

fore, result in a radius relationship different from that found for cation exchangers.

Preliminary results⁷ 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 consider-

(7) B. Soldano, H. Rosenstock and Q. V. Larsen, in press.

ably 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.

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OAK RIDGE, TENN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

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

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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 Glueckauf² 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 $\log (\gamma_1)_s \rightarrow 0$ as $\sum_i (m_i)_s \rightarrow 0$, while the activity coefficients for the ions in the resin phase are defined by $\log (\gamma_i)_r \rightarrow 0$ as $\sum_i (m_i)_r \rightarrow 0$ 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 assum-

ing 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 Brønsted'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

(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.

employed for such evaluations. Later the basis and the consequences of some of the steps will be discussed in greater detail.

External Activity Coefficients.—In this study, the outside solution was maintained always at 0.1 *N* total concentration in order that the reasonable assumption of equality of the outside solution activity coefficients could be made. Any error introduced is felt to be negligible and in any event could be calculated. This assumption eliminates $\log(\gamma_1/\gamma_2)_s$ from equation 1.

It should be pointed out here that the use of 0.1 *N* outside solutions also eliminates, or reduces to a small amount, the electrolyte entering the resins because of the Donnan effect. Thus it is generally permissible to assume merely equivalent exchange of ions between resin and outer solution. However, selectivity data for 1 or 2% DVB resins must therefore be accepted with some reservation.

Pressure-Volume Term.—The evaluation of the pressure-volume work has been performed by Glueckauf,² by Boyd⁴ and by Gregor⁵ and follows fairly elementary lines. Its contribution results from the assumption that the only difference at constant molality between an uncross-linked and a cross-linked exchanger as far as water absorption is concerned is the superposition of a hydrostatic pressure on the interior of the cross-linked exchanger, with a consequent elevation of the water activity inside the resin. It can be shown⁴ thermodynamically that

$$P\bar{V}_w = RT \ln(a'_w/a_w)m \quad (3)$$

where \bar{V}_w is the partial molal volume of water at the resin molality *m*, a'_w is the activity of water in isopiestic equilibrium with the cross-linked resin at *m*, and a_w is the activity of water in isopiestic equilibrium with an effectively uncross-linked resin to produce the same molality. Since the swelling pressure can be calculated from equation 3, only the difference in the partial molal volume of the ions must be known in order to obtain the complete pressure-volume work term. As a simplification the assumption will be made that $(\bar{V}_1 - \bar{V}_2) \cong (\bar{V}_1^0 - \bar{V}_2^0)$ where \bar{V}_i^0 refers to ionic partial molal volumes at infinite dilution. To be rigorously correct the ionic partial molal volumes under the actual experimental conditions should be used in order to keep the activity coefficients independent of pressure. For water, however, the difference is small, and it may well be small for differences between the partial molal volumes of ions. Moreover, since the pressure-volume term under the present convention never contributes more than a few per cent. to the selectivity term, these assumptions are probably adequate.

Activity Coefficients of Pure Resin Salt Forms.—The logarithm of the ratio of activity coefficients of the mixed resin salt forms in equation 1 remains to be calculated. This is accomplished indirectly by first calculating the ratio of the activity coefficients of the two pure resin salt forms from measured osmotic coefficients of those same salt forms and then relating these activity coefficients to those

actually existing inside a resin mixture by means of a modified Harned's rule.

The osmotic coefficients obtained by equilibrating very slightly cross-linked anion resins (*ca.* 0.5% DVB) in their pure forms with water vapor of varying activity have been shown⁷ to be related to molality by the following equation. The theoretical basis for this equation has been proposed by G. Scatchard.⁸

$$\phi = f(m) + am/(1 + bm) \quad (4)^9$$

where ϕ is the osmotic coefficient and *m* is the molality, *i.e.*, the number moles of ions per 1000 g. of water.¹⁰ The quantities *a* and *b* are constants which are characteristic for each ion. The function $f(m)$ is similar to that employed by Glueckauf in equation 2 and must describe the behavior of the osmotic coefficient in the dilute concentration range. At the present time, the form of $f(m)$ is unknown; that knowledge awaits the quantitative description of the properties of a collection of highly charged (infinitely long) linear polymer molecules.

The measured osmotic coefficients are converted to the pure resin salt activity coefficients in the following manner. Combining the definition

$$(r\phi) = \frac{-2.3 \times 55.5}{m} \log a_w$$

with equation 4 results in

$$-2.3 \times 55.5 \log a_w = mf(m) + am^2/(1 + bm) \quad (5)$$

Applying the Gibbs-Duhem equation

$$-55.5 \, d \log a_w = a/2.3 [2m/(1 + bm) - bm^2/(1 + bm)^2] dm + g(m) dm \quad (6)$$

$$= m \, d \log a_r^0$$

where $g(m)$ is the form of $f(m)$ after the differentiation and a_r^0 is the activity of the pure resin salt. Thus

$$d \log \gamma_r^0 + d \log m = a/2.3 [2/(1 + bm) - bm/(1 + bm)^2] dm + \frac{g(m)}{m} dm \quad (7)$$

If the $\log m$ term is included in $g(m)$ and the resulting expression integrated between $m = 0$ and $m = m$, one obtains

$$\log \gamma_r^0 = a/2.3b [\ln(1 + bm) + bm/(1 + bm)] + F(m) \quad (8)$$

If now the *assumption* is made that the difference in $F(m)$ for any two ions is negligible, the subtraction of equation 8 for one salt form from that for another at the same molality results in the following expression for the ratio of activity coefficients of two pure salt forms.

$$\log(\gamma_1^0/\gamma_2^0)_r = a_1/2.3b_1 [\ln(1 + b_1m) + b_1m/(1 + b_1m)] - a_2/2.3b_2 [\ln(1 + b_2m) + b_2m/(1 + b_2m)] \quad (9)$$

(7) B. Soldano and Q. V. Larson, *THIS JOURNAL*, **77**, 1331 (1955).

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

(9) It should be pointed out that for anion exchangers above 2 molal, the values of $f(m)$ were found to be negligibly small by the authors.

(10) Experimentally one obtains not ϕ but the product $v\phi$, from the definition $v\phi = -55.5 \log a_w/m$, *v* being the number of ions into which the given salt dissociates and a_w the water activity in the system. However, *m* is defined here as the total concentration of counterions neutralizing a charged polymer molecule of essentially infinite molecular weight and thus the value of *v* is effectively included in *m*; then *v* can be set equal to unity in equation 4 and in the subsequent treatment.

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

(5) H. P. Gregor, *THIS JOURNAL*, **73**, 642 (1951).

(6) B. B. Owen and S. R. Brinkley, *Chem. Revs.*, **29**, 461 (1941).

It must be emphasized that the identity of the $F(m)$ terms holds only insofar as the original $f(m)$ terms are identical, and, therefore, one cannot state definitely that equation 9 will result in absolute values of $\log(\gamma_1^0/\gamma_2^0)_r$.

Activity Coefficients of Mixed Resin Salt Forms.

—The above ratios of pure activity coefficients must be related to those for the mixed salts existing in the exchanger. This was attempted earlier by using Harned's rule, which is embodied in the equation

$$\log(\gamma_1/\gamma_2)_r = \log(\gamma_1^0/\gamma_2^0) + \alpha_{21}m_1 - \alpha_{12}m_2 \quad (10)$$

α_{21} and α_{12} are interaction coefficients, which, if the rule is obeyed, are constant at a given molality ($m = m_1 + m_2$)¹¹; m_1 is the molality of the more osmotically active species and m_2 is the molality of the less osmotically active species. Combining equations 1 and 10, equation 11 is obtained

$$\log(\gamma_1/\gamma_2)_r = \log D - P \frac{(\bar{V}_1^0 - \bar{V}_2^0)}{2.3RT} = \log(\gamma_1^0/\gamma_2^0)_r + \alpha_{21}m_1 - \alpha_{12}m_2 \text{ at a total } m = m_1 + m_2 \quad (11)$$

A strict test of equation 11 requires selectivity measurements at a constant total molality and varying ratios of the two ions. Unfortunately, such a test is not entirely possible since the resin total molality in general varies with loading at a given cross-linking, *i.e.*, upon passing from one pure form through mixtures to the other pure form. However, it was found for the anion systems studied that modified interaction coefficients determined from trace selectivity measurements at various cross-linkings, and consequently various molalities, could be related to molality in the following manner

$$\alpha_{21}(m) = \alpha_{21}^0/R_2(m) \quad (12a)$$

$$\alpha_{12}(m) = \alpha_{12}^0/R_1(m) \quad (12b)$$

Here m is the total molality of the resin, α_{21}^0 and α_{12}^0 are constants independent of molality. Collecting terms

$$\log(\gamma_1/\gamma_2)_r = \log(\gamma_1^0/\gamma_2^0)_r + (\alpha_{21}^0/R_2)m_1 - (\alpha_{12}^0/R_1)m_2 \quad (13)$$

where

$$R_2(m) = \ln(1 + b_2m) + b_2m/(1 + b_2m)$$

$$R_1(m) = \ln(1 + b_1m) + b_1m/(1 + b_1m)$$

The basis for the particular device of equations 1 will be discussed later. It should be pointed out, however, that by using equation 13 it becomes possible to calculate the selectivities under all conditions merely from a knowledge of the two constants α_{12}^0 and α_{21}^0 . In principle these are obtainable from only two selectivity experiments and osmotic measurements.

Experimental

Three separate experiments are involved. (1) The osmotic coefficients of the pure 0.5% DVB resin salt forms are measured as a function of the internal molality, *i.e.*, moisture content, of the resins. (2) The exchange selectivity is measured for the resins in equilibrium with an external mixed aqueous electrolyte solution whose total concentration is 0.1 *N*. (3) The internal molality of the mixed salt form of the cross-linked resins as they exist at equilibrium is measured under the conditions of the actual selectivity experiment.

(11) H. S. Harned and B. B. Owen, *J. Phys. Colloid Chem.*, **57**, 461 (1954).

The osmotic coefficients of the pure salt forms were determined by equilibrating 0.5% DVB resins isopiastically with a series of saturated salt solutions of known water activity. The method is described in detail elsewhere.⁴ The moisture content of these equilibrated resins was found by heating them to constant weight at 68° in a vacuum oven over P₂O₅; increasing the temperature to 72° caused no further significant weight change. The practical mean molal osmotic coefficients were calculated from the usual definition

$$\phi = -\log a_w/0.00782m \quad (14)$$

where a_w is the known activity of the equilibrated water and m is the internal resin molality defined here as the number of exchange sites on the resin per 1000 g. of water.

Selectivity measurements were performed as follows: 25 ml. of 0.1 *N* solutions containing varying proportions of the sodium salts of the two anions of interest, one of which was radioactively tagged, were equilibrated for one day with a known amount (approximately 0.3 meq.) of the exchanger. The equilibrium solution was separated from the resin by filtration through a sintered glass disk so that a maximum amount (about 24.5 ml.) of the solution was received in a 50-cc. test-tube. The resin was washed repeatedly with distilled water until 100 ml. was accumulated. The resin, the filtrate, and 25 ml. of the wash solution were placed in separate test-tubes and the three tubes counted in an H. P. ion chamber. One to 2% correction was applied to the resin counts to normalize the resin volume with that of the two solutions. Material balances of the tagged species within 0.2 to 0.3% were obtained by this technique. Whenever possible, separate analytical or radiochemical determinations were made for the second species. The concentration of the second species was mainly obtained by difference. Selectivity values are precise to 2% or less since resin capacities and moisture contents were determined to 0.2%.

The moisture contents of the resins under the selectivity conditions were determined by isopiastically equilibrating the above washed resins with the appropriate 0.1 *N* solution. The resin molalities are practically a linear function of ion mole fraction, *i.e.*, so-called equivalental loading, so that only the molalities of the pure resin forms are reported in Tables I–III.

Swelling pressures were determined as indicated above, and the values for the pure resin forms in equilibrium with 0.1 *N* external solutions are given in Tables I–III. Pressures for the mixed forms were calculated by assuming that the pressure varies linearly with the mole fraction. This assumption is valid if the equivalental volume of a mixed form is a linear function of exchanger composition.

Capacities of the resins were determined by equilibrating a weighed amount of the moisture-free chloride form with at least a 100-fold or more excess of NaNO₃ solution. After phase separation, the resin was washed repeatedly with distilled water; filtrate and washings were combined and titrated potentiometrically for chloride.

The resins used for this study were of the Dowex-2 anion exchanger type (dimethylethanol quaternary ammonium structure); divinylbenzene (DVB) content (¹/₂ to 16%).

Discussion

The selectivities of three pairs of monovalent anions (Br–F), (Br–Cl) and (Br–I) were measured as a function of resin composition and degree of cross-linking (Tables I–III). The selectivity in general increased with increasing cross-linking. This phenomenon was most pronounced when the resin was completely in the salt form of less adsorbed ion. As the resin composition was altered to that of the more adsorbed ion, the selectivity fell in all cases. In fact, when the resins were completely in the latter form, there were only minor differences in selectivity over a wide range of cross-linking.

A primary concern of this paper, however, is the determination of the applicability of equations 11 and 13 to the calculation of ion-exchange selectivities as a function of the two aforementioned variables. The basic problem is one of relating the ac-

TABLE I

THE EFFECT OF RESIN COMPOSITION AND CROSS-LINKING ON THE Br-F SELECTIVITY

F = Eq. fraction of resin in the fluoride form; D = (Br^-/F^-) resin/ (Br^-/F^-) outside; M = no. of moles of anion per 1000 g. of water inside a resin which is in equilibrium with an external 0.1 N salt solution; P = swelling pressure in atmospheres; $(\bar{V}^{\circ}_{F^-} - \bar{V}^{\circ}_{Br^-}) = -27.1$ cc. per mole.

	Pure Br ⁻ resin	1% DVB						Pure F ⁻ resin
F	0	0.14	0.44	0.58	0.82	0.97	1.0
D	6.4	8.4	10.0	13.8	17.9	19.2
M	4.65							2.36
P	0							31
	Pure Br ⁻ resin	2% DVB						Pure F ⁻ resin
F	0	0.12	0.39	0.54	0.61	0.78	0.98	1.0
D	8.0	11.3	13.6	15.0	19.6	27.4	29.0
M	5.51							2.9
P	44.0							81
	Pure Br ⁻ resin	4% DVB						Pure F ⁻ resin
F	0	0.09	0.27	0.46	0.60	0.74	0.98	1.0
D	9.5	11.7	14.9	18.0	21.8	30.7	31.7
M	5.94							3.4
P	50							110
	Pure Br ⁻ resin	8% DVB						Pure F ⁻ resin
F	0	0.05	0.13	0.32	0.45	0.75	0.96	1.0
D	18.4	20.9	31.0	39.8	67.0	95.0	100.9
M	10.04							5.4
P	136							235
	Pure Br ⁻ resin	16% DVB						Pure F ⁻ resin
F	0	0.05	0.09	0.17	0.25	0.57	0.75	0.95
D	...	26.4	28.4	32.0	40.8	74.4	108.0	156.7
M	11.48							7.8
P	175							438

TABLE II

THE EFFECT OF RESIN COMPOSITION AND CROSS-LINKING ON THE Br-I SELECTIVITY

F = Eq. fraction of resin in the Br⁻ form; D = (I^-/Br^-) resin/ (I^-/Br^-) outside; $(\bar{V}^{\circ}_{Br^-} - \bar{V}^{\circ}_{I^-}) = -11.6$ cc. per mole.

	Pure I ⁻ resin	4%					Pure Br ⁻ resin
F	0	0.28	0.49	0.73	0.95	1
D	4.44	4.63	4.95	5.32	5.81
M	12						5.94
P	47						50
	Pure I ⁻ resin	8%					Pure Br ⁻ resin
F	0	0.26	0.29	0.44	0.68	0.94	1
D	5.32	5.71	5.70	5.82	6.49	7.2
M	15						10.04
P	87.4						13.6
	Pure I ⁻ resin	16%					Pure Br ⁻ resin
F	0	0.21	0.49	0.71	0.85	1
D	5.87	6.45	7.14	8.0	8.62
M	15.3						11.48
P	104						175

tivity coefficient ratio of the pure salt forms obtained from osmotic coefficient measurements $\log(\gamma_1^0/\gamma_2^0)_r$ to the actual activity coefficient ratio of the mixed resin $\log(\gamma_1/\gamma_2)_r$. In the absence of any theory which would give this dependence in resins, Harned's rule was first applied. The actual determination of the interaction coefficients, α_{12} and α_{21} , equation 11, from the experimental data is simplified greatly by setting the molality of one of the

TABLE III

EFFECT OF RESIN COMPOSITION AND CROSS-LINKING ON THE Br-Cl SELECTIVITY

F = Fraction of resin in the bromide form; D = $(Br^-/Cl^-)_r/(Br^-/Cl^-)$ outside; $(\bar{V}^{\circ}_{Cl^-} - \bar{V}^{\circ}_{Br^-}) = -6.9$.

	Pure Cl ⁻ resin	1%					Pure Br ⁻ resin
F	0.0	0.22	0.29	0.51	0.69	0.78	1.0
D	2.33	2.35	2.3	2.26	2.24	2.22
M	2.41						4.65
P	18					
	Pure Cl ⁻ resin	2%					Pure Br ⁻ resin
F	0.0	0.20	0.32	0.54	0.80	1.0
D	2.58	2.6	2.56	2.58	2.60
M	3.79						5.51
P	42						44
	Pure Cl ⁻ resin	4%					Pure Br ⁻ resin
F	0.0	0.23	0.35	0.59	0.80	1.0
D	2.85	2.79	2.73	2.61	2.52
M	4.42						5.94
P	55						50
	Pure Cl ⁻ resin	8%					Pure Br ⁻ resin
F	0.0	0.25	0.41	0.65	0.85	1.0
D	3.65	3.59	3.51	3.41	3.3
M	7.1						10.04
P	136						136
	Pure Cl ⁻ resin	16%					Pure Br ⁻ resin
F	0.0	0.31	0.50	0.73	0.88	1.0
D	4.36	4.09	4.1	4.12	3.95
M	8.8						11.48
P	198						175

components (monitored by means of radioactivity) effectively equal to zero (e.g., 10^{-8} molal or lower). Equation 11 then becomes

$$\log(\gamma_1/\gamma_2)_r = \log D - \frac{P\Delta\bar{V}^0}{2.3RT} = \log(\gamma_1^0/\gamma_2^0)_r - \alpha_{21}m_1 \text{ at total } m \cong m_1 \quad (15)$$

or

$$\log(\gamma_1/\gamma_2)_r = \log D - \frac{P\Delta\bar{V}^0}{2.3RT} = \log(\gamma_1^0/\gamma_2^0)_r - \alpha_{12}m_2 \quad m \cong m_2 \quad (16)$$

Such trace concd. measurements with resins of varying cross-linking permit the determination of the α 's as a function of molality. These apparent "interaction coefficients," shown in Fig. 1, vary greatly with concentration. It should also be pointed out that absolute values of α_{12} and α_{21} are dependent upon the assumption that $F(m)$ is the same for two ions. Solution interaction coefficients also vary considerably with concentration, but there is a tendency for them to become constant at high concentration, about 2 M . Since the resin concentrations vary from 2 to 15 molal, one would normally expect constant interaction coefficients in the resin. Thus the application of Harned's rule, a corollary of Brønsted's general theory of specific interaction, results in a situation wherein the interaction coefficients are constantly decreasing with increasing resin molality.

To circumvent this difficulty the concept of variable interaction coefficient equations (12a) and (12b) is introduced. It appears not to be unreason-

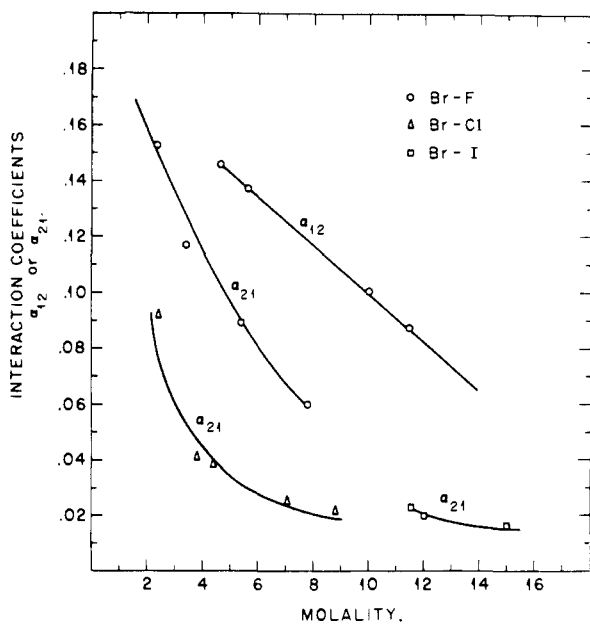


Fig. 1.—The dependence of the interaction coefficients on resin molality.

able to make the interaction coefficients a function of the activity coefficient of the ion. Moreover, since the interaction coefficients decrease with molality, an inverse relationship is more appropriate. Only two traces selectivity experiments with any cross-linked resin are then needed to evaluate the α_{12}^0 and α_{21}^0 in equation 13. Once these two constants are determined, the selectivities for the system should be calculable at any cross-linking or any resin composition merely by a knowledge of the osmotic coefficients of the pure salt forms. This procedure was employed in making a comparison between experimentally measured and calculated selectivities for

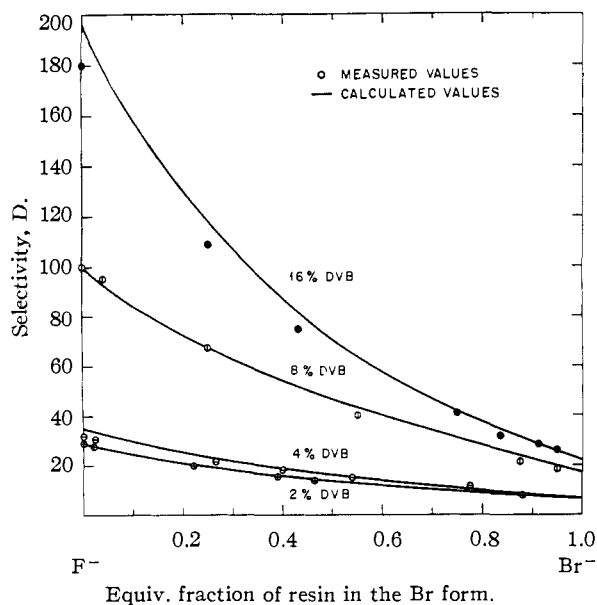


Fig. 2.—Calculated (on the basis of the two experimental points with equation 13) and measured selectivities for Br-F system.

the Br-F system (Fig. 2), Br-I (Fig. 3) and Br-Cl (Fig. 4).

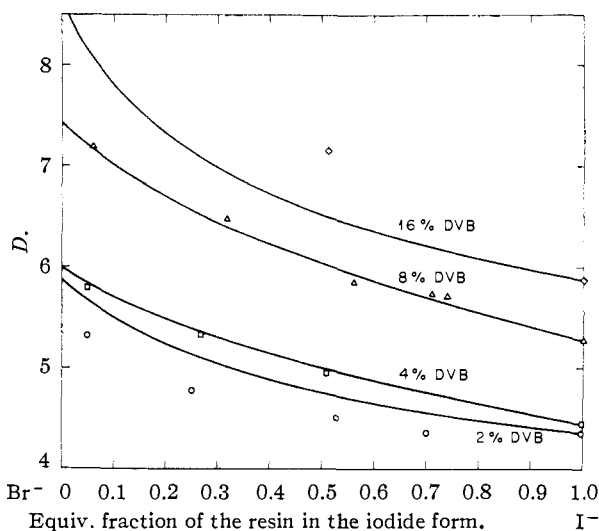


Fig. 3.—Calculated (on the basis of the two experimental points with equation 13) and measured for the Br-I system.

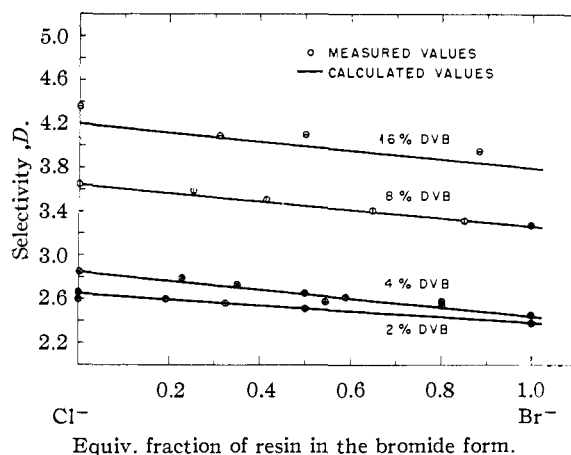


Fig. 4.—Calculated (on the basis of the two experimental points with equation 13) and measured for the Br-Cl system.

Agreement of the measured selectivities (Table I) with the calculated values (Fig. 2) for the bromide-fluoride system is good. In this system, the variation of the selectivity, values 4 to 200, with cross-linking and concentration is considerable. Furthermore, the variation of selectivity with the resin environment at any cross-linking is in itself large. Therefore, one has a system which makes the greatest demands on any theoretical approach.

The Br-I system (Table II, Fig. 3) shows only a fair degree of correlation between measured and calculated values. The system was studied because it contained two ions which have b values, Table IV and equation 4, of opposite sign. For this particular system it was found that only one interaction coefficient, α_{21} , varied with molality as in equation 13 and that α_{12} was truly constant, *i.e.*, $\alpha_{12}^0 = \alpha_{12}$. Thus a system of mixed signs in b results in one variable and one constant interaction coefficient. One is

led to predict that in the case of a system containing two negative b values both interaction coefficients should be constant.

The bromide-chloride system (Table III and Fig. 4) shows fairly good agreement, with the possibility that deviations may become apparent in a low cross-linked region. This is to be expected since the assumption has been tacitly made in this whole thesis that at 0.1 N the Donnan electrolyte in the resin is negligible. At low cross-linking this is probably an oversimplification. One other factor should be emphasized in this discussion; the molality of any system must be known accurately. An empirical relationship was employed to obtain the molality of intermediate mixtures between the pure salt forms, namely, that the molality of a resin mixture is linearly dependent on the molality of the two pure salt forms. For the bromide-fluoride system, this assumption was verified. A slight deviation in the case of the bromide-iodide system can account for discrepancies noted between the calculated and measured selectivities of that particular system. On the whole, however, the treatment appears to closely approximate the actual experimental conditions.

Interaction Coefficients.—Having established that interaction coefficients of the type used in equations 12 and 13 permit an extensive correlation of resin selectivity and osmotic data, it is of interest to inquire into their possible significance and their relationship with interaction coefficients observed in normal aqueous electrolyte mixtures. At least two factors indicate that the coefficients employed here are not of the same nature as the usual Harned coefficients. First, the variation of the resin coefficients with molality (Fig. 1) is much greater than for the solution type; furthermore, the latter generally approach constancy at about two or three molal. Second, if a true Harned's rule is obeyed by a system, it is a thermodynamic conse-

quence that the sum ($\alpha_{12} + \alpha_{21}$) be a constant, independent of molality.¹² That this is not the case here is obvious from equation 13.

It was found, however, that the values of α_{12}^0 might be amenable to calculation. For the anion systems investigated, the following relationship appears to hold

$$\alpha_{12}^0 = (a_1/b_1 \times 2.3 - a_2/b_2 \times 2.3)(b_1 + b_2) \quad (17)$$

where a and b (Table IV) are specific constants for each salt form in the general osmotic coefficient equation 4. The calculated and experimentally determined α_{12}^0 values (Table IV) agree quite closely. The real significance of this result is the implication that the osmotic coefficients of the pure salt resins should suffice to determine the activity coefficient ratios of mixed resin systems and therefore ion exchange selectivities.

TABLE IV
A COMPARISON OF MEASURED AND CALCULATED INTERACTION COEFFICIENTS

	Br-F	Exchange Br-I	Br-Cl
Experimentally detd. α_{12}^0	+0.1192	-0.02	-0.0026
Calcd. α_{12}^0 from eq. 17	+0.1196	-0.02	-0.0035

where

Ion	a	b
I ⁻	0.0147	-0.010
Br ⁻	.0635	+ .02
Cl ⁻	.153	.05
F ⁻	.54	.10

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(12) E. Glueckauf, McKay and Mathieson, *J. Chem. Soc.*, S299 (1948).

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Osmotic Approach to Ion-exchange Equilibrium. II. Cation Exchangers

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Selectivities of cation exchangers were measured both as a function of resin cross-linking and composition. A general method is proposed to calculate cation-exchange selectivities from osmotic coefficient measurements of weakly cross-linked resins.

Previous investigations had shown¹ that osmotic coefficient measurements could be successfully correlated with anion-exchanger selectivities. It was considered of interest, therefore, to determine whether this treatment also could be applied to cation exchangers.

The experimental procedures in the present work consisted of (1) measurements of osmotic coefficients of the "pure" resin "salt forms"; (2) determination of moisture characteristics of cross-linked cation-exchange systems, both pure and

mixed; and (3) measurement of selectivities for various types of ion exchange pairs. A "pure" resin salt form is a resin which is completely in one salt form, e.g., all NaR. With the exception of the determinations of the moisture content of the resins, the experimental techniques were identical with those used for the anion-exchange systems. Since cation-exchange resins have higher thermal stability than anion-exchange resins, they were heated overnight at 105° under a vacuum in the presence of P₂O₅. Table I lists the values of the molality of the pure resin salts that were found to be in equilibrium with 0.1 M salt solutions under these

(1) B. Soldano and D. B. Chesnut, *THIS JOURNAL*, **77**, 1334 (1955).