in the partition method introduces a complicating factor that cannot be readily evaluated.

No data were found in the literature which could be compared unambiguously with those reported in Table II. The nearest case was the benzene solution values recorded in the last column of the table. A rough parallelism is noted in the trend of the two sets of values, and, neglecting the case of benzoic acid, the benzene values are larger by a factor of 10–20. Differences not only of the constants but of the heats of association are to be expected[29] on the basis of relative affinity of the solvent for the monomer molecules.

This study was undertaken as one phase of a program envisaging the examination of interactions of various acid–base systems in a relatively constant medium by means of the infrared absorption technique. Measurements in carbon tetrachloride on pyridine and diethyl ether with some of the acids listed above have been carried out and will be reported at a later date.

DURHAM, NORTH CAROLINA

[29] M. E. Hobbs and W. W. Bates, THIS JOURNAL, **74**, 746 (1952).

[CONTRIBUTION FROM THE INSTITUTE OF SCIENCE AND TECHNOLOGY, UNIVERSITY OF ARKANSAS]

Prediction of Cation-exchange Equilibria

BY J. L. PAULEY

RECEIVED JULY 15, 1953

This paper offers an explanation for the selectivity of ion-exchange resins, based upon a consideration of the coulombic forces acting on the system. Herein, the resin is considered to be a series of negative point charges randomly distributed and the cations are held at an average at their closest distance of approach (which may be considered to be the sum of the radii of the "adsorbed" hydrated cation and the resin anion). Hence, the free energy change involved in the exchange of the cations, and thus K_{eq}, may be determined from the work necessary to remove each of the two types of cations involved from this distance of closest approach to infinity against the coulombic attractive forces acting between the cation and the resin anion. Calculations were made for several uni-univalent exchanges and one uni-divalent exchange, and the calculated K_{eq} was found to agree favorably with that obtained experimentally.

The exchange capacity, *i.e.*, the ability of one ion to replace another on an ion exchanger, varies according to the radii of the hydrated ions.[1] The order of absorption in general is that of the lyotropic series Cs > Rb > K > Na > Li.

Nachod and Wood[2] have compared equilibrium exchange capacities with the "a_0" values of the Debye–Hückel equation for activity coefficients which have been related to hydrated radii. They have found nearly quantitative correlation within valence types as expressed by the equation

$$R = \alpha \times 28.3 \times \text{E.E.} + \beta\,(23.5 + 5.3V)$$

where R = radius of hydrated ion, α and β are constants depending on exchanger, V = valence of entering ion, and E.E. = equilibrium exchange capacity.

Boyd, Schubert and Adamson[3] have shown that exchange constants are related to the free energies of hydration of the cations involved, and have suggested that the free energies of hydration, and thus of exchange, should be governed by electrical interactions according to Coulomb's law. They have found close correlation between free energies of hydration and exchange constants in the systems investigated.

Gregor[4] has examined the consequences of combining Donnan's equations concerning membrane equilibria with an assumed simple relationship between swelling pressure and volume of the exchange resin, wherein the stress caused by the swelling is considered to obey Hooke's law. The relationships developed in many cases have been found to describe the properties of ion exchangers rather closely.

It is a reasonable assumption that, in any completely rigid treatment of free energies or equilibrium constants of ion-exchange reactions, the variation in degree of swelling with ionic form of the exchange resin should be considered. It might also be expected that this factor should become increasingly important with increasing cross linkage and swelling pressure of the resin.

In this paper, the contribution to the free-energy difference for the exchange reaction of the change in swelling pressure for different ionic forms has been neglected. It would be expected that this assumption would be justified completely only if the amount of cross-linking is negligible. As a first approximation, it has been assumed that for moderately cross-linked exchangers this contribution, if not completely negligible, is small compared to the electrical interactions involved.

In general, it has been assumed that the ions of the resin phase may be considered to be completely disassociated, with their activities determined by interionic attractions approximately as expressed by the Debye–Hückel theory. It should not be expected, however, that this treatment would be applicable to the resin phase, inasmuch as the resin anion is attached somewhat firmly to the resin walls and a spherically–symmetrical arrangement of ions about it could hardly be expected. Also, steric or space requirements will largely rule out the attainment of a spherically–symmetrical atmosphere for the cations of the resin phase, or for the salt ions coming from the solution phase which are found in the resin phase.

---

[1] R. Kunin and R. J. Meyers, "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 22 ff.

[2] F. C. Nachod and W. J. Wood, THIS JOURNAL, **67**, 629 (1945).

[3] G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

[4] H. P. Gregor, *ibid.*, **70**, 1293 (1948); H. P. Gregor and J. I. Gregman, *ibid.*, **70**, 2370 (1948).

For a particular sulfonated polystyrene resin assumed to be more or less typical, the wet resin is found to be 40% water,[5] and to have an exchange capacity of 3.0 meq. per gram. Considering that each of the anionic groups is in contact with the imbibed water, and that the density of water remains constant in the resin phase, this corresponds to 0.4 cc. of water in one gram of the resin; thus, the volume of the pores in one gram of resin is 0.4 cc. The 3.0 meq./gram corresponds to $3.0 \times 6 \times 10^{20}$ anionic groups, or 18×10^{20} groups. This amounts to $4 \times 10^{23}/18 \times 10^{20}$ cubic ångströms per group, or about 222 cubic ångströms. This corresponds to a cube 6.05 Å. on an edge available to each hydrated cation.

From the above, it can be seen that the motion of the ions will be severely limited and that nothing approaching the Debye–Hückel model for an ionic atmosphere can be expected. And, since thermal motion is a strictly random motion, it seems reasonable to predict that, on an average, the resin cations would remain very nearly at their distance of closest approach to the resin anion.

From these factors, the author has postulated as a standard state, or as an average equilibrium state, the resin cations bound more or less firmly to the anionic groups of the resin, the distance between the charge centers being the distance of closest approach of the cation and anion. This distance of closest approach has been taken to be the sum of the radius of the hydrated cation and the radius of the oxygen anion.

The choice of the value to be used for the anion radius is difficult. Bernal and Fowler[6] have assumed the radii of anions in solution to be equivalent to their crystallographic radii. If the anion is non-hydrated, as they have suggested, this would appear to give a maximum value for ionic bonding. Equilibrium constants have been calculated using the crystallographic radius of oxygen, 1.32 Å., the covalent radius of oxygen, 0.22 Å., and an intermediate arbitrary value of 1.00 Å. Because this factor is constant in all cases, there is no change in the relative order of exchange; only the magnitude of the exchange constant is affected. Also, the values of K_{eq} calculated for an anion radius of 0.22 and 1.32 Å. bracket the observed values; thus, the choice of the proper intermediate value would produce extremely close correlation between observed and calculated values. The choice of such a value has been deliberately avoided because, although such a radius is not entirely unreasonable, there is little justification, in the light of our present knowledge of ionic radii in solution, for the choice of any particular intermediate numerical value.

This choice of radii has been made on the basis of several known facts: (1) It is known, from transference, mobility and other data, that cations in solution are hydrated. (2) On the basis of the assumptions of Bernal and Fowler,[6] anions in solutions in general may be assumed to be non-hydrated and their radii to be their crystallographic radii. (3) In the derivation of the Debye and Hückel equations, it was found that the introduction of a term corresponding to the radius of the hydrated ion concerned is necessary at appreciable concentrations. (4) Walton,[7] *et al.*, in a paper given at the 1953 A.C.S. Meeting in Los Angeles, have shown on the basis of studies with various copper and silver amine complexes that there is no change in amine–metal ratios within the solution or resin phase, and that the replacing of water by ammonia has slight effect upon the exchange constant. From this they assume that in the resin phase the ions exist in the hydrated or solvated form. (5) Swelling data for highly cross-linked resins indicate that the degree of swelling is in the order Li > NH_4 > Na > K > Rb > Cs, which is the order of decreasing radii of hydrated ions. (6) The inversion of order or equalization of exchange capacities found at higher temperatures, higher concentrations, or in media of low dielectric constant, is consistent with the viewpoint of solvated ions. (7) This viewpoint offers a consistent explanation of the hitherto almost unexplained ionic preference of exchanges when treated by the methods of this paper.

If this model is taken as a first approximation, we can consider that the potential and consequently the standard-state free energy of the resin ion–hydrated cation pair will be governed by the Coulomb law

$$V = \frac{Z_1 Z_2 \epsilon^2}{rD}$$

where r is distance of closest approach of the exchange-resin anion and associated hydrated cation. It also will be assumed that, for dilute solutions, the activities of the cations not associated with the resin are equal to their concentrations.

On the basis of the above assumptions, considering the reaction

$$A^+ + B^+R^- = B^+ + A^+R^-$$

the reaction can be divided into two parts

$$B^+R^- = B^+ + R^-, \text{ and} \quad (1)$$

$$\Delta F_0 = \int_{r_B + r_R}^{\infty} \frac{Z_B Z_R \epsilon^2}{r^2 D}\,dr = \frac{Z_B Z_R \epsilon^2}{(r_B + r_R)D}$$

$$A^+ + R^- = A^+R^- \quad (2)$$

$$\Delta F_0 = \int_{\infty}^{r_A + r_R} \frac{Z_A Z_R \epsilon^2}{r^2 D}\,dr = \frac{-Z_A Z_R \epsilon^2}{(r_A + r_R)D}$$

where Z represents the charge of the ions, r_A and r_B are radii of corresponding hydrated cations, r_R is the effective radius of resin anion, ϵ is the electronic charge, and D is the dielectric constant of the medium.

Now, introducing N, Avogadros number, to give the molar free energy change, the ΔF_0 for the overall reaction can be given

$$N\Delta F_{01} + N\Delta F_{02} = \Delta F_0(\text{tot.})$$

Thus

$$\Delta F_0\ (\text{tot.}) = \frac{N^2}{D}\left(\frac{Z_B Z_R}{r_B + r_R} - \frac{Z_A Z_R}{r_A + r_R}\right)$$

and from the relationship: $\Delta F_0 = -RT \ln K_{\text{eq}}$ the equilibrium constant can be determined.

In order to compare the equilibrium constants

---

[5] G. E. Boyd, G. K. Rollefson and R. E. Powell, Ed., *Ann. Rev. Phys. Chem.*, **2**, 320 (1951).

[6] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[7] H. F. Walton, R. H. Stokes and R. H. Lang, paper presented at 123rd Meeting A.C.S., Los Angeles, Calif., March, 1953.

obtained in this manner with those found in the literature, the above relationships are written as

$$-\log K = \frac{N\epsilon^2}{2.3RTD}\left(\frac{Z_{\mathrm{B}}Z_{\mathrm{R}}}{r_{\mathrm{B}} + r_{\mathrm{R}}} - \frac{Z_{\mathrm{A}}Z_{\mathrm{R}}}{r_{\mathrm{A}} + r_{\mathrm{R}}}\right)$$

$$\epsilon = 4.8 \times 10^{-10} \text{ e.s.u.}$$

$$D = 78.54$$

$$T = 298°$$

$$\mathrm{R} = 8.32 \times 10^{7} \text{ ergs/degree/mole}$$

$$N\epsilon^2(10^{-8})/2.3RTD = 3.09\ (r \text{ in Å})$$

Different values have been obtained for the hydrated ion radii of cations by different authors according to the methods of measurement used. In Table I, values given by three different investigators have been listed. If the picture given of the exchange resin pore size is approximately correct, the values in the first two columns, obtained from ionic mobility studies, would appear to be much too large. The values in the third column are from the "a_0" values of the Debye–Hückel equations as determined by Bernal and Fowler,[6] and are such that ionic mobility should not be seriously hampered by the pore size of the resin. The choice of these values for calculation of $K_{\mathrm{eq's}}$ seems reasonable also, because they were obtained for a more nearly analogous situation: the distance of closest possible approach of oppositely charged ions in solution.

TABLE I

IONIC RADII OF HYDRATED CATIONS

Ion	Radius, Å.[10]	Radius, Å.[8]	Radius, Å.[9]
Na^+	5.6	7.90	2.16
K^+	3.8	5.32	1.82
Rb^+	3.6	5.09	1.66
Li^+		10.0	2.85
NH_4^+		5.37	
Cs^+		5.05	1.19
Ca^{++}		9.6	2.94
H^+		11.0	3.03

Radius of resin anion = 1.32 Å.

An example of the calculations is reproduced below

For the exchange: $Na^+ + KR = K^+ + NaR$

$$\begin{aligned}\log K_{(\mathrm{eq})} &= -3.1\left(\frac{1}{3.14} - \frac{1}{3.48}\right)\\ &= -3.1\ (0.32 - 0.29)\\ &= -0.093\\ K_{\mathrm{eq}} &= 0.80\end{aligned}$$

Boyd[3] gives for this exchange $K = 0.62 \rightarrow 0.72$.

For the exchange: $2Na^+ + CaR_2 = 2NaR + Ca^{++}$

$$\begin{aligned}\log K_{\mathrm{eq}} &= -3.1\left(\frac{4}{4.26} - \frac{2}{3.48}\right)\\ &= -3.1\ (0.939 - 0.575)\\ &= -1.13\\ K_{\mathrm{eq}} &= 0.08\end{aligned}$$

Walton[11] gives 0.32–0.52 for this exchange.

Table II presents values obtained for K_{eq} in this manner compared to experimentally observed values. In obtaining these observed values, the difficulty of defining an activity coefficient for the ions in the resin phase arises. Lacking any certain knowledge of these activity coefficients, it has been assumed, in obtaining experimental values, that the activity coefficients of both exchanging cations in the resin phase are at least similar in magnitude and will effectively cancel.

TABLE II

CALCULATED VALUES FOR EQUILIBRIUM CONSTANT FOR SEVERAL EXCHANGES USING "a_0" VALUES DETERMINED BY ROBINSON AND STOKES[8] AND DIFFERENT ANIONIC RADII, COMPARED TO OBSERVED VALUES

	Calcd. K_{eq}.				
	$r_{\mathrm{R^-}}$ = 0.22	$r_{\mathrm{R^-}}$ = 1.32	$r_{\mathrm{R^-}}$ = 1.00		Obsd. values of K_{eq}.
$Na^+ + KR$	0.61	0.80	0.76		0.62
$Rb^+ + KR$	1.35	1.14	1.16		1.37
$Rb^+ + NaR$	2.22	1.42	1.53		2.05
$Na^+ + LiR$	1.95	1.40	1.49		1.72
$2Na^+ + CaR_2$	0.05	0.08	0.06	(B)	0.32[a]
$K^+ + LiR$	3.17	1.75	1.97		2.65
$Cs^+ + KR$	2.25	1.27	2.07		1.88
$Na^+ + HR$	2.22	1.50	1.62	(A)	1.20[a]
$Cs^+ + HR$	6.73	1.73	2.49	(A)	2.04
$Rb^+ + HR$	6.73	1.73	2.49	(A)	2.22

[a] Ionic strength = 0.1. All others, ionic strength = 0.001. A, data of Bauman[12]; B, data of Walton[11]; other data from Boyd.[3]

The validity of the numerical values of K_{eq} for those exchanges involving H^+ ions as calculated here is highly questionable, as it has been noted that H^+ occurs between Na^+ and Li^+ in the exchange series, although the hydrated ion undoubtedly has a larger radius than does the lithium ion. It is interesting, however, that the calculated order of exchange is the same as that observed and the value of K_{eq} calculated is, at least for r_{R} equal to 1.00 and 0.22 Å., larger than that observed. This would be expected if the acid form of the exchange resin were incompletely disassociated, as has been suggested.

In this treatment, all second-order coulombic interactions have been neglected. It is not implied, however, that such second-order effects are unimportant, because it is probable that the anionic groups are separated by only 4 to 10 Å. But, in the light of existing knowledge concerning the internal arrangement of ion-exchange resins, there is little justification for an attempt to calculate these effects numerically. However, it is noteworthy that, for any reasonable model of the resin interior, these second-order coulombic interactions can serve only to reinforce the selectivity of the resin. This increases the numerical value of K_{eq} for the exchange of a hydrated ion with a small radius for a hydrated ion of larger radius. It also will be noted that, if we accept the assumption of Bernal and Fowler[6] that the proper value for the anionic radius is the crystallographic radius of the ion, these second-order effects will make the calculated values of K_{eq} agree more closely with observed values.

The degree of cross-linking of the resin mentioned before, also will determine to some extent the rigor of the foregoing treatment. The change in swelling pressure of the resin resulting from cation exchange, and also the relative ability of the ions to diffuse through the resin, will become of increasing

---

(8) H. J. Jenny, *J. Phys. Chem.*, [2] **36**, 2217 (1932).

(9) R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).

(10) Wiklander, *Annuals, Roy. Agr. Coll. Sweden*, **14**, 1 (1946).

(11) H. F. Walton, *J. Phys. Chem.*, **49**, 471 (1945).

(12) W. C. Bauman and J. Eichorn, THIS JOURNAL, **69**, 2830 (1947).

importance in determining the equilibrium ionic distribution as the degree of cross-linking of the resin is increased. Conversely, if there is essentially no cross-linking, as for linear polyelectrolytes, it might be expected that the free energy of exchange would approximate that to be expected from the Debye–Hückel treatment of electrolytes in solution, since the limitation of motion of the cations resulting from volume available within the pores of the resin no longer would be a governing factor.

Thus, it might be expected that this treatment in its present form would describe most nearly the ionic distribution for exchanges involving moderately cross-linked resins and cations whose sizes are not such as to make their ability to diffuse through the resin pores the controlling factor in determining their equilibrium distribution.

Acknowledgment.—The author acknowledges the helpful coöperation of Professors E. S. Amis, M. K. Testerman and H. Chessin of the University of Arkansas, and Dr. F. C. Nachod of Sterling-Winthrop Research Institute.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Role of the Solvent in Radical Decomposition Reactions: Phenylazotriphenylmethane

BY MARILYN G. ALDER[1] AND JOHN E. LEFFLER[2]

RECEIVED SEPTEMBER 14, 1953

A well-known property of radical dissociation reactions is insensitivity of the rate to changes in solvent. However, the insensitivity of the rate is not necessarily due to absence of strong interaction between the solvent and either the starting or transition states. In the present example there is an important interaction with the solvent and the small effect on the rates is due to simultaneous large but compensating changes in enthalpy and entropy of activation.

Introduction

The insensitivity of the rates of radical decomposition reactions to changes in solvents has usually been considered to be the result either of complete absence of interaction of the reagents with the solvent or of equivalent interaction of the solvent with both the ground and transition states of the reagent. The comparative rarity of ideal mixtures makes the former explanation implausible. On the other hand, it is hard to believe that all radical dissociation transition states should be solvated to exactly the same extent as their ground states. Some differences in electronic configuration and polarizability should exist. In the case of aromatic systems, the formation of complexes[3] with the reagent should put partial charges on the reagent molecule. These should affect the bond strength in much the same way as a substituent. Unless the average solvation state of the reagent molecules happens to coincide with the one corresponding to the lowest strength of the bond to be broken, there should be a change in solvation on attaining the transition state. We now present evidence for such an effect in the decomposition of phenylazotriphenylmethane in a series of solvents.

Experimental

Phenylazotriphenylmethane was synthesized by the method of Gomberg and Berger.[4] Crystallization from ether gave material melting with decomposition at 111–113°. The decomposition temperature is not sensitive to the presence of the hydrazo compound in small amounts. The hydrazo compound may be removed by shaking with lead dioxide until no further increase in optical absorption is observed. The absorption spectrum was similar in all five solvents. The consistent band maximum at 420 mμ agrees well with that at 420.5 mμ reported by Burawoy using hexane as a solvent.[5] The optical extinction at this wave length was used in following the decomposition of the azo compound.

All of the solvents used were freshly distilled. Samples of the solutions were outgassed and sealed in ampoules under one atmosphere of nitrogen and kept frozen in Dry Ice-acetone until used. The kinetic measurements were made by placing the sealed ampoules in thermostated baths (±0.02°). At the end of a measured time interval, the ampoule was removed, quenched in Dry Ice–acetone, warmed to room temperature, opened, and the optical density of the contents measured at 420 mμ. Because variations in the optical analysis, in the degassing and sealing procedure, and in the amount of colored by-products, made it impossible to obtain high precision in the rate constants, these were determined over a very wide temperature range to obtain sufficiently precise activation parameters. Each rate constant represents a considerable number of separate experiments, a different degassed ampoule being used for each time interval and at least two initial concentrations being represented. The colored by-product amounted to less than 10% of the initial optical density and was corrected for by using an equation 1 derived from the assumption that the colored by-product was formed continuously. The same equation may be derived if the assumption is made that the by-product was all present at the beginning of the run.

$$\log \frac{(\epsilon_A - \epsilon_B')[A]_0}{2.30D - \epsilon_B'[A]_0} = \frac{kt}{2.30} \qquad (1)$$

$$\epsilon'_B = \frac{2.30D_\infty}{[A]_0} \qquad (2)$$

where

$[A]_0$ = initial concn. of phenylazotriphenylmethane
ϵ_A = extinction coeff. of phenylazotriphenylmethane
D = optical density at time t
t = time in seconds
k = first-order rate constant, sec.$^{-1}$
ϵ_B' = a pseudo-extinction coeff. for the impurity responsible for the infinity color
D_∞ = the optical density at infinite time

Figure 1 illustrates the application of equation 1 to the data for the decomposition of phenylazotriphenylmethane in

---

[1] Office of Naval Research Post-doctoral Research Associate, 1951–1952.

[2] To whom requests for reprints should be addressed.

[3] Note for example the contribution of ionic structures to the wave functions of molecular complexes: R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[4] M. Gomberg and H. W. Berger, *Ber.*, **36**, 1088 (1903).

[5] A. Burawoy, *J. Chem. Soc.*, 1865 (1937).