2p carbon orbitals were employed to calculate the interaction between a vibrating proton and one π-orbital, and a rough molecular orbital calculation was used to obtain the density of the odd electron at each carbon and oxygen atom. The calculated interaction constant was about an order of magnitude too small. This lack of agreement is not considered to be a fundamental inconsistency, however, because distortions that might occur in the shape of the 2p orbitals could account for the discrepancy without seriously affecting the over-all shape and properties of the wave function.[31] It is not believed that this disagreement between theory and experiment is inconsistent with the interpretation of relative interaction constants for similarly situated protons in different molecules as relative electron densities at the protons.

A similar calculation for duroquinone, assuming non-vibrating methyl groups, gives a result that is two to three orders of magnitude too small. Hyperconjugation, which was neglected in this calculation, causes delocalization of the methyl group electrons into the π-orbitals of the ring. If this phenomenon were taken into account, the magnitude of the calculated interaction constant should be increased and although calculations of this type have not yet been performed, we believe that these measurements may represent the first direct evidence for hyperconjugation.

The complete interpretation of the proton hyperfine splitting in spectra from radicals containing more than one ring has not been accomplished as yet, and it may not be possible to analyze these complex spectra until extensive knowledge of the magnitudes of the splittings in simple compounds is obtained. As the number of rings is increased, the density of the odd electron at the protons is reduced to such an extent that it is not possible to obtain complete resolution of the component lines and, as the number of protons is increased, the range of intensities become so large that it is difficult to detect the weakest components.

The observation of paramagnetic resonance spectra is clearly a sensitive method for detecting and identifying free radical intermediates. The studies performed on the *p*-benzosemiquinone ion, for example, have shown that this ion is more stable than might have been supposed.[32] By the use of this technique, the equilibrium measurements on semiquinones carried out by Michaelis and his collaborators can be extended to relatively unstable systems. Kinetic studies of auto-oxidations can be elucidated by using the paramagnetic intensity to follow the course of the reaction, and rapid reactions can probably be studied by the use of a stirred-flow reactor. We also believe that the method will be useful in determining the nature of the side reactions that occur in many quinone systems.

NEW YORK, N. Y.

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[31] Jarrett and Sloan (see ref. 16) have recently proposed a different mechanism. An indirect coupling between the electron and proton moments through the chemical bond has been suggested, similar to the coupling between nuclear moments observed in nuclear magnetic resonance spectra, but no quantitative estimates of the effect have been made.

[32] L. Michaelis and S. H. Wollman, *Science*, **109**, 313 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies on Ion-exchange Resins. XIII. Selectivity Coefficients of Quaternary Base Anion-exchange Resins Toward Univalent Anions

BY HARRY P. GREGOR, JACK BELLE[1] AND R. A. MARCUS

RECEIVED NOVEMBER 11, 1954

Selectivity coefficients of a quaternary base ammonium anion-exchange resin toward a number of univalent anions have been measured. In some systems the selectivity coefficients varied little with composition, while in others a marked dependence was observed. Examples of the former included systems made up of various pairs of ions from Group A—halide, acetate, iodate and nitrate, or of pairs of ions from Group B—thiocyanate, perchlorate, di- and trichloroacetate, trifluoroacetate, toluenesulfonate and naphthalenesulfonate. Examples of systems where the selectivity coefficient changed markedly were made up of an anion from Group A with one from Group B. These data were interpreted in terms of two postulated types of specific interactions (ion-pair formation) of these ions with those of the resin matrix. The ion-pairs of Group A were assumed to be randomly distributed in the resin phase, while those of Group B were assumed to occur in the form of "patches," *i.e.*, form clusters. The effect of temperature on the distribution coefficient was small; the concentration of the solution (when dilute) had a negligible effect upon the selectivity.

The previous paper in this series showed that the exchange capacity of a quaternary ammonium base-anion exchange resin was the same for a number of univalent anions and that the swelled volume of the resin phase in different exchange states appeared to be a function of interactions between the movable exchange anions and the fixed groups.[2] This paper describes the selective uptake of one anionic species over another for various combinations of ions with resins of different degrees of cross-linking, and the effect upon this selectivity by variations in the ionic strength of the equilibrating solution and the temperature of the system. These results are interpreted in terms of two different mechanisms of ion-pair formation.[3]

Experimental

A series of benzylethanoldimethylammonium anion exchange resins (Dowex 2, Dow Chemical Co., Midland, Michigan) was used in this study. These resins were identical with ones used in the previous paper[2] and are desig-

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[1] Taken in part from the Dissertation submitted by Jack Belle in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, October, 1952.

[2] H. P. Gregor, J. Belle and R. A. Marcus, THIS JOURNAL, **76**, 1984 (1954).

[3] H. P. Gregor, *ibid.*, **73**, 3537 (1951).

nated by their percentage divinylbenzene (DVB) contents as DVB 1, 2, 4, 8 and 16. In general, unless otherwise specified, all of the experimental conditions were the same as described previously, *i.e.*, employing dilute (0.01–0.1 molal) solutions and room temperatures (24–26°). Sodium or potassium salts were used, except where specified otherwise.

The selectivity coefficient K_d is defined in the conventional manner

$$K_d = K_2^1 = \left(\frac{M_1}{M_2}\right)\left(\frac{m_2}{m_1}\right)$$

where K_2^1 is the selectivity coefficient for a particular exchange process, here the displacement of anion (2) from the resin by anion (1) from the solution, the M's refer to molalities of the anions in the resin phase, and the m's to molalities of the respective ions in the solution phase. This system of notation, where upper case letters refer to terms in the resin phase and lower case letters to corresponding terms in the solution phase, will be used in this paper. The mole fraction of the total exchange capacity of the resin in a particular anionic state (as chloride, for example) is designated X_{Cl}.

Selectivity coefficients were determined by either a column or a shaking procedure. In the former, a known solution was passed through a small (1 g.) bed of resin to equilibrium, the resin phase separated from the solution either by centrifugation or suction, the ions eluted from it and analyzed. The halide, thiocyanate and iodate ions were determined with the silver electrode; hydroxide was titrated. Other ions could be calculated by difference, since the capacity of the resin is the same for all of the anions studied.[2]

With the shaking procedure, a weighed amount of resin in a specific anionic state was shaken with a given portion of a standardized solution of another anion. After equilibrium, the resin and solution phases were separated and each analyzed. These procedures are the same as those described by Gregor and Bregman.[4] The K_d values reported in this paper are reproducible to at least ±5%. In every case they are equilibrium values. Routinely, each experiment was allowed to proceed for at least three times the period of time required for equilibration before the resin and solution phases were separated. Also, it was firmly established that the same equilibrium state was reached regardless of the direction from which it was approached.

TABLE I

SELECTIVITY COEFFICIENTS AS A FUNCTION OF FRACTION OF EXCHANGE CAPACITY IN CHLORIDE STATE

X_{Cl}	K_d	X_{Cl}	K_d	X_{Cl}	K_d
Iodide		Thiocyanate		Perchlorate	
		Resin DVB 2			
0.08	0.092	0.11	0.091	0.03	0.032
.46	.11	.48	.17	.50	.11
.85	.097	.89	.88	.87	.62
		Resin DVB 8			
Fluoride		Bromide		Iodide	
0.15	15.0	0.22	0.29	0.07	0.076
.56	11.5	.49	.40	.49	.055
.90	9.70	.88	.34	.88	.029
Thiocyanate		Perchlorate		Iodate	
0.05	0.054	0.04	0.036	0.27	4.22
.47	0.22	.52	.11	.60	4.11
.98	4.12	.74	.26	.83	4.80
Nitrate		Hydroxide		Acetate	
0.08	0.37	0.20	4.48	0.13	6.80
.47	.33	.53	1.91	.49	6.43
.78	.36	.94	1.15	.86	5.90
Chloroacetate		Dichloroacetate		Trichloroacetate	
0.28	6.41	0.19	0.39	0.09	0.12
.47	6.04	.50	0.46	.56	0.43
.88	4.76	.94	2.13	.92	2.97
Trifluoroacetate		*p*-Toluenesulfonate		β-Naphthalene sulfonate	
0.08	0.46	0.07	0.073	0.12	0.017
.48	0.46	.49	0.12	.53	0.049
.84	1.24	.90	1.12	.99	3.11

Selectivity coefficients for exchange of various anions with the chloride ion as a function of X_{Cl} for DVB 2 and 8 resins using dilute solutions are given in Table I. Table II presents selectivity coefficient data for various combinations of ions other than chloride with resin DVB 8. Some calculated values of K_2^1, *i.e.*, K_d are also given; these will be discussed in a later section. Examination of these tables shows that all of the systems studied could be divided into two groups, sharply differentiated from one another. One set of systems had K_d values which did not vary markedly, if at all, over the entire range of X values. For the other set, K_d varied sharply with X, sometimes as much as 100-fold.

Tables I and II give but a limited number of the experimental points determined. Figure 1 shows K_d plotted against X_{Cl} for those systems (involving the chloride ion) where K_d was relatively constant, showing all experimental points determined using the DVB 8 resin, while Fig. 2 gives detailed data for systems where K_d varied sharply with X_{Cl}, and also where ions other than chloride were involved.

TABLE II

SELECTIVITY COEFFICIENTS WITH VARIOUS PAIRS OF ANIONS FOR RESIN DVB 8

Ions (1)	Ions (2)	X_1^1	K_2^1 (Exp.)	K_2^1 (Calc.)
IO_3	CH_3COO	0.19	1.73	
		.50	1.69	1.5
		.83	1.65	
Br	I	.15	0.18	0.25
Br	OH	.74	2.84	3.3
Br	NO_3	.09	0.93	
		.50	1.00	1.0
		.98	0.94	
SCN	CCl_3COO	.11	2.43	
		.47	1.79	1.4
		.83	1.13	
SCN	ClO_4	.036	0.63	
		.42	0.59	0.5
		.87	0.57	
SCN	I	.61	1.55	1.8

Figure 3 shows how K_d measured for various ions against the chloride ion at $X_{Cl} \cong 0.5$ varied with the percentage DVB for a series of resins. Table III shows K_d values measured at two temperatures, 5 and 25°, for resins DVB 2, 8 and 16 and for the chloride ion measured against the iodide, perchlorate and acetate ions.

TABLE III

SELECTIVITY COEFFICIENTS AGAINST CHLORIDE AS A FUNCTION OF TEMPERATURE FOR DVB RESINS

Anion	Resin DVB	5° X_{Cl}	5° K_d	25° X_{Cl}	25° K_d
Iodide	2	0.47	0.083	0.46	0.11
	8	.42	.042	.49	.055
	16	.47	.031	.50	.065
Perchlorate	2	.44	.032	.32	.048
	8	.48	.044	.47	.070
	16	.52	.030	.38	.035
Acetate	2	.57	5.45	.46	4.96
	8	.58	10.3	.49	6.43
	16	.56	13.3	.59	10.2

As expected, the ionic strength of the solution phase (in dilute solutions) had a slight, if any, effect upon K_d values. For example, with resin DVB 8 and chloride–perchlorate exchange $K_{ClO_4}^{Cl}$ was 0.062–0.066 in the X_{Cl} range of 0.43–0.46 while the solution ionic strength was varied from 0.001

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(4) H. P. Gregor and J. I. Bregman, *J. Colloid Sci.*, **6**, 323 (1951).

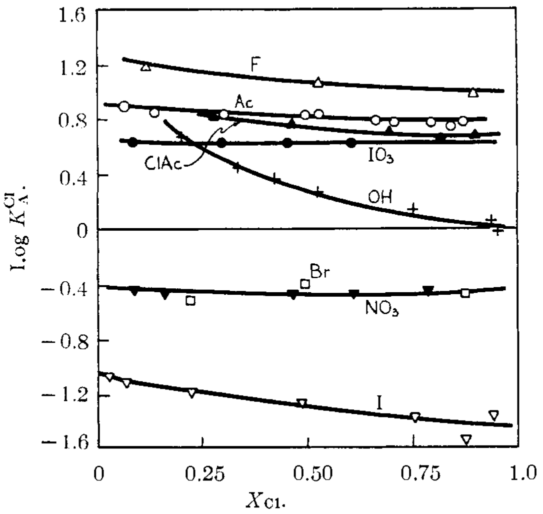


Fig. 1.—Selectivity coefficients measured against chloride with resin DVB 8 for the following anions: fluoride (△); acetate (○); chloroacetate (▲); iodate (●); bromide (□); nitrate (▼); iodide (▽); hydroxide (+).

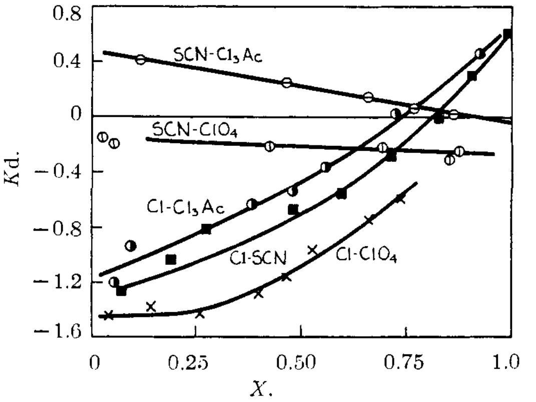


Fig. 2.—Selectivity coefficients measured against chloride with resin DVB 8 for the following anions: trichloroacetate (◑); thiocyanate (■); perchlorate (×). Other selectivity coefficient curves are for thiocyanate over trichloroacetate (⊖) and over perchlorate (⦶).

to 0.1. Chloride–acetate and chloride–trichloroacetate exchange equilibria were similarly unaffected.

Discussion

Most of the selectivity coefficients measured in this study are quite different from unity, and in some cases vary to a considerable degree with the resin composition. This situation is quite different from that with cation exchange processes, where reasonable explanations based upon "pressure–volume" effects, upon analogies with ionic activity coefficients in solution, and upon adsorption of organic cations have been presented.[4,5–9] The data obtained for anion exchange processes which are presented here and elsewhere[2] strongly suggest that a different major factor is operative in the case of anion-exchange resins. A consideration of differences in specific interactions between various anions and the resin cationic group is indicated.

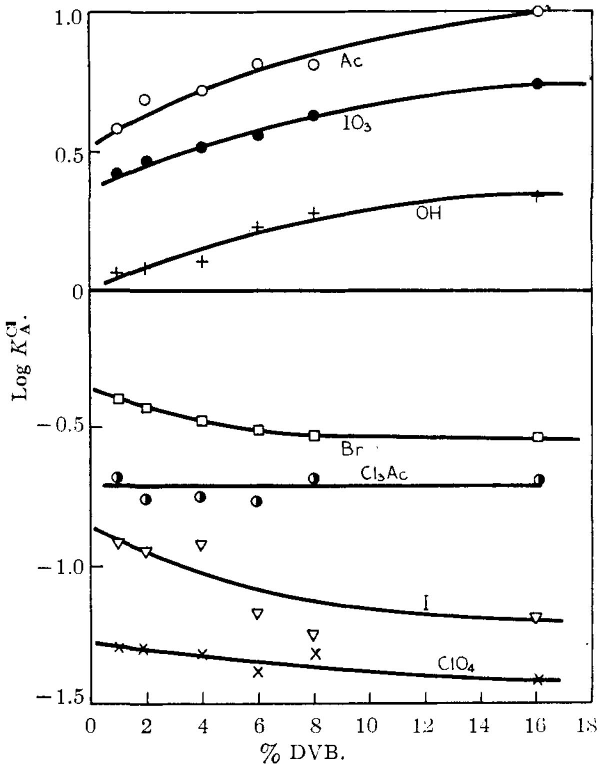


Fig. 3.—Selectivity coefficients measured against chloride for various DVB resins at $X_{Cl} \cong 0.5$ for the following anions: acetate (○); iodate (●); hydroxide (+); bromide (□); trichloroacetate (◑); iodide (▽); perchlorate (×).

If one assumes that ion-pair formation occurs, then the ease of ion-pair formation inferred in this manner coincides with that inferred in a similar fashion from data on the dependence of resin volume on the nature of the anion present.[2] Moreover, this correlation can be made roughly quantitative.

Method of Calculation.—Ion-pair dissociation constants will be estimated from selectivity coefficient data as follows. Consider first an ideal system where the resin phase consists of a three-dimensional network of fixed, positive exchange groups (R^+) which are compensated for electrically by exchange anions A^- and B^-. Association or ion-pair formation can take place between fixed and movable ions to form RA and RB ion-pairs. The resin phase also contains W_W grams of solvent (water), and is in equilibrium with a dilute solution phase containing A^- and B^- salts.

Several cases present themselves. First, consider a system where the interaction between a fixed cation and a movable anion is independent of the formation of ion-pairs on neighboring resin sites. The occurrence of ion-pairs will then be *random* throughout the network, comparable to the adsorption of a gas on a lattice where the adsorption is not a function of whether the neighboring site is occupied or free. For the process $RA = R^+ + A^-$,

[5] H. P. Gregor, THIS JOURNAL, **70**, 1293 (1948).

[6] W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

[7] F. Glueckauf, *Proc. Roy. Soc.* (*London*), **214**, 207 (1952).

[8] B. R. Sundheim, M. H. Waxman and H. P. Gregor, *J. Phys. Chem.*, **57**, 974 (1953).

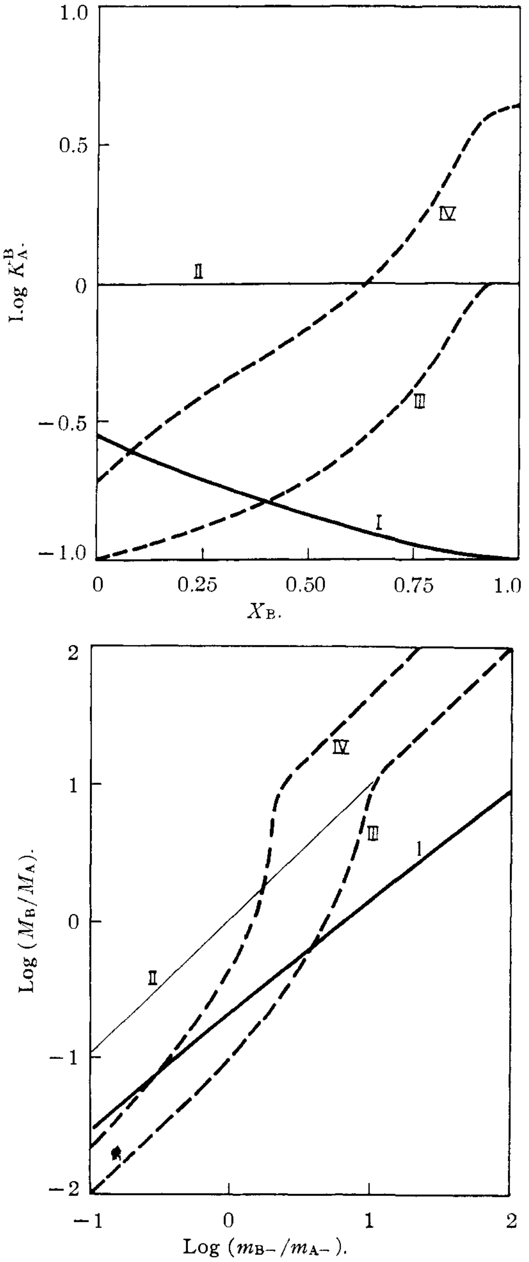
[9] H. P. Gregor and M. Frederick, *Ann. N. Y. Acad. Sci.*, **57**, 87 (1953).

the practical (molal) dissociation constant R_A is clearly given by

$$R_A = \left(\frac{M_{R^+}M_{A^-}}{M_{RA}}\right) = \frac{N_{R^+}N_{A^-}}{N_{RA}} \times \frac{1000}{W_W}$$

where N is the number of moles. All of these symbols refer to components in the resin phase. Activity coefficients are assumed to be unity; these are described in another paper.[10]

For systems where either or both ions form *random* ion-pairs, it can be shown readily that K_d is fairly independent of the ionic composition of the resin. In Figs. 4 and 5 calculated curves are given for two systems: curve I, $R_A = 0.1$ and $R_B = \infty$, *i.e.*, anion B does not associate; curve II, $R_A = R_B = 0.1$. The units of R are moles/1000 g. of water.



Figs. 4 and 5.—Calculated curves for selectivity of anions A and B for the following sets of postulates: I, $R_A = 0.1$, B not associated; II. $R_A = 0.1$, $R_B = 0.1$; III, $C_A = 0.1$, B not associated; IV, $C_A = 0.1$, $R_B = 0.1$.

The selectivity coefficient K_d may be calculated on the basis of this model in terms of R_A and R_B in the following way. Neglecting "pressure-volume" effects, the molality of unpaired ions in the resin phase is related to the molality of these ions in the external solution according to Donnan conditions, and one obtains in this manner the equation $M_{A^-}/M_{B^-} = m_{A^-}/m_{B^-}$. Then

$$K_d = K_B^A = \left(\frac{M_A}{M_B}\right)\left(\frac{m_{B^-}}{m_{A^-}}\right) = \frac{M_{A^-} + M_{RA}}{M_{B^-} + M_{RB}}\left(\frac{m_{B^-}}{m_{A^-}}\right) \quad (1)$$

where the subscript A or B refers to the *total* amount of that species in the resin phase. The two additional conditions are: (1) electroneutrality in the resin phase, or $M_{R^+} = M_{A^-} + M_{B^-}$; (2) $M_{RA} + M_{RB} + M_{R^+} = 1$ molal.

That these assumptions will explain part of the data can be seen by making a judicious choice of R constants and obtaining approximate fits of calculated curves with the experimental values of Fig. 1.

This assumption of *random* ion-pairing does not explain the data of Fig. 2. Interactions other than those between one anion and one resin cation may also be postulated. For example, strong coulombic and van der Waals forces may exist between adjacent ion-pairs such that the paired ions would essentially form a *clustered* or separate phase, *i.e.*, ion-pair formation at sites adjacent to those already occupied is assumed to be energetically preferred to a significant degree. The equilibrium expressions for this system are $C_A = M_{A^-}$ and $C_B = M_{B^-}$, where C_A is the constant for dissociation of the RA ion-pair in the *clustered* system. This expression applies only when $M_A \geqq C_A$; when M_A is less than C_A no ion-pairs RA are present and similar considerations apply to RB. The behavior of many heterogeneous systems is described by this type of equation: the system calcium carbonate–calcium oxide–carbon dioxide is typical.

It can be shown that with systems where either anion forms a *clustered* ion-pair K_d will vary strongly with the mole fraction. In Figs. 4 and 5, curve III is for a system where $C_A = 0.1$ and $R_B = \infty$, and curve IV for $C_A = 0.1$, $R_B = 0.1$.

For a system where anion B forms *random* ion-pairs and anion A forms *clustered* ion-pairs (curve IV), and where the total amount of A present is equal to or greater than C_A or $M_A \geqq C_A = M_{A^-}$, the expression relating the ratio of these ions in the resin phase to the ratio of their solution molalities is

$$2C_A\frac{m_{B^-}}{m_{A^-}} = -R_B + [(R_B + C_A)^2 + 4X_BR_B]^{1/2} \quad (2)$$

Curves based on systems where both RA and RB would form separate phase *clusters* are rather similar in shape to curve IV. However, as can be seen from the data, the selectivity coefficients of such pairs of anions are instead relatively independent of the mole fraction, as shown in Fig. 2. Such behavior readily can be explained if both anions form a *cluster* which approximately consists of an ideal "solid" solution rather than of two separate "solid"

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(10) M. Gottlieb and H. P. Gregor, THIS JOURNAL, **76**, 4639 (1954).

phases. The dissociation constants in this case would take the form

$$S_A = (M_A X_{RA}) = C_A X_{RA}$$

where

$$X_{RA} = \frac{N_{RA}}{N_{RA} + N_{RB}}$$

Clearly, the selectivity coefficient for these "$C - C$" systems can then be calculated in terms of these C's, which in turn can be evaluated from "random-clustered" ($R - C$) ion-pair data. It thus becomes possible to use $R - C$ data to calculate the $C - C$ curves. This has been done and the results are described later.

Each method of plotting used in Figs. 4 and 5 has certain advantages. The log K_d *vs.* X plot is widely used; in particular it points up the differences between systems which do show and those which do not show large changes in K_d with X. However, the nature of this plot masks experimental errors, particularly when K_d is determined by the shaking procedure, for errors which make X large also make K_d large, and conversely. The plot used in Fig. 5 is superior because: (a) the slope of the line is equal to K_d at any point (in the logarithmic plot $\log K_d = \log (M_B/M_A) - \log (m_{B^-}/m_{A^-})$, etc.); (b) variations in K_d with changes in the composition of the resin phase show up clearly; (c) it is sensitive as regards showing up erroneous experimental points.

The curves where the selectivity coefficient varies with the molar ratio in the resin essentially contain only one characteristic, namely, the value of K_d and so cannot be used to evaluate absolute values of these postulated ion-pair constants. The curves where K_d varies appreciably with external molar ratio need several parameters to describe them by means of an equation and hence can be used to estimate the absolute values of the R and C constants. These R constants can then be employed in the $R - R$ curves to determine the R's of other ions.

The constants R_B and C_A were estimated from curves where K_d varied with mole fraction in the following way. Selecting a given point on this curve, R_B was calculated for various assumed values of C_A using equation 2, thus yielding a curve of R_B *vs.* C_A. This calculation was repeated for two other, widely different points on the data curve. The region of intersection of all three R_B *vs.* C_A curves yields the relatively unique values of R_B and C_A.

Evaluation of Dissociation Constants from Selectivity Coefficient Data.—Since practical (molal) dissociation constants were calculated, data on the water content of the resin phases was needed. In a previous paper in this series[2] it was shown that the molality of exchange anions in the resin phase of a DVB 8 resin were as follows: 4.3 for chloride; 5.2 to 6.0 for dichloroacetate, trichloroacetate, trifluoroacetate, toluenesulfonate and naphthalenesulfonate; 7.5 for thiocyanate; 9.2 for perchlorate. Comparable values for a DVB 2 resin did not differ from these by more than 20%, because while the water content was greater due to the greater degree of swelling, the greater exchange capacity of the resin (3.86 compared to 2.25 mmoles/g.) compensated for this. Further, since the values of W_w are approximately linear functions of the mole fractions, the taking of an average value of W_w = 200 g. for most of the anions introduces but a small error; however, for the chloride–thiocyanate system W_w was taken as 170, and for chloride–perchlorate W_w = 150.

Turning first to the data for systems where K_d did vary sharply with resin phase composition, consider those in which the chloride ion was involved. Figure 6 shows experimental points and curves fitted to these points calculated for systems where one ion (chloride) is assumed to form a *random* ion-pair and the other anion a *clustered* ion-pair. While data were obtained in the range $X_{Cl} > 0.9$ ($M_B/M_A > 10$), they were not included because of the relatively large experimental errors that arise here, since ion A usually was determined by difference. For resins DVB 2 and 8, a single value for R_{Cl}, 0.65, was found to fit all these systems. With resin DVB 8 (except as noted) the C constants for the other anions were as follows: thiocyanate, 0.25; thiocyanate (DVB 2), 0.20; perchlorate (also for DVB 2), 0.10; dichloroacetate, 0.35; trichloroacetate, 0.35; trifluoroacetate, 0.35; *p*-toluenesulfonate, 0.15; *β*-naphthalenesulfonate, 0.050. Each of these values is probably accurate to but ±10%. It is seen from Fig. 6 that the fit of experimental to curves calculated using the above constants is reasonable except with the dichloroacetate and the trifluoroacetate systems.

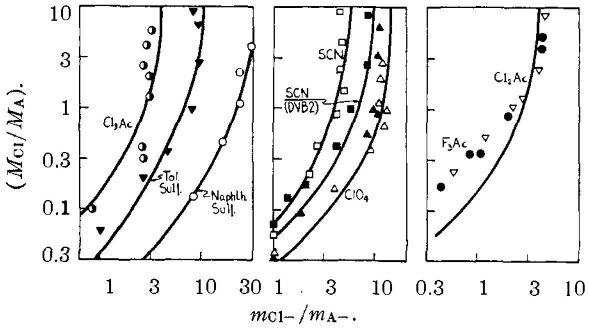

Fig. 6.—Experimental points and curves calculated based upon the postulate of *random-clustered* systems for anion-exchange processes with resin DVB 8 and chloride with the following anions: trichloroacetate (◑); *p*-toluenesulfonate (▼); *β*-naphthalenesulfonate (○); thiocyanate (□), with DVB 2 (■); perchlorate (△), with DVB 2 (▲); dichloroacetate (▽); trifluoroacetate (●).

Before evaluating ion-pair dissociation constants for systems where both ions form *random* ion-pairs, it is of value to calculate the maximum value that K_A^{Cl} (A is any anion) can have if R_{Cl} = 0.65 as just calculated and anion A does not associate. At X_A = 0.5, K_d (max.) = 5.6. Since K_F^{Cl} = 11.6 and K_{Ac}^{Cl} = 6.5 it would appear that a significant discrepancy exists. However, a consideration of pressure–volume effects shows that this discrepancy is apparent rather than real because in systems which are largely dissociated high osmotic pressures prevail and pressure–volume effects act to exclude the larger or unassociated ion from the resin phase. From relative humidity data and comparisons with sulfonic acid resins of comparable cross-linking (the chloromethylation reaction introduces additional cross-linking), the osmotic pressures which prevail can be estimated at about 150–200 atm.[8,9]

Using the appropriate differences in volumes of resins in different anionic states given previously,[2] our selectivity coefficients corrected to zero osmotic pressure become: $K_{\mathrm{F}}^{\mathrm{Cl}}$, 5.1; $K_{\mathrm{Ac}}^{\mathrm{Cl}}$, 4.3; $K_{\mathrm{ClAc}}^{\mathrm{Cl}}$, 4.6; $K_{\mathrm{IO_3}}^{\mathrm{Cl}}$, 2.7. These pressure–volume corrections are very approximate; the accuracy of the corrected K_{d} values is estimated to be ±20%. Therefore, one can conclude that there is little, if any, association in the case of the fluoride, acetate and chloroacetate resins. The values of R_{A}, calculated on the assumption of $R - R$ systems and $R_{\mathrm{Cl}} = 0.65$ are as follows: iodate, 3.6; bromide, 0.20; nitrate, 0.17; iodide, 0.025. The pressure–volume term can be neglected in these latter systems because even the chloride state resin is about 70% associated so that the osmotic pressure is relatively small.[11]

Using the R and C values just calculated for the various anions, the selectivity coefficients of other systems composed of different combinations of these same anions can be predicted. Table II shows a comparison of predicted and experimental values. The first four are for $R - R$ systems. The next two values are for systems where the ions were "*clustered*" when paired with chloride, but are assumed to form a "solid solution" or $S - S$ system when paired together. Thiocyanate–iodide exchange is an example of an $R - C$ system; here the calculated value of 1.8 compares favorably with the experimentally determined value of 1.55.

General Discussion.—While one might attempt to correlate ion-pair dissociation constants with such physical properties as ionic polarizability or molar refraction, this does appear possible at this time. In general, the selective uptake of an ion increases as does its molar refraction. However, since the geometry of an ion is sure to be an important factor, comparisons should be made only for ions of similar geometry and size. Figure 7 shows a plot of log K_{d} for the halides (measured against chloride) as a function of their molar refraction.[12] The relationship between K_{d} and the molar refraction is not a general one, however. For example, the molar refraction is 11.0 for nitrate and 13.2 for perchlorate; K_{d} values for these ions would fall approximately along the curve of Fig. 7. However, for acetate the molar refraction is 13.6 and the value does not fall along the curve. Here molar refraction by itself is not a valid criterion, probably because of size and geometry factors; these considerations presumably apply to the other unsymmetrical ions.

In addition to the simple ion–ion coulombic forces which are present, ion–dipole and van der Waals interactions are appreciable in these systems. Evidence of this may be found in the adsorption of iodide and iodine by sulfonic acid cation-exchange resins, and by the strong uptake of organic ions by the same resin, the effect increasing with increasing molecular weight of the ion.[4] These forces may also contribute to ion-pairing and it would then be predicted that ion-pairing would increase with the polarizability of the exchange ion, with the closeness of approach of the ions and with organic substitution in the anion.

At first glance the strong preference of the resin for the perchlorate ion appears surprising. However, this interaction in these quaternary ammonium resins is consistent with the low solubilities of the quaternary ammonium perchlorates. For example, tetramethylammonium perchlorate is soluble only to 0.03 M, while the iodide is soluble to 0.25 M.

The parameter which appears to determine whether an anion will give selectivity coefficient curves with chloride ion of the $R - R$ or $R - C$ type is the ionic size. With the exception of the perchlorate, the anions giving the $R - R$ curves are small, those giving the $R - C$ curves are large. *Clustering* interactions presumably occur largely along the polymer chain where the fixed groups are about 3–4 Å. apart. Since the forces that make for *clustering* are very short range ones, it is important that the associated ion-pairs be large enough to affect association at an adjacent site. If a resin were prepared in which the fixed exchange sites were far enough apart, it would be predicted that all anions would associate in the *random* system.

Since the formation of ion-pairs is reflected in both volume and selectivity coefficient data, these data are interrelated, although not necessarily in a simple manner. Figure 8 shows a plot of log $K_{\mathrm{A}}^{\mathrm{Cl}}$ as a function of V_{e}, the swelled volume of the resin in the various anionic states.[2] The selectivity coefficients (at $X_{\mathrm{Cl}} \rightarrow 0$) are used instead of dissociation constants because of the different forms of R and C constants. Data for most of the systems are found to fall approximately along the same line; a large value of V_{e} corresponds to a low degree of selective uptake, and the converse is also true. However, with the large trichloroacetate or aryl sulfonate anions one finds a large swelled resin volume together with a *high* degree of selectivity. Apparently here the size of the anion itself is such as to make the resin swell.

The effects of changes in temperature upon the selectivity coefficients with three sets of anions on resins of three different degrees of cross-linking were shown in Table III. It is evident that K_{d} for these systems is fairly independent of temperature. There is a small tendency for the system to become more random (K_{d} approach unity) with increasing temperature in that the ionic preference decreases. This effect applies to both *clustered* and *random* ion-pairs, also where one ion is not appreciably associated.

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(11) It should be pointed out that the osmotic pressures which could reasonably be encountered in these systems would have but a negligible effect upon the dissociation constants themselves, because here the thermodynamic expression for the closed system is

$$\frac{\partial \ln R_{\mathrm{A}}}{\partial \pi} = -\frac{(\bar{V}_{\mathrm{A}^-} + \bar{V}_{\mathrm{R}^+} - \bar{V}_{\mathrm{RA}})}{RT}$$

where π is the osmotic pressure and the $\bar{V}$'s the partial molar volumes. Since electrostriction usually occurs in these systems, ΔV is small and negative, and dissociation would increase with π. The fact that we are dealing with an *open osmotic system* here means that where R_{A} is small (strong association), the gel will contract and make for the formation of more ion-pairs but with the same value of R_{A}.

(12) Taken from A. Kruis and W. Geffcken, *Z. physik. Chem.*, B**34**, 51 (1936); H. Kohner and H. Gressman, *ibid.*, **144A**, 137 (1929).

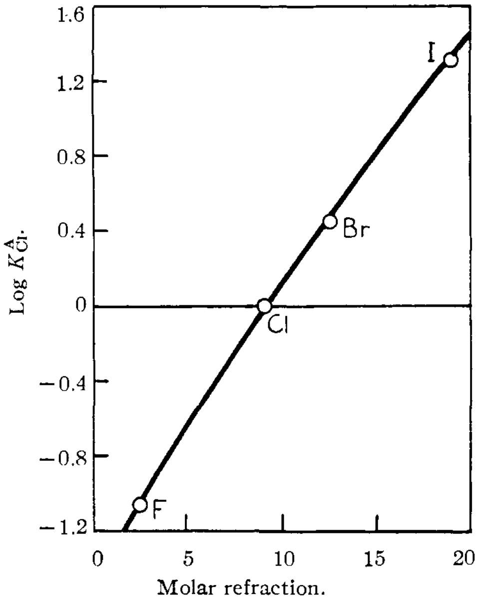

Fig. 7.—Selectivity coefficients for halide exchange with DVB 8 resin as a function of ionic molar refraction.

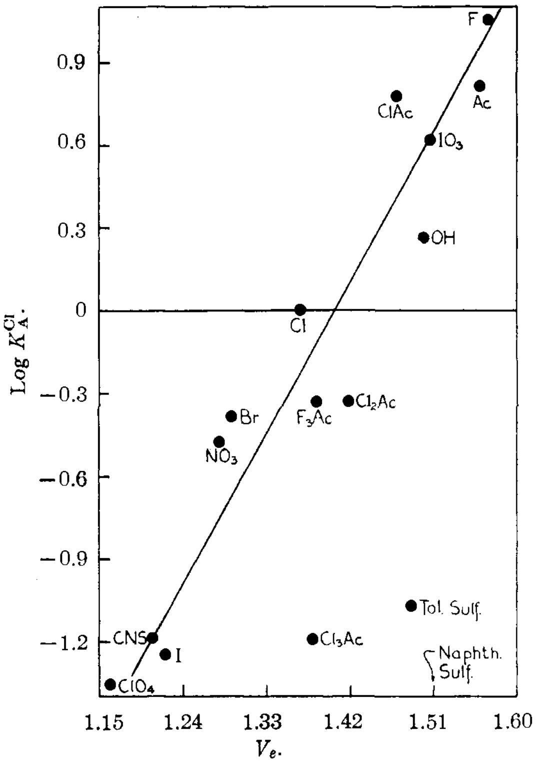

Fig. 8.—Selective uptake of the chloride ion over various anions with a DVB 8 resin, as a function of the swelled volume of the resin in the corresponding anionic states. All values taken at $X_{\mathrm{A}} \to 1$.

As regards the effect of cross-linking, as shown in Fig. 3, the uptake of the favored ion is increased with increasing cross-linking. $K_{\mathrm{Ac}}^{\mathrm{Cl}}$ increases from 3.8 to 10 as the DVB content of the resin goes from 1 to 16%, while $K_{\mathrm{Cl}}^{\mathrm{I}}$ increases from 9.6 to 16 and $K_{\mathrm{Cl}}^{\mathrm{ClO_4}}$ increases from 48 to 62. In the chloride–trichloroacetate system where ΔV is nearly zero, K_{d} is independent of cross-linking, as expected. Pressure–volume effects appear to be a major factor only in the absence of ion-pairing.

There is an obvious parallel between the extent of ion-pair formation as described here and the well known Lyotropic or Hofmeister series of colloid chemistry, where adsorbability at polar–apolar interfaces by anions and the coagulation of positively charged colloidal particles by anions follow the series: naphthalenesulfonate > benzenesulfonate > thiocyanate > iodide > bromide > chloride > fluoride. The forces making for these effects are presumably similar, although in ordinary colloidal systems the *clustering* effect is probably not present because of the low charge density on the surface. The general effects which exist in the ion-exchange resin systems are considerably stronger because the density of active sites in the resins is very high.

A direct comparison of our data and those of other authors is made difficult by the large differences which exist between resin samples prepared by essentially the same procedures. Wheaton and Baumann[13] have studied selectivity coefficients for Dowex 2 and Dowex 1 (both DVB 8) resins, the latter being of the benzyltrimethylammonium type. They found with Dowex 2 that $K_{\mathrm{F}}^{\mathrm{Cl}} = 7.7$ and $K_{\mathrm{I}}^{\mathrm{Cl}} = 0.14$; both values are smaller by a factor of about two than ours. The behavior of a similar anion-exchange resin, Amberlite IRA 400, which is also of the benzyltrimethylammonium type was investigated by Kunin and McGarvey,[14] who found that $K_{\mathrm{I}}^{\mathrm{Cl}} = 0.33$ and $K_{\mathrm{SCN}}^{\mathrm{Cl}} = 0.5$. These selectivities are in the same direction as those observed by us, but are very much smaller in magnitude, about one-tenth as large.

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[13] R. M. Wheaton and W. C. Baumann, *Ind. Eng. Chem.*, **43**, 1088 (1951).

[14] R. Kunin and F. X. McGarvey, *ibid.*, **41**, 1265 (1949).