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 consequence 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 resinates 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

	Exchange		
	Br–F	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

Acknowledgment.—The authors wish to acknowledge the valuable suggestions and informative discussions of Professor G. Scatchard concerning this work. They also wish to acknowledge the services rendered by Dr. G. Myers.

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

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

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

BY B. SOLDANO, Q. V. LARSON AND G. E. MYERS

RECEIVED MARCH 15, 1954

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 shown[1] 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 P_2O_5. 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

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

Table I

Moisture Characteristics of Cross-linked Pure Resin Salt Forms

%DVB	Values of resin molality over 0.1 N salt soln.						
	H^+	K^+	Na^+	Li^+	Cs^+	NH_4^+	Ag^+
2	1.06		1.95	1.60	2.90	1.36	
4	2.4	2.94	3.02	2.80	4.30	3.05	4.7
8	4.58	5.99	5.98	5.09	6.95	5.78	8.07
12	6.9	8.91	8.66	7.72	9.25	8.70	11.36
16	7.6	10.5	10.1	8.43	10.9	9.16	12.05
24	10.36	14.05	14.0	12.43	16.9	11.82	16.48

conditions. In the calculation of the moisture content of the "mixed resins forms" at $a_w \sim 0.1\ m$, the assumption was made that for monovalent ion systems the resin moisture varied linearly with resin composition. That this assumption seems reasonable is demonstrated by Fig. 1 which shows that it holds at all loadings and cross-linkings for the Na–Cs system.

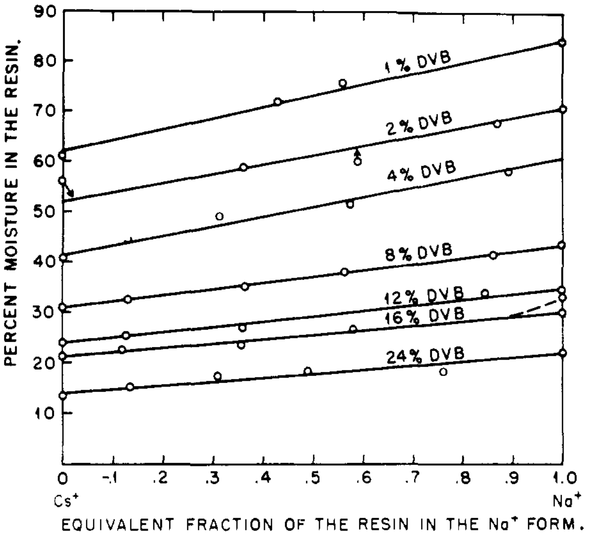

Fig. 1.—The moisture variation with cross-linking of mixed monovalent cation exchangers.

Discussion

Derivation of the Activity Coefficient Ratio of the "Pure Salt Forms."—Selectivities for monovalent systems can be thermodynamically related to the resin activity coefficients by the equation

$$\log D - P\Delta \bar{V}^0/2.3RT = \log (\gamma_1/\gamma_2)_r + \log (\gamma_2/\gamma_1)_0 \quad (1)$$

where

$$D = \frac{(m_1/m_2)_{\text{resin}}}{(m_1/m_2)_{\text{outside soln.}}}$$

$\log (\gamma_1/\gamma_2)_r$ = the ratio of the activity coefficients of the two mixed resin salts, $\log (\gamma_2/\gamma_1)_0$ = the ratio of the activity coefficients of the two mixed salts in the external phase (this term approaches zero when the outside concentration is maintained below 0.1 m), and $P\Delta\bar{V}^0/2.3RT$ = the swelling pressure of the system times the difference in the partial molal volumes of the ions at infinite dilution.

In order to make the activity coefficients independent of pressure, the actual partial molal volumes of the ions in the resin must be used, not those at infinite dilution. For water, however, the difference is small, and it may be safe to assume that the difference between the partial molal volumes of two ions is not much different at infinite dilution than under the actual experimental conditions. Since the former values have been measured by Brinkley and Owens they will be used, subject to the above reservation. Moreover, since in most cases the pressure volume correction is small, any errors in the estimate should not introduce any serious discrepancies in the following treatment.

Previous investigations[2] have shown that cation exchange osmotic coefficients could be described over a concentration range of 1.5 to 15 molal by the function

$$\phi = a_1 m/(1 + b_1 m) + \phi_0 \quad (2)$$

where a_1 and b_1 are constants characteristic of each ion and $\phi_0 = B$ is the "apparent" extrapolated value of ϕ at infinite dilution. Since the osmotic coefficient describes the water activity over the desired concentration range, the application of the Gibbs–Duhem equation should permit the evaluation of the activity coefficients of the pure resin salt forms. It can be shown[1] that

$$\log \gamma_1^0 = a_1/2.3b_1\ [\ln (1 + b_1 m) + b_1 m/(1 + b_1 m)] + F_1(m) \quad (3)$$

where γ_1^0 is the activity coefficient of 0.5% DVB pure salt resinate, $F_1(m)$ is the $f_1(m)$ after the application of the Gibbs–Duhem equation. Since the ratio of the activity coefficients of the pure salt forms is desired, one can write

$$\log (\gamma_1^0/\gamma_2^0)_r = a_1/2.3b_1\ [\ln (1 + b_1 m) + b_1 m/(1 + b_1 m)] - a_2/2.3b_2\ [\ln (1 + b_2 m) + b_2 m/(1 + b_2 m)] \quad (4)$$

provided $F_1(m) - F_2(m) \cong 0$ in the range where equation 3 is employed.

Relationship of log $(\gamma_1^0/\gamma_2^0)_r$ to log $(\gamma_1/\gamma_2)_r$.—The basic problem in correlating osmotic coefficient measurements with ion-exchange selectivities is the determination of the relationship of the activity coefficient ratio of the pure salt forms to the activity coefficients of the mixed resin salts. One may initially attempt to solve this problem by assuming the applicability of *Harned's rule*

$$\log D - P\Delta V/2.3RT = \log (\gamma_1/\gamma_2)_r = \log (\gamma_1^0/\gamma_2^0)_r - \alpha_{12}m_2 + \alpha_{21}m_1 \quad (5)$$

α_{12} and α_{21} are interaction constants, m_1 is the molality of the species which is osmotically more active, and m_2 is the molality of the other species.

When the "trace selectivity" technique is employed, whereby one of the two ions in any selectivity experiment is maintained at the trace level inside the ion exchanger, equation 5 can be reduced to

$$\log (\gamma_1/\gamma_2)_r = \log (\gamma_1^0/\gamma_2^0)_r - \alpha_{12}m_2 \text{ at concn. } m = (m_1 + m_2) \cong m_2 \quad (6)$$

or alternately to

$$\log (\gamma_1/\gamma_2)_r = \log (\gamma_1^0/\gamma_2^0)_r + \alpha_{21}m_1 \text{ at concn. } m = (m_1 + m_2) \cong m_1 \quad (7)$$

If trace selectivity measurements are made as a function of the degree of resin cross-linking (equivalent to altering the resin molality, shown in Table I) the applicability of equations 6 and 7 can be tested. In ordinary aqueous solutions the values of α_{12} and α_{21} tend to become constant for many sys-

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[2] B. Soldano and Q. V. Larson, This Journal, **77**, 1331 (1955).

tems for concentrations greater than one or two molal.

Previous investigations[1] have indicated that the nature of ion-exchange interaction coefficients might be dependent on the sign of the b constant associated with each ion. With this in mind representative systems were studied which permitted the testing of this concept. If the method were successful, an attempt would then be made to determine the applicability of equation 5. This could be done by altering the resin environment and the degree of resin cross-linking.

The selectivities of the Na–Li system as a function of resin loading and cross-linking were studied first (Table II). This pair of ions was chosen because the Na^+ had a negative b value and the Li^+ a positive b value.[2] In the case of the anion-exchange resins, such a combination could be represented by one constant and one variable interaction coefficient. The results of "trace selectivity" experiments employing equations 6 and 7 revealed that the two interaction coefficients for this system varied considerably with molality (Fig. 2). To circumvent this difficulty, the following equation was tested

$$\log (\gamma_1/\gamma_2)_r = \log (\gamma_1^0/\gamma_2^0)_r - \alpha_{12}m_2 + \beta_{12}m_2^2 + \alpha_{21}m_1 + c \quad (8)$$

where α_{12}, α_{21}, β_{12} are constant interaction coefficients and $c = -0.04$.

TABLE II

THE EFFECT OF RESIN COMPOSITION AND CROSS-LINKING ON THE SELECTIVITY OF THE Na–Li SYSTEM

$D = (Na^+/Li^+)_{resin}/(Na^+/Li^+)_{outside\ soln.}$; F = fraction of the resin in the sodium form.

Cross-linking, %								
2	F	0	0.16	0.45	0.63	0.79		
	D	1.12	1.10	1.07	1.14	1.07		
4	F	0	0.2	0.44	0.73	0.92		
	D	1.40	1.42	1.44	1.46	1.48		
8	F	0	0.22	0.48	0.70	0.86		
	D	1.72	1.75	1.8	1.84	1.87		
12	F	0	0.10	0.25	0.50	0.62	0.88	
	D	2.15	2.14	2.15	2.03	2.00	2.00	
24	F	0	0.10	0.26	0.55	0.63	0.88	0.91
	D	3.25	3.00	2.74	2.33	2.23	1.92	1.90

Such a representation accurately described the trace selectivity data at all cross-linkings for resins completely in the Na^+ form. However, as the resin environment was varied toward that of the pure Li^+ form, serious deviations arose between the calculated and experimentally measured selectivities. Since the addition of a cubic term in equation 8 does not appear promising, a device similar to that employed for anion-exchange systems[1] will be proposed.

$$\log D - P\Delta\bar{V}^0/2.3RT = \log (\gamma_1/\gamma_2)_r = \log (\gamma_1^0/\gamma_2^0)_r - \alpha_{12}m_2 + \alpha_{21}m_1 + c \quad (9)$$

$$\alpha_{12} = \alpha_{12}^0 \bar{R}_1^2$$

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

where m is the total molality of the mixed resin system and $c = -0.05$. Since R_1 varies with molality, α_{12} is a variable, whereas α_{21} and α_{12}^0 are true constants.

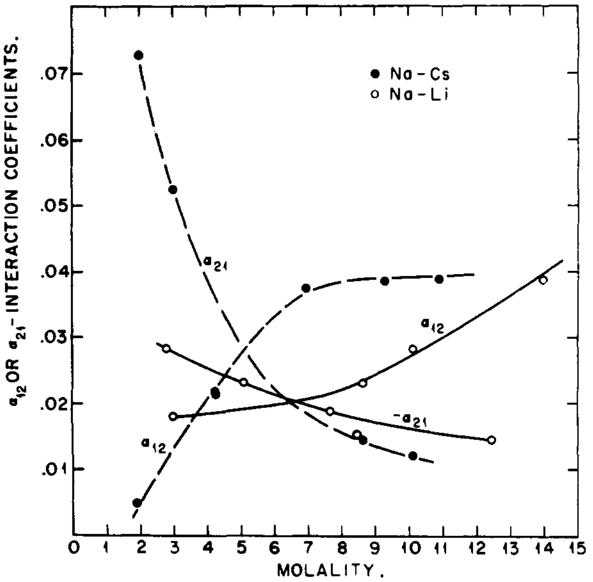

Fig. 2.—The variation of the interaction coefficient with molality.

Using the above device and the values of α_{12}^0 and α_{21} listed in Table III a comparison was made of the calculated and measured selectivities as a function of resin environment and cross-linking. As shown in Fig. 3, there appears to be a reasonable correlation between the two values. In fact, two trace experiments with any resin could, in principle, permit the calculation of all the selectivities. It may be pertinent to point out, moreover, that this treatment assumes one variable and one constant interaction coefficient.

TABLE III

INTERACTION COEFFICIENTS[a] MEASURED BY TRACE EXPERIMENTS

Dm_2/m_1	c	α^0_{12}	α_{21}	β_{12}
Cs*/K	+0.07	....	−0.024	0
Cs/Na*	+ .13	0.052	0	0
Cs*/Na	+ .13	....	0	0
Cs*/H	+ .13		0.007	0
Cs*/Li	+ .13	....	0.0600	0
Ag*/Na	+ .14	....	0.07	0
Ag/Na*	+ .14	− .0066	....	
Ag*/H	+ .13		.013	0
Ag/Cs*	+ .01	− .0095	....	0
K/Na*	0	+ .020	....	0
Na*/H	− .04	....	− .059	0
Na*/Li[b]	− .05	....	− .012	0
NH_4*/Cs	+ .13	+ .00346		
Cs*/NH_4	+ .13		− .00828	0
NH_4/Na*	+ .03	+ .0176	....	0
Na/Li*	− .05	− .0051	....	+0.00289

[a] Calculated by means of equation 5 where the starred term is the trace component. [b] $\alpha_{12}^0 = 0.173$ for alternative method.

At this point there appears to be no justification for the use of $c = -0.05$ other than that it appears to be needed. Later it will be shown that the c constants are characteristic of certain systems. In most cases, the value of c is of negligible importance and can be predicted.

Since the values of b for most of the cations are

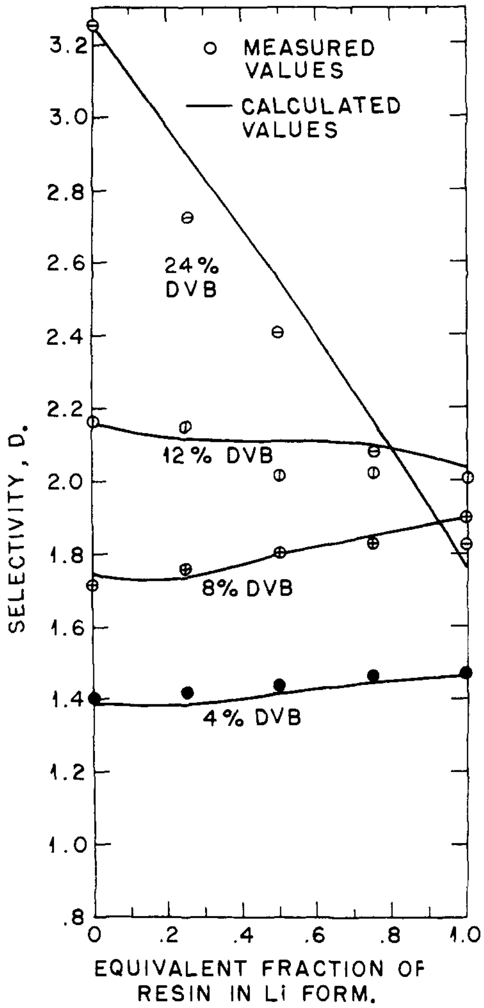

Fig. 3.—Calculated and observed selectivities of the Na–Li system.

negative, a thorough study was made of a system both of whose ions have negative b values. It was felt that the behavior of this system would be most representative of monovalent sulfonic cation-exchange systems in general. The Na–Cs system was chosen for this purpose. This system commanded additional interest because the $P\Delta\bar{V}°/2.3RT$ correction might be of some consequence due to the relatively large value of $\Delta\bar{V}°$. The "trace selectivity" technique was employed with equations 6 and 7 to measure the values of α_{12} and α_{21} (Fig. 2) as a function of molality. The observed wide variation of the interaction coefficients with molality was completely eliminated when a value of 0.13 was inserted for c in equation 9. Using the two constant interaction coefficients listed in Table III, a comparison has been made (Table IV) of the calculated and measured selectivities for Na–Cs system (corrected for $P\Delta\bar{V}°/2.3RT$ as a function of the two general variables). The two values agree closely.

"Trace Selectivity."—In order to obtain a better understanding of the nature of the constant c and the behavior of interaction coefficients in general, the "trace selectivity" technique along with equations 6 and 7 was used for the study of a number of ion pairs as a function of resin cross-linking. For the most part, if constant interaction coefficients and a value of c (Table III) were used, the calculated selectivities closely approximated the measured values (Table V) over a concentration range of two to twelve molal.

Table IV

The Effect of Resin Composition and Cross-linking on the Selectivity of the Cs–Na System

DVB, %	Type D	F, Fraction of NaR 0	0.25	0.50	0.75	1	$P\Delta\bar{V}^0/2.3RT$ $F = 0$	$F = 1$
2	Measd.[a]	1.35	1.44	1.53	1.63	1.73		
	Calcd.	1.33	1.45	1.54	1.62	1.69	0.0097	0.0129
4	Measd.	1.33	1.48	1.65	1.84	2.04		
	Calcd.	1.33	1.48	1.65	1.80	1.91	.0178	.0225
8	Measd.		1.51	1.84	2.24	2.72		
	Calcd.	1.33	1.61	1.94	2.31	2.72	.0292	.0485
12	Measd.	1.26	1.64	2.14	2.80	3.63		
	Calcd.	1.27	1.69	2.21	2.85	3.67	.0615	.0876
16	Measd.	1.37	1.72	2.29	3.06	4.07		
	Calcd.	1.13	1.64	2.27	3.08	4.15	.0705	.1073

[a] Refers to experimentally determined D corrected for $P\Delta\bar{V}°/2.3RT$ as shown in equation 5. $D = (Cs^+/Na^+)_{resin}/(Cs^+/Na^+)_{soln}$.

The only variable interaction coefficients were those of the Na–Li system and the value of α_{12} for the Na–H system. Even in the latter cases, however, the value of α_{21} is without exception a constant. In general the constancy of both interaction coefficients appears to be characteristic of most monovalent ionic systems. The agreement in Table V is good considering the concentration range covered. In the 24% cross-linking range, however, the correlation falls off because of the relationship $am/(1 + bm)$ no longer successfully represents the behavior of the osmotic coefficients. Since most cation exchangers are not as concentrated as this, the difficulty is usually of minor importance.

An important problem, however, still remains. It is evident that the interaction coefficients calculated by means of equations 6 and 7 would vary greatly with concentration if the empirical constants c listed in Table III were eliminated. The origin of these constants is not known at the present time. There are, however, several reasonable possibilities. In the first place, until a method is devised to determine the nature of the function ϕ_0 in equation 2, there is no assurance that the assumption

$$F_1(m) - F_2(m) = 0$$

is completely valid. Moreover, the possibility exists that the constants might be a necessary theoretical requirement for relating $\log (\gamma_1^0/\gamma_2^0)_r$ to $\log (\gamma_1/\gamma_2)_r$ in cation-exchange systems. This would indicate that Harned's rule without a constant is non-operative in these systems. Finally there is the strong possibility that some of the values of c may be influenced by the fact that the limiting values of ϕ_0 for all systems are not equal to 0.4. Additional evidence will be presented to show that this latter contingency may be the determining factor in the value of the constant in any system involving Ag^+. It is pertinent to point out for the present that the value of ϕ_0 for Ag^+ is equal to 0.25 compared to the usual value of 0.40 for most simple monovalent ions.

TABLE V

COMPARISON OF MEASURED[a] AND CALCULATED SELECTIVITIES FOR TRACE EXPERIMENTS

System		DVB, %					
		2	4	8	12	16	24
Cs*/H	Measd.	1.92	3.26	6.92	15.15	22.6	92.2
	Calcd.	1.97	3.13	5.72	15.7	22.5	89.4
	$P\Delta\bar{V}/2.3RT$	0	0.013	0.05	0.11	0.135	0.243
Cs*/K	Measd.	1.14	1.175	1.21	1.22	1.3	
	Calcd.	1.15	1.175	1.20	1.21	1.31	
	$P\Delta\bar{V}/2.3RT$	0	0.0058	0.014	0.0248	0.0350	
Cs*/Li	Measd.	2.63	4.48	10.46	20.4	41.7	132
	Calcd.	2.74	4.80	11.05	29.0	38.0	132
	$P\Delta\bar{V}/2.3RT$		0.013	0.05	0.11	0.135	0.243
Cs*/Ag	Measd.		0.91	0.828	0.756	0.713	
	Calcd.		0.90	0.828	0.736	0.713	
	$P\Delta\bar{V}/2.3RT$		0.016	0.0264	0.0472	0.0546	
Ag*/Na	Measd.	2.3	3.50	7.2			
	Calcd.	2.43	3.34	8.18			
	$P\Delta\bar{V}/2.3RT$	0					
Ag/Na*	Measd.	1.59	2.46	3.4	5.35	5.95	
	Calcd.	1.58	2.43	3.29	5.63	5.88	
	$P\Delta\bar{V}/2.3RT$	0	0	0	0	0	
Na*/Li	Measd.		1.40	1.72	2.16	2.4	3.25
	Calcd.		1.39	1.75	2.16	2.26	3.25
	$P\Delta\bar{V}/2.3RT$						
K/Na*	Measd.	1.15	1.29	1.38	1.57	1.635	
	Calcd.	1.16	1.29	1.44	1.52		
	$P\Delta\bar{V}/2.3RT$	0	0.006	0.015	0.0268	0.036	
Na*/H	Measd.	1.03	1.13	1.34	1.82	2.08	5.10
	Calcd.	1.07	1.19	1.25	1.81	2.15	4.47
	$P\Delta\bar{V}/2.3RT$	0	0	0.0037	0.00784	0.0095	0.0171
Ag*/H	Measd.	1.89	2.91	5.1		26.1	92.8
	Calcd.	1.95	3.27	6.16		25.7	100
	$P\Delta\bar{V}/2.3RT$	0	0	0	0.005	0.0064	0.0115
Cs*/NH_4	Measd.	1.355	1.50	1.57	1.74	1.78	
	Calcd.	1.40	1.46	1.60	1.71	1.74	
	$P\Delta\bar{V}/2.3RT$		0.0022	0.006	0.009	0.0118	
NH_4/Na*	Measd.	1.12	1.17	1.25	1.39	1.46	1.33
	Calcd.	1.11	1.17	1.3	1.37	1.61	1.37
	$P\Delta\bar{V}/2.3RT$		0.01	0.04	0.058	0.076	0.092

[a] The measured selectivity corrected by the $P\Delta V/2.3RT$ values listed.

Fortunately the constant does not present any difficult operational problems. An examination of Table III reveals the following facts. All the systems involving the Na^+ ion, with the exception of Ag^+ and Cs^+, require a constant $c = 0.04$ in equation 6; those involving Cs^+ or Ag^+ require a value of $c = 0.13$. If Ag^+ and Cs^+ compose a system, the constant practically disappears. One can, in fact, correlate the values of c with the absolute values of b found for each ion with the exception of the Na–K system.

In principle, therefore, only two trace selectivity measurements with any resin should permit the calculation of the selectivities for the system at any cross-linking and resin environment. Moreover, there is evidence that only one measurement is needed because one can show that[3]

$$(\alpha_{12} - \alpha_{21}) = (2/2.3m)(\phi_1 - \phi_2) \qquad (10)$$

where α_{12}, α_{21} are the interaction coefficients, and $\phi_1 - \phi_2$ is the difference in the osmotic coefficients of the pure salt forms of the two ions at molality m.

When equation 10 is used in conjunction with experimentally measured values of α_{21}, the following values of α_{12} were found for the Na–Cs system: at $m = 2$, $\alpha_{12} = 0.05$; at $m = 5$, $\alpha_{12} = 0.054$; and at $m = 10$, $\alpha_{12} = 0.049$. The average of these values agrees very closely with the value experimentally determined for this system, *i.e.*, $\alpha_{12} = 0.05$.

Equation 5 failed only in the case of the Ag^+–Na^+ system to relate α_{12} to α_{21}. Previously it was stated that the origin of c for Ag^+ might be different. If the following equation is used, no difficulty is experienced.

$$(\alpha_{12} - \alpha_{21}) = 2/2.3\frac{(\phi_1 - \phi_2)}{m} - c \qquad (11)$$

where $c = 0.14$. It becomes increasingly evident that the value of c in the entire treatment is influenced by at least two factors. In any case, there appears to be no difficulty in calculating one interaction coefficient if the other is known.

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(3) H. S. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 462.

Nature of the Interaction Coefficients.—No attempt appears to have been made to correlate observed ion-exchange interaction coefficients with known physical properties of ions. If such correlations exist they may be of significance in themselves and will be of value in permitting the calculation of mixed resin activity coefficients from pure activity coefficients. In Table VI are listed the experimentally measured values of α_{12} and those calculated using the empirical equation

$$|\alpha_{12}| = (r_1 - r_2/2)^3 \qquad (12)$$

where r_1 and r_2 refer to the crystal radii in ångströms of the two cations that compose the system. The two values agree fairly well over a considerable range. The most surprising fact about equation 12 is that crystal radii in ångströms give the value for the interaction coefficients needed in general equations 6 and 7. Since the interaction coefficients have the dimensions of liters per equivalent it is obvious that other terms are required in equation 12. The important implication does remain, however, that a knowledge of the osmotic coefficients of the pure salt forms probably will permit the ultimate calculation of monovalent ion selectivities for cross-linked exchangers.

TABLE VI

COMPARISON OF CALCULATED AND MEASURED α_{12} VALUES

System	Experimentally measured α_{12}	Calcd. $\|\alpha_{12}\|$ by eq. 12	System	Experimentally measured α_{12}	Calcd. α_{12} by eq. 12
Cs-Li	+0.16-0.18[a]	0.162	K-Na	+0.02	0.0068
Cs-Na	+ .052	.052	Cs-NH_4	+ .00346	.0012
Ag-Na	− .0066	.004	Na-Li	− .005	.005
Ag-H	+ .045[a]	.045	NH_4-Na	+ .0176	.0186
Ag-Cs	− .0095	.0099			

[a] α_{12} values calculated from measured values of α_{21} using equations 10 and 11.

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. M. H. Lietzke in the preparation of this manuscript.

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Hydrogen Electrode–Silver Chloride Electrode System at High Temperatures and Pressures[1]

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RECEIVED OCTOBER 14, 1954

A knowledge of the behavior of the hydrogen electrode at high temperatures and pressures will ultimately afford a means of measuring the *p*H of aqueous solutions above 100°. In the present paper it is shown how calculated curves can be plotted demonstrating the behavior of the hydrogen electrode–silver chloride electrode system at temperatures up to 250° and pressures up to 40 atmospheres. The agreement between calculated potentials, which are based on extrapolation of data obtained at lower temperatures, and experimental data obtained directly at the higher temperatures is shown and discussed. A mechanism is proposed to account for deviations between the calculated and experimental values at the higher temperatures and pressures.

Introduction

The behavior of the hydrogen electrode at high temperatures and pressures is of considerable importance since it will ultimately afford a means of measuring the *p*H of solutions above 100°. When the hydrogen electrode itself cannot be used in *p*H measurements, for example in solutions where the hydrogen gas might cause chemical reduction, other electrodes, such as metal, metal oxide or special glass electrodes, could be calibrated against the hydrogen electrode in stable solutions. In the present paper it is shown how a series of calculated curves can be plotted demonstrating the behavior of the hydrogen electrode–silver chloride electrode system at high temperaures and pressures in hydrochloric acid solution. The agreement between the calculated values and the experimental data of Choudhury and Bonilla[2] is also shown and discussed.

Theoretical

E^0 of the Electrode System.—In order to obtain E^0 values at temperatures above 100° the E^0 values obtained by Harned and Ehlers[3] for the hydrogen electrode–silver chloride electrode system were extrapolated. The equation used was

$$E^0 = 0.22239 - 645.52 \times 10^{-6}(t - 25) - 3.284 \times 10^{-6}(t - 25)^2 + 9.948 \times 10^{-9}(t - 25)^3 \quad (1)$$

where t is the temperature in degrees centigrade. Equation 1 was derived from data obtained between 0 and 60°. At 95° the E^0 value calculated agrees with the experimental value to within 0.1 mv. The value of E^0 decreases from 0.22239 v. at 25° to 0.02603 v. at 250°.

The Activity Coefficient of HCl at High Temperatures.—The mean ionic activity coefficient of hydrochloric acid was calculated by two methods. In the first method equation 2 was integrated over the interval from 0° to the desired temperature.

$$\left(\frac{\partial \ln \gamma\pm}{\partial T}\right)_m = -\frac{\bar{L}_2(T)}{\nu RT^2} \qquad (2)$$

$\bar{L}_2$ is the partial molal heat content of HCl in a solution of the specified concentration. The equation was solved only for a solution of HCl which was 0.01689 *m* at 25°. This value was taken so that a direct comparison could be made between the calculated potential values and the experimental values of Choudhury and Bonilla.

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(1) This paper is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) R. N. Choudhury and C. F. Bonilla, thesis submitted by R. N. Choudhury in partial fulfillment of the requirements for the degree of Master of Science, Columbia University, May 1, 1952.

(3) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933).