For this reason, tracer ReO_4^- , WO_4^{2-} , and CrO_4^{2-} were measured vs. Cl^- as the macro anion, and tracer $\text{Cr}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_6^{4-}$ were determined vs. macro concentrations of CN^- .

Experimental

Reagents.— The resins used in the present experiments were two batches of Dowex 1, a strong-base resin, one of 10% and the other of 8% DVB cross linking. They had capacities of 3.04 and 3.46 meq/g dry resin, respectively.

The chloride solutions employed were made from reagent-grade salts, used without further purification. The concentrations of these solutions were determined by the Volhard method.¹⁰ The cyanide solutions were made from Baker and Adamson KCN, reagent grade, and the stock solution was determined by the Denigès-Liebig method,¹⁰ using a visual end point.

The 3.87 day $^{186}\text{ReO}_4^-$ tracer was obtained from Oak Ridge, as was the 27.8 day $^{51}\text{CrCl}_3$. The latter was diluted with 10^{-3}M stable CrCl_3 , oxidized with Na_2O_2 , and then boiled to destroy the peroxide. The oxidation to CrO_4^{2-} could be followed by the change in color to the yellow of CrO_4^{2-} . The batch experiments with this ion were done at pH 8-10. Below pH 8, HCrO_4^- forms and dimerizes. The 73.2 day $^{185}\text{WO}_4^{2-}$ came from Oak Ridge in dilute KOH; the experiments with it were performed in slightly basic solution.

The three tracer cyano complexes were prepared from radioactive ^{59}Fe , ^{60}Co and ^{51}Cr , supplied by Oak Ridge as the chlorides in HCl. A small amount of each tracer was added to water and taken to near dryness several times to remove the HCl. About one gram of KCN was then added, and the mixture heated until the KCN fused. After cooling, the solid was dissolved in 0.01M KOH. The concentrations of the cyano complexes were less than 10^{-6}M in the batch experiments performed, and the pH was 11-12.

Procedure.— In the batch experiments, 5, 10, or 20 ml of a chloride or cyanide solution of known concentration, to which 50 μl of tracer had been added, were

shaken overnight with small amounts (10-150 mg) of resin in 25 ml glass-stoppered flasks or 60 ml glass-stoppered bottles. Duplicate 2 or 3 ml aliquots of the equilibrium solution were withdrawn through glass-wool filters into screw-cap vials, and were then gamma-counted in a 2" x 2" NaI(Tl) well-type scintillation counter, using a single-channel analyzer. A standard solution was treated in the same way, but without any resin being added. After correcting the counting rates for background, the value of D, the distribution ratio for the tracer species could be obtained,

$$D = \frac{[(c/m/ml \text{ stand. sol.}) - (c/m/ml \text{ equil. sol.})](ml \text{ of sol.})}{(c/m/ml \text{ equil. sol.})(g \text{ dry resin})} \quad (5)$$

Results

The results of the distribution experiments with alkali chloride solutions (mainly NaCl) from 0.02 to 0.5m and tracer ReO_4^- , CrO_4^{2-} , and WO_4^{2-} are shown in Fig. 1. Similarly, Fig. 2 gives the plots of $\log D$ vs. KCN solutions from 0.1 to 1m. Since for the tracer ion, $D' = [\bar{B}]/[B] = D/\text{swc}$, where swc stands for specific water content (g water/g dry resin), substitution into the appropriate form of eq. 2 for heterovalent exchange yields

$$D' = \mathcal{K}_{B/A} \frac{[\bar{A}]^n}{[A]^n} \frac{\bar{\gamma}_A^n \gamma_B}{\bar{\gamma}_B \gamma_A^n} = K_{B/A} \frac{[\bar{A}]^n}{[A]^n} \quad (6)$$

In dilute solutions where resin invasion is negligible, $[\bar{A}] = \bar{C}/\text{swc}$, where \bar{C} is the capacity of the resin (meq/g dry resin), $\frac{\gamma_B}{\gamma_A} \rightarrow 1$, and for tracer concentrations of B, $\frac{\gamma_A}{\gamma_B} = \text{constant}$. Then

$$D' = \left(\mathcal{K}_{B/A} [\bar{A}]^n \frac{\bar{\gamma}_A^n}{\bar{\gamma}_B} \right) [A]^{-n} = K_{B/A} \frac{[\bar{A}]^n}{[A]^n} \quad (7)$$

and the terms inside the parentheses are a constant. So D' and D depend inversely on the n^{th} power of the aqueous-phase macro-ion concentration, $[A]$.

Since the log-log plots of D vs. molality in Figs. 1 and 2 are straight lines with the proper slope n , the conditions described in the previous paragraph must hold, and $K_{B/A}$ can be evaluated from the plots by means of eq. 7 with the additional knowledge of the resin capacity, \bar{C} , and the specific water content, swc. These values of $K_{B/A}$ are given in Table I; note that the first three are for Cl^- -form X10 resin, and that the second group is for CN^- -form X8 resin.

Discussion

Before discussing what the results indicate about the choice between models stressing ion pairing in the resin phase and models stressing the differential hydration of the ions, one should note the effect of "electroselectivity" in heterovalent exchange. That is, as discussed in Ref. 11, the Donnan potential of the ion-exchange resin acts on the counter ions with a force proportional to their charge. Thus the counter ion of higher charge is more strongly attracted by the ion exchanger. And because the Donnan potential increases with dilution of the external solution and with increasing concentration of the resin-fixed ions, the attraction for the higher-charged ions follows the same pattern. Since in most ion-exchange operations the external solution is dilute compared to the resin phase, this leads to the empirical observation that resins prefer the ion of higher charge. But, in fact, if the external solution is made quite concentrated, this order can be reversed. This type of selectivity, called electroselectivity,¹¹ is not intrinsic to the exchanger, but follows merely from the difference in ionic charge of the two ions and the difference in concentration of the two phases. It can be seen more simply, perhaps, as an example of Le Chatelier's Principle in the equilibrium



where ion type A is univalent (for simplicity) and ion type B is n-valent. If the external solution is made much more dilute than the resin phase, the equilibrium reacts so as to try to put more ions into the external phase and decrease the number of ions in the exchanger. This means a shift to the right, favoring ion B in the exchanger and ion A in the external solution.

However, the value of the equilibrium quotient, or selectivity coefficient, for eq. 8,

$$K_{B/A} = \frac{[\bar{B}] [A]^n}{[\bar{A}]^n [B]} \quad (9)$$

does give a direct measure of the intrinsic selectivity even for heterovalent exchanges. A complication is that the value of $K_{B/A}$ may vary with resin composition. To circumvent this, the ions to be compared can be in tracer quantities in the presence of macro amounts of a third ion which thus dominates the composition in both phases. Experimentally it is more convenient to measure $K_{B/A}$ for one tracer ion at a time in the presence of the same macro species, and this is what has been done in the present study.

Table I lists the values of the equilibrium quotients found. Actually, there is some uncertainty as to the most appropriate way to compare heterovalent exchanges. A fairer comparison than the values of K directly might be $K^{1/ab}$, or $K_{B/A}^{1/n}$ in the present case, so that the equilibrium is normalized to one equivalent of exchange; these values are also listed. It can be seen from either set of values that there is a marked decrease in resin selectivity with an increase in the charge on the anion.

So at least with a strong-base resin, electrostatic ion pairing in the resin phase does not determine the order of selectivity. On the contrary, resin selectivity appears to go with the inverse order of the hydration energies of the ions. This is, in fact, what would generally be expected from a model for ion-exchange selectivity based on the difference in hydration energies of an ion between the two phases,⁸ as this difference should be roughly proportional to the hydration energy in the better phase, in pure water itself, at least for lowly and moderately cross-linked resins. Thus we believe it is

more correct in the present systems to speak of selective binding of the ions into the external aqueous phase, rather than of ion pairing in the resin phase.

Finally, carrying this hydration argument to an extreme provides a possible explanation for the difference in $K_{B/A}$ for CrO_4^{2-} and WO_4^{2-} and for $\text{Co}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{CN})_6^{3-}$. The tungsten(VI) and chromium(III) are more electro-positive than the chromium(VI) and cobalt(III), respectively; as a result, the electron densities on the surfaces of WO_4^{2-} and $\text{Cr}(\text{CN})_6^{3-}$ are a little higher than those on CrO_4^{2-} and $\text{Co}(\text{CN})_6^{3-}$. This means slightly greater hydration by water, and so somewhat greater binding of WO_4^{2-} and $\text{Cr}(\text{CN})_6^{3-}$ into the dilute external aqueous phase and somewhat smaller values of $K_{B/A}$, as observed.

Footnotes and References

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- (1) G. E. Boyd, J. Schubert, and A. W. Adamson, J. Am. Chem. Soc. 69, 2818 (1947).
- (2) H. P. Gregor, J. Am. Chem. Soc. 73, 642 (1951).
- (3) T. R. E. Kressman and J. A. Kitchener, J. Chem. Soc. 1190 (1949).
- (4) K. W. Pepper and D. Reichenberg, Z. Elektrochem. 57, 183 (1953).
- (5) J. L. Pauley, J. Am. Chem. Soc. 76, 1422 (1954).
- (6) H. P. Gregor, J. Belle, and R. A. Marcus, J. Am. Chem. Soc. 77, 2713 (1955).
- (7) F. E. Harris and S. A. Rice, J. Chem. Phys. 24, 1258 (1956).
- (8) B. Chu, D. C. Whitney, and R. M. Diamond, J. Inorg. Nucl. Chem. 24, 1405 (1962); B. Chu, Thesis, Cornell University, Ithaca, New York (1959).
- (9) G. Eisenman, Biophys. J. Suppl. 2, 259 (1962).
- (10) H. A. Laitinen, Chemical Analysis, (McGraw-Hill, New York, 1960).
- (11) F. Helfferich, Ion Exchange, p. 156 (McGraw-Hill, New York, 1962).

Table I. Selectivity Coefficients for Tracer Anions on Dowex 1

Tracer anion of charge n	X10 Resin		$K_{B/A}^{1/n}$
	Macro-anion	$K_{B/A}$	
ReO_4^-	Cl^-	570	570
WO_4^{2-}	Cl^-	0.10	0.32
CrO_4^{2-}	Cl^-	0.23	0.48
	X8 Resin		
$\text{Cr}(\text{CN})_6^{3-}$	CN^-	2.0	1.3
$\text{Co}(\text{CN})_6^{3-}$	CN^-	22	2.8
$\text{Fe}(\text{CN})_6^{4-}$	CN^-	0.073	0.52

Figure Captions

Fig. 1. Plot of D for tracer ReO_4^- , CrO_4^{2-} , and WO_4^{2-} vs. Cl^- molality; lines are drawn with slopes of -1, -2, and -2, respectively. Data are for X10 resin, and for NaCl solutions except for symbols indicating LiCl, 0; Cs Cl, \blacksquare ; $(\text{CH}_3)_4\text{NCl}$, \blacktriangle .

Fig. 2. Plot of D for tracer $\text{Co}(\text{CN})_6^{3-}$ (\blacktriangle), $\text{Cr}(\text{CN})_6^{3-}$ (\blacksquare), and $\text{Fe}(\text{CN})_6^{4-}$ (\bullet) vs. KCN molality for X8 resin; lines are drawn with slopes of -3, -3, and -4, respectively.

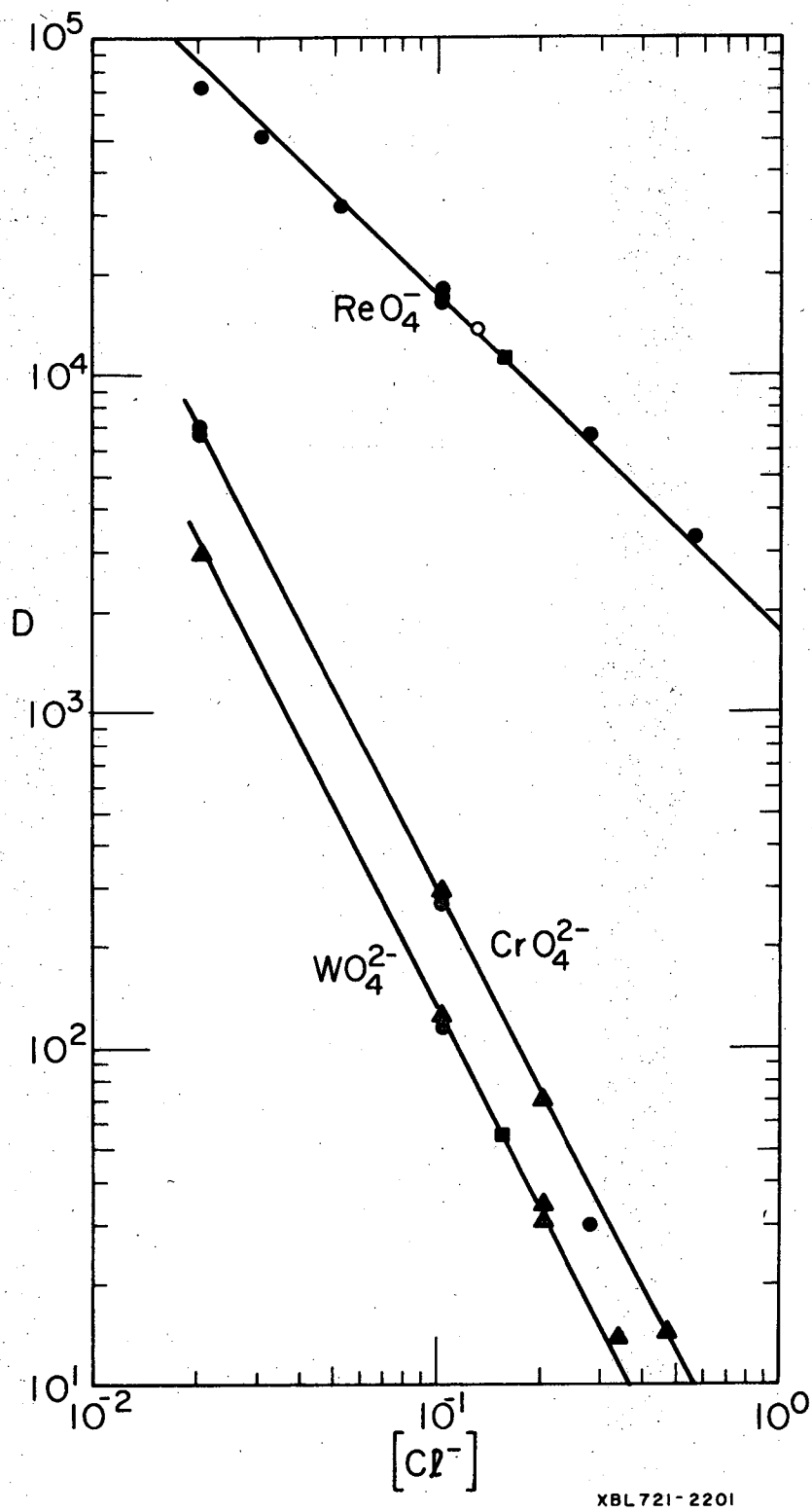
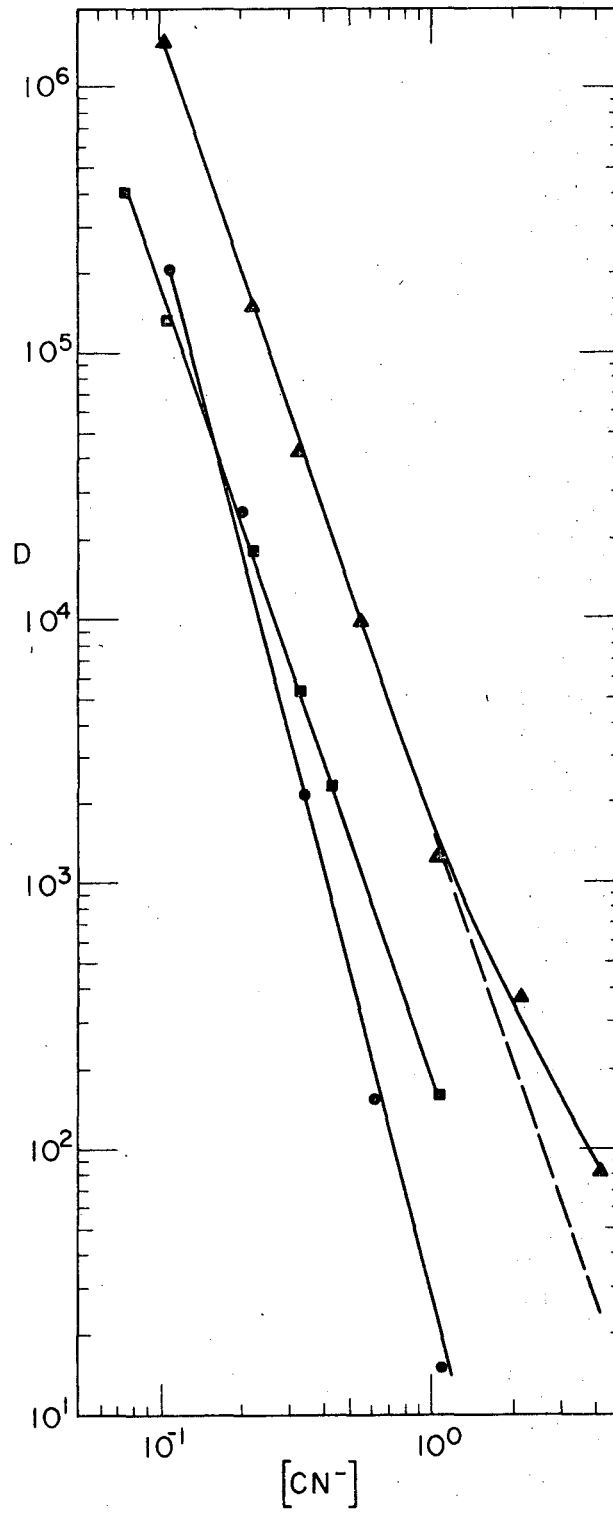


Fig. 1



XBL721-2202

Fig. 2

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