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Osmotic Behavior of Anion and Cation Exchangers

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RECEIVED MARCH 15, 1954

The osmotic coefficients of both anion and cation exchangers are defined by a two parameter equation. The two parameters are found to be interdependent. By this approach the osmotic coefficients are related to the crystal radii of ions.

The osmotic coefficients of ion exchangers are very useful in interpreting ion exchange behavior. It is of considerable interest, therefore, to determine whether these coefficients can be characterized and systematized for both the anion and cation types.

Experimental

Various salt forms of approximately 0.5% DVB cation and anion exchangers were equilibrated with water vapor of fixed activities. The experimental techniques for the preparation of the resins and for the isopiestic measurements have been described in detail previously.[1]

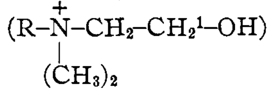
Discussion

The determination of the moisture uptake of an ion exchanger as a function of water activity should permit the calculation of osmotic coefficients. For an aqueous solution, by definition $\nu\phi = -\log a_w/0.00782m$, where ϕ = the practical osmotic coefficient, ν = the number of ions into which the resin salt dissociates, a_w = the activity of the water vapor, and m = the stoichiometric molality of the resin salt in equivalents per 1000 grams of water. However, for an ion-exchange resin the complete equation is

$$\log a_w = -0.00782\nu\phi m + \frac{0.00782\pi}{RT} \qquad (1)$$

Glueckauf[2] has assumed, as do the authors of this paper, that for a 0.5% DVB resin the osmotic pressure π is negligible throughout the concentration range about 2 to 30 molal. This assumption is not valid at very low concentrations but it becomes better as the concentration increases, and the osmotic pressure term becomes negligible at about 2 molal. The lower limit is dependent upon the particular resin salt form. The deviations moreover increase with decreasing concentration. For example, based upon the estimate[1] that $\pi = 0$ for a NaR resin form when the equivalent volume V_e = 300 ml., a fully swollen 0.5% DVB resin (V_e = ~2800 ml.) will have a π = 20 atmospheres at m = 0.4. At NaR m = to 2.7, π = 1. This calculation assumes a linear relation between π and V_e, a relation which tends to give higher than measured values for π for weakly (2% or lower) cross-linked preparations. Using these extreme limits, however, one finds that the pressure term is appreciable only for the F^-, Cl^- and Br^- values at the lowest measured values of m for each ionic form. For all the remaining salt forms and most important at the higher concentrations (>2m) the pressure term is negligible. Since the osmotic coefficients in this treatment are evaluated over a considerable concentration range (2–30 molal) neglecting the above corrections should not adversely affect the conclusions although a caution should be noted.

Previously Glueckauf[2] for cation exchangers and Boyd and Soldano[1] for anion exchangers had shown that the value of ν in ion exchangers appeared to be unity, whereas for 1–1 electrolytes ν = 2. The behavior was interpreted to indicate that the poly-ion did not affect the thermodynamic properties of the ion exchangers. The validity of this assumption cannot be rigorously established until osmotic coefficients for long chain polyelectrolyte sulfonate systems have been successfully determined at extreme dilutions. However, the decidedly different behavior at comparable concentrations of ion exchange systems from that of the alkali halide type appears to make the assumption of unity a good one. Moreover, if ν is different from unity, it would only alter the values found in this treatment by a constant factor and thus introduce no complications. Throughout the present discussion the value of ν will be considered to be unity.

Anion Exchangers.—The effect of molality upon the osmotic coefficients of Dowex 2 (a dimethylethanol quaternary ammonium ion resin type  $(\mathrm{R{-}\underset{(CH_3)_2}{\overset{+}{N}}{-}CH_2{-}CH_2{-}OH})$ is shown in Fig. 1. As expected the osmotic coefficients of the salt forms, at any fixed molality, range in the following order: $F^- > Cl^- > Br^- > I^- > ClO_4^-$. Moreover, all the

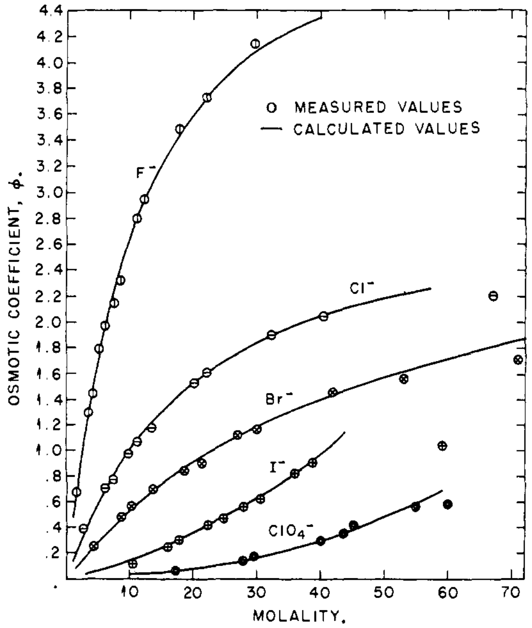


Fig. 1.—Comparison of calculated with measured osmotic coefficients for Dowex 2.

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[1] G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

[2] E. Glueckauf, *Proc. Roy. Soc.* (*London*), **A214**, 207 (1952).

curves tend to extrapolate to an apparent value of $\phi = 0$ at $m = 0$. By definition the value of ϕ must equal unity at infinite dilution if ν is equal to unity. Moreover, there is no physical reason to expect the ionized resin to be osmotically inactive at higher dilutions. There is, therefore, reason to believe that the concentration term and the pressure term in equation 1 become equal at low dilutions. It appears, however, that in the range where *practical measurements* can be made the value of the common "apparent" intercept ϕ_0 is equal to zero for the anion exchanger. Moreover, it was found that all the osmotic coefficients for Dowex 2 could be represented by the general equation[3,4]

$$\phi = \frac{am}{(1 + bm)} + \phi_0$$

where a and b are constants characteristic of each salt form and m is the stoichiometric molality of the resin. The relationship characterizes the behavior of the fluoride form of the resin (Fig. 1) from 2 to approximately 30 molal. For the perchlorate form it is valid as far as 60 molal. The osmotic coefficients[1] of Dowex 1 (a trimethyl quaternary ammonium ion resin type ($R-\overset{+}{N}-(CH_3)_3$) are completely satisfied by the same relationship over comparable concentration ranges.

An inspection of the characteristic values of a and b for various salt forms in the two types of anion exchangers (Table I) reveals that the values of a are always positive, although the quantity may vary from +0.54 for the fluoride ion to +0.0035 for the perchlorate ion. The characteristic b values range from +0.1 for the fluoride form of the resin to −0.013 for the perchlorate form.

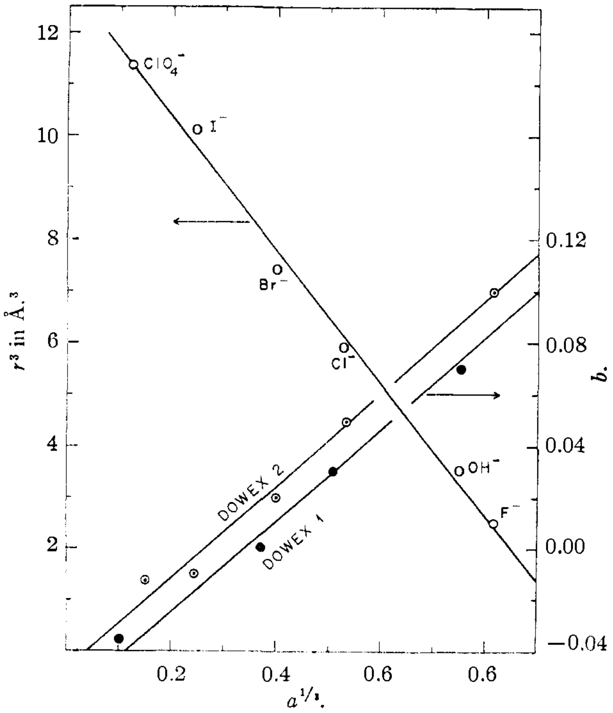

Fig. 2.—The dependence of a and b and the crystal radius for anion exchangers.

Table I

The Variation of a and b with Salt Form and Resin Structure[a]

Ion	a for Dowex-2	b for Dowex-2	a for Dowex-1	b for Dowex-1	Crystal radius, Å.
ClO_4^-	0.0035	−0.013	0.001	−0.035	2.25
I^-	.0147	− .010	...	.....	2.16
Br^-	.0635	+ .02	.051	.0	1.95
Cl^-	.153	.05	.135	+ .03	1.81
OH^-	....	.....	.426	.07	1.53
F^-	.54	.10	.578	.12	1.36

[a] $\phi_0 = 0$ for both Dowex-1 and 2.

The significance of these two constants is shown in Fig. 2. In the first place, a is definitely a function of b. Although it cannot be stated with absolute certainty that the function of $a^{1/3}$ *vs.* b will be exactly linear for all conceivable cases, there is no doubt that the two constants are interdependent. Thus a single parameter equation can be used to calculate the osmotic coefficient for any anion resin salt over a wide range of concentration at least (1.8 to 30 molal).

Equally important, moreover, is the fact that the value a can be related to the crystal radius of an ion. Thus it becomes possible to systematize the osmotic coefficients of the resin salts in a manner analogous to that of Cobble.[5] These osmotic coefficients can be used to calculate the activity coefficient ratio[6] of any monovalent ion pair, a necessary requirement for the calculation of ion-exchange selectivities.

Since the two types of anion exchangers differ only slightly in the structure of the functional group, it is not surprising that the values of a are not significantly different. The parallelism of the two plots (Fig. 2) suggests that a structural correlation of exchange properties based upon functional groups may be possible. It would appear, in any case, that the basic differences between the two types of exchangers is reflected primarily in the values of b.

Cation Exchangers.—When equation 1 is applied to various salt forms of cation exchangers of the sulfonic type, it is apparent (Fig. 3) that the range of validity (2–15 m) is more limited than in the case of the anion exchangers. Fortunately, this concentration range is sufficiently large to include most of the exchange systems experimentally encountered. It should be pointed out that the very lowest values in Fig. 3 are subject to a pressure volume correction comparable to that found for anion exchange systems. A study was made to determine the effect of cation size, structure, and charge on the value of a, b and ϕ_0. As shown in Table II, there are several basic differences between cation and anion exchangers. In the first place, the values of b are negative for all the simple cations with the exception of the Li^+ ion. This behavior is also exhibited by the multivalent cations. Only in the case of the complex quaternary ammonium cat-

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(3) G. Scatchard and R. C. Breckenridge, *J. Phys. Chem.*, **58**, 596 (1954).

(4) The assumption is made that below a certain degree of cross-linking (Ca 0.5%: DVB), the osmotic coefficients are independent of the DVB content and are solely a function of molality.

(5) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443 (1953).

(6) B. Soldano and D. Chesnut, This Journal, **77**, 1334 (1955).

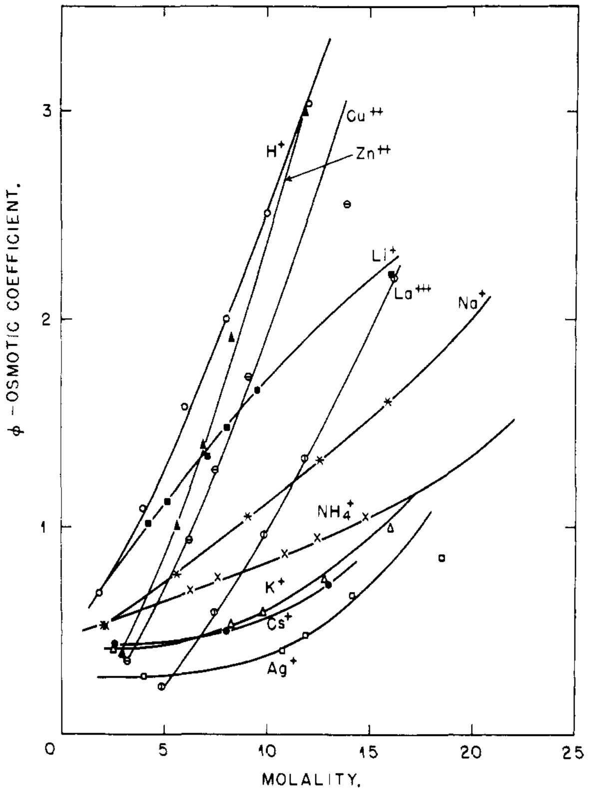

Fig. 3.—Comparison of calculated with measured osmotic coefficients for salt forms of Dowex 50. Solid lines are calculated curves; points are experimental.

ions are positive values of b encountered comparable to those found for anion exchangers. In fact, the b value for $N^+(CH_3)_4$ ion, $b = +0.09$, is not much different from a value of +0.10 found for the fluoride form of Dowex 1 ($R{-}N^+(CH_3)_3F^-$).

TABLE II

THE OSMOTIC COEFFICIENT PARAMETERS FOR CATION EXCHANGE RESINS

Ion	a	b	Crystallographic radius, Å.	ϕ_0
H^+	0.17	−0.02	0.58	0.40
Li^+	.157	.02	.60	.40
Na^+	.065	− .01	.95	.39
NH_4^+	.0307	− .015	1.48	.47
K^+	.0098	− .050	1.33	.40
Cs^+	.0068	− .055	1.69	.41
Ag^+	.007	− .055	1.26	.25
Tetramethylammonium ion	.3255	.09	2.44	.00
Tetraethylammonium ion	.467	.10	2.93	− .22
La^{+++}	.098	− .026	1.15	− .32
Zn^{++}	.208	− .021	0.74	− .28
Cu^{++}	.166	− .022	.81	− .22

Another significant difference between the two basic types of ion exchangers lies in the values of ϕ_0. For most of the simple cations, with the exception of Ag^+, a value of $\phi_0 = \sim 0.40$ is found. This is in direct contrast with the value of $\phi_0 = 0$ for most anion exchangers. It is of interest to point out that the cation $N^+(CH_3)_4$ also has a value of $\phi_0 = 0$. The differences in the apparent osmotic intercept between anion and cation exchangers may reflect differences in degree of association for the two types. The stronger cation exchanger would presumably be much less associated than the anion exchanger.

The values of $a^{1/3}$ for cation exchange systems appear to also be linearly dependent on the values of b. Moreover, this relationship appears to be charge dependent although an insufficient number of multivalent ions have been studied to establish a relationship. Just as in the case of the anion exchangers, a can be related to measurable physical properties of cation exchangers. The values a/z where z is the valence of the cation are linear functions of the reciprocals of the cation crystal radii (Fig. 4).

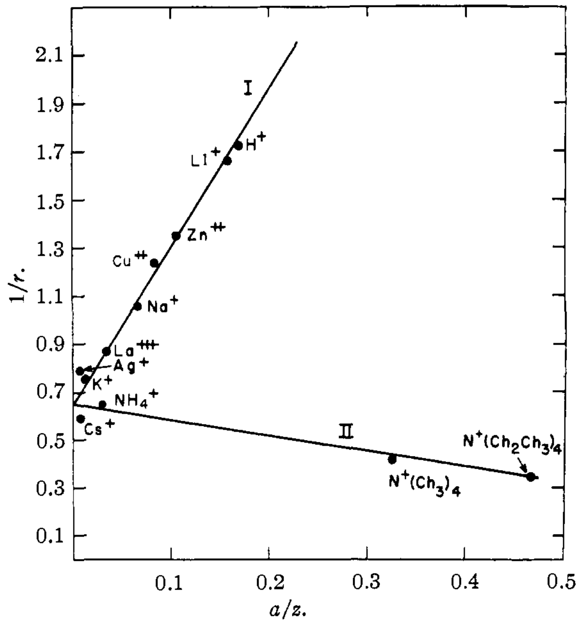

Fig. 4.—Dependence of a on the crystal radius of salt forms of Dowex 50.

It should be pointed out the osmotic coefficients of the multivalent ions were calculated on an equivalent basis and not on the conventional molarity basis. If the latter scale has been used, the value of a for a divalent ion would be increased by four, and for a trivalent ion by nine. On a molarity basis one can write that (Fig. 4, curve I)

$$a \sim \left(\frac{z^2}{r} - c\right) l \qquad (2)$$

where

z = the valence of the cation
r = the crystal radius of the cation
l = number of equivalents per mole of cation
c = 0.65.

The form of relationship (2) is suggestive of an ion dipole phenomenon. This behavior appears to be different from that found for anion exchangers. The larger size of the latter type's functional group and the anions themselves (save for the F^- and OH^- ions) preclude any pronounced ion hydration. One would expect in these systems that dispersive effects would be more important and, therefore, result in a radius relationship different from that found for cation exchangers.

Preliminary results[7] with the sulfonic-type resins indicate that while $c = 0.65$ in equation 2 is independent of variations in resin capacity, the values of a are definitely affected. Hence, it becomes of interest to extend this approach to ion exchangers containing different functional groups in order to determine the effect of functional group size on the constant c.

Finally, the behavior of the quaternary ammonium salts (curve II, Fig. 4) appears to be considerably different from the smaller cations. The large size of these cations prevents any possibility of a simple ion hydration mechanism predominating.

In general, it would appear that ion exchangers, because of the high concentrations obtainable, will be very valuable in studying the properties of concentrated solutions.

Acknowledgment.—The authors wish to acknowledge the valuable discussions and suggestions of Professor G. Scatchard, and the invaluable assistance of Dr. M. D. Silverman in preparing the manuscript.

OAK RIDGE, TENN.

[7] B. Soldano, H. Rosenstock and Q. V. Larsen, in press.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Osmotic Approach to Ion-exchange Equilibrium. I. Anion Exchangers

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RECEIVED MARCH 15, 1954

Anion exchange selectivities have been measured for the (Br–F), (Br–Cl) and (Br–I) systems both as a function of resin composition and degree of cross-linking. A method is proposed for the calculation of these selectivities as a function of the two aforementioned variables by means of osmotic coefficient measurements of weakly cross-linked anion exchangers.

The factors affecting ion-exchange selectivity have been intensively investigated and reviewed during the last decade.[1]

In 1952 Glueckauf[2] made the valuable proposal that osmotic coefficient measurements of weakly cross-linked (0.5% DVB) pure resin salt forms could be used to determine the activity coefficient ratios of the ions in an ion exchanger. Basically his approach was to relate the selectivities to the osmotic coefficients by means of an equation similar to the following

$$\ln D = \frac{(\pi_r - \pi_s)(\bar{V}_1 - \bar{V}_2)_r}{RT} + \ln (\gamma_1/\gamma_2)_r - \ln (\gamma_1/\gamma_2)_s \quad (1)$$

where D is the selectivity in terms of molality m, r and s refer to the resin and solution phase, respectively, $\bar{V}_1$ is the partial molal volume of the ion 1 in the resin at that concentration, $(\pi_r - \pi_s) = P$ is the resin swelling pressure, and the γ's are the ion activity coefficients in the appropriate phases. The mean molal activity coefficients of the ions in the aqueous solution are defined at a pressure of 1 atmosphere by the condition that $\log (\gamma_i)_s \rightarrow 0$ as $\sum\limits_i (m_i)_s \rightarrow 0$, while the activity coefficients for the ions in the resin phase are defined by $\log (\gamma_i)_r \rightarrow 0$ as $\sum\limits_i (m_i)_r \rightarrow 0$ and $P \rightarrow 1$ atmosphere.

Glueckauf showed that moisture adsorption data for the pure resins permit a determination of P, and of the osmotic coefficients of the aqueous solution within the resin. He was able to relate the pure salt form osmotic coefficients to $\log (\gamma_1^0/\gamma_2^0)_r$, the activity coefficient ratio for the two pure resin salt forms. Then, by using Harned's rule and assuming that the interaction coefficients α_{12} and α_{21} are equal in magnitude but of opposite sign, he arrived at values of $\log (\gamma_1/\gamma_2)_r$, the activity coefficient ratio for the mixed salt forms existing in the selectivity experiment. An analytic expression for the osmotic coefficient is required in order to employ the Gibbs–Duhem equation to determine ion activity coefficients. Glueckauf proposed that for a pure resin salt form

$$(\phi - 1) = -f(m) + am \quad (2)$$

where $f(m)$ covered the resin concentration range (approximately 0 to 2 molal) inaccessible to isopiestic measurements and was assumed to be common to all ions, and a was specific for each resin form. Equation 2 is analogous to the one parameter equation for electrolytes proposed by Guggenheim and a consequence of Brönsted's theory of specific interaction.[3] However, Guggenheim's formulation was itself unsatisfactory above ionic strengths of about 0.1, and, consequently, it is not to be expected that it should apply well to the exchange resins where concentrations over the range of interest may reach 15 molal. Further, the assumption that Harned's rule may apply cannot be accepted *a priori*, nor can the assumption that $\alpha_{12} = -\alpha_{21}$. Although the osmotic approach had not yet evolved to a point where it was demonstratively more advantageous, it was felt that this approach to the problem of ion-exchange selectivity offered real promise. For this reason, a determined effort was made in this Laboratory to obtain accurate osmotic and selectivity data with a hope of extending this concept.

Theory.—The problem is one of evaluating each of the terms in equation 1. For purposes of clarity, a brief outline will be presented covering the means

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[1] (a) W. C. Bauman and J. Eichorn, THIS JOURNAL, **69**, 2830 (1947); (b) W. J. Argersinger, Jr., A. W. Davidson, O. D. Bonner, *Trans. Kansas Acad. Sci.*, **53**, 404 (1950); (c) H. P. Gregor, THIS JOURNAL, **73**, 642 (1951); (d) K. Kraus and G. Moore, *ibid.*, **75**, 1457 (1953); (e) G. E. Boyd, *Ann. Rev. Phys. Chem.*, **2**, 309 (1951).

[2] E. Glueckauf, *Proc. Roy. Soc.* (*London*), **A214**, 207 (1952).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 386.