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Influence of Electrolyte Uptake on the Equilibrium Constant for the Sodium–Hydrogen Exchange on Dowex 50

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The influence of the inclusion of electrolyte uptake on the calculated thermodynamic equilibrium constant for the sodium–hydrogen exchange on Dowex 50 has been investigated. It was found that the contribution of the electrolyte uptake term is significant in the determination of the activity coefficient, f, for each pure resin in a solution of the corresponding salt at molality m. In the case studied, however, if these coefficients are included in the calculation, log K is not appreciably affected by neglect of the electrolyte uptake in the exchange itself. For the sodium–hydrogen exchange an adequate approximation to these log f terms is given by the negative of the product of the water uptake (the number of moles of water per equivalent of resin) and the logarithm of the activity of water in the binary solution.

Introduction

When a particle of cation-exchange resin is placed in a solution of electrolyte whose cation is different from that in the resin, three processes are known to occur: first, equivalent cation exchange takes place until equilibrium is reached; second, water is taken up by the resin; and third, some electrolyte, in addition to that which is exchanged, is taken out of the external solution and remains associated with the resin particle. Of the processes mentioned, the cation exchange itself has been of primary interest.

For an exchange involving the monovalent cations A^+ and B^+, then, at equilibrium

$$A^+ + BRes \rightleftarrows B^+ + ARes \qquad (1)$$

The thermodynamic equilibrium constant, expressed in terms of activity coefficients and concentrations, may be written

$$K = \frac{N_A m_B f_A}{N_B m_A f_B}\left(\frac{\gamma_{BX}}{\gamma_{AX}}\right)^2 = K_a(f_A/f_B) \qquad (2)$$

where N_A and N_B represent the concentrations of A^+ and B^+ in the resin phase, expressed in this paper as the number of moles of A^+ or B^+ per equivalent of resin, and m_A and m_B are the molalities of the salts AX and BX in the solution. The activity coefficients in the resin phase are represented by f_A and f_B, and the mean ionic activity coefficients of AX and BX in solution by γ_{AX} and γ_{BX}.

Argersinger, Davidson and Bonner,[1] and independently Ekedahl, Högfeldt and Sillén,[2] have shown that combination of the Gibbs–Duhem equation for the resin phase with the definition of K yields expressions from which activity coefficients of the resin components may be calculated, provided the activity coefficients in the mixed solution are known.

In this early work only the cation-exchange equilibrium was considered. Later Davidson and Argersinger[3] took into account that water transfer also accompanied the exchange. The inclusion of water transfer in the exchange treatment was shown to yield a single value of K for the sodium–hydrogen exchange at external solution molalities of 0.1, 0.3 and 1.0. The improvement, although apparently effective, as reflected by the constancy of K at three ionic strengths, was still subject to the objection that the third factor in the exchange process, namely, electrolyte uptake, had not been taken into account.

In a theoretical paper, Gaines and Thomas[4] have presented a thermodynamic treatment of ion exchange, in the second part of which (Case B) they have included the contributions of both water and sorbed electrolyte. Their work represents an approach similar to that which has been made in this Laboratory, except that some new terms, which can be determined experimentally, have been included to correct for the electrolyte uptake.

The purpose of the present work was to compare the two treatments in some detail, and to determine the magnitude of the corrections imposed by the inclusion of electrolyte uptake in the sodium–hydrogen exchange.

Davidson and Argersinger pictured each resin type as being associated with a certain number of moles of water. The exchange process, then, was considered to include water transfer between the external solution and the resin. The standard state of each resin type was the pure water-saturated resin. Their expression for log K is equivalent to

$$\log K = \int_{N_{ARes}=0}^{N_{ARes}=1} \log K_a \, dN_{ARes} + \int_{N_{ARes}=0}^{N_{ARes}=1} (n_B - n_A) \log a_w dN_{ARes} \qquad (3)$$

where n_A and n_B are the "saturation constants," *i.e.*, the number of moles of water per equivalent of resin taken up by each pure resin type, and a_w is the activity of water. In this case, where no electrolyte uptake is considered, N_A (the number of moles of A^+ per equivalent of resin) is the same as N_{Ares}, the mole fraction of ARes.

The number of moles of water per equivalent of resin in the exchange, N_w, is related to the saturation constants by the equation

$$N_w = n_A N_{ARes} + n_B(1 - N_{ARes}) \qquad (4)$$

When the saturation constants are considered constant at any given molality, the equilibrium constant above may be expressed in terms of N_w by the equation

$$\log K = -(n_A \log a_w)_{N_{ARes}=1} + (n_B \log a_w)_{N_{ARes}=0} + \int_{N_{ARes}=0}^{N_{ARes}=1} \log K_a \, dN_{ARes} + \int_{N_{ARes}=0}^{N_{ARes}=1} N_w \, d \log a_w \qquad (5)$$

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[1] W. J. Argersinger, Jr., A. W. Davidson and O. D. Bonner, *Trans. Kansas Acad. Sci.*, **53**, 404 (1950).

[2] E. Ekedahl, E. Högfeldt and L. G. Sillén, *Acta Chem. Scand.*, **4**, 556 (1950).

[3] A. W. Davidson and W. J. Argersinger, Jr., *Ann. N. Y. Acad. Sci.*, **57**, 105 (1953).

[4] G. L. Gaines, Jr., and H. C. Thomas, *J. Chem. Phys.*, **21**, 714 (1953).

which corresponds to equation 17 of Gaines and Thomas, for Case A, in which electrolyte sorption is assumed not to occur.

Gaines and Thomas considered the resin phase to consist of four components, *i.e.*, A^+, B^+, X^- and water. They applied the complete and detailed conditions for thermodynamic equilibrium in the entire exchange system and derived differential expressions for the resin activity coefficients. The standard state for each resin was defined in terms of the pure resin saturated with water, that is, in equilibrium with an infinitely dilute solution of electrolyte with common cation. The evaluation of the resin activity coefficients at an arbitrary state of the exchange system requires that the differential relations be integrated from the standard states to the arbitrary state of the system; the evaluation of the equilibrium constant for the exchange process requires the integration of the differential relations from the standard state of one resin component to the standard state of the other resin component. As Gaines and Thomas point out, the functions integrated are point functions of position on the isothermal exchange surface, and hence any convenient path between two specified states may be chosen. Gaines and Thomas made three different choices as convenience dictated; in each the path included segments from the standard state of either resin to a state in which the pure resin is in equilibrium with a solution of electrolyte with common cation at a finite concentration. In addition, a path across the isothermal exchange surface was chosen at constant total solution molality (Case A, general), constant solvent activity (Case A, special instance), or constant uptake of negative ion (Case B, general). These three conditions are of course not generally equivalent; the choice is to be made on the basis of the relative simplicity of the results and the availability of the requisite exchange data. In this paper integration at constant ionic strength is chosen because this restriction seems most easily satisfied experimentally.

The differential relations which determine complete equilibrium, equations 32, 33 and 34 of Gaines and Thomas, were combined and integrated at constant ionic strength to yield $\log f_A$ and $\log f_B$ at a given resin composition in the exchange system. When these are incorporated into the definition of $\log K$, Gaines and Thomas' equation 14, one obtains, instead of their equation 38

$$\log K = \frac{N(Q) - N(S)}{2.303} + \log \frac{f_A(Q)}{f_B(S)} - N_X(Q) \log K_A(Q) + N_X(S) \log K_B(S) + \int_S^Q \log K_B \, dN_X + \int_S^Q \log K_a dN_A + \int_S^Q N_w \, d\log a_w \quad (6)$$

where

$$K_A = \frac{N_A N_X}{m_A m_X (\gamma_{AX})^2} \quad (7)$$

and a similar equation defines K_B. The term N is $N_A + N_B + N_X$, where N_X is the number of moles of anion sorbed per equivalent of resin. State Q represents pure ARes in equilibrium with pure AX solution of molality m, and state S is similarly defined for BRes.

The terms $\log f_A(Q)$ and $\log f_B(S)$ refer to the activity coefficients of the respective pure resins in contact with a solution containing electrolyte with a common cation at molality m. The values of these activity coefficients are calculated by means of the equations

$$\log f_A(Q) = -\log N_A(Q) - \int_{a_w = 1}^{a_w(Q)} (N_w - 55.51 \, N_X/m_X) \, d\log a_w$$
$$\log f_B(S) = -\log N_B(S) - \int_{a_w = 1}^{a_w(S)} (N_w - 55.51 N_X/m_X) \, d\log a_w \quad (8)$$

which are derived for the present case precisely as Gaines and Thomas derived their equation 42′.

Equations for the exchange when the electrolyte sorption is not taken into account are easily derived from the above by setting N_X equal to zero and recognizing that now $N_A + N_B = 1$. Thus

$$\log K = \log \frac{f_A(Q)}{f_B(S)} + \int_S^Q \log K_A dN_A + \int_S^Q N_w \, d\log a_w \quad (9)$$

and

$$\log f_A(Q) = -\int_{a_w = 1}^{a_w(Q)} N_w \, d\log a_w; \quad \log f_B(S) = -\int_{a_w = 1}^{a_w(S)} N_w \, d\log a_w \quad (10)$$

Equation 9 is very similar to equation 5. Each results from three integration steps:

(a) From the standard state of pure ARes saturated with water to state Q, where pure ARes is in equilibrium with a solution of AX of specified molality. The integration yields in the one case $\log f_A(Q)$ and in the other $-(n_A \log a_w)_{N_{ARes}=1}$. If the saturation constant n_A were independent of external molality, then these quantities should be identical.

(b) From state Q *via* exchange at constant total molality to state S, where pure BRes is in equilibrium with a solution of BX of the specified molality. The integration, as it must, yields identical terms in the two cases.

(c) From State S to the standard state of pure BRes saturated with water. The terms $\log f_B(S)$ and $-(n_B \log a_w)_{N_{BRes}=1}$ result, respectively, in the two cases.

In this paper experiments are described which determine all those quantities (N_A, N_B, N_X, N_w, which may be considered functions of m_A and m_X as independent variables) required for the application of the complete equations 6 and 8. These measurements cover the entire range included in the integration path, and are made for each of several different paths involving exchange at different values of the constant total ionic strength. The alternative formulations which ignore electrolyte sorption, equation 5 and equations 9 and 10, are then tested with the same experimental data and the effects of the approximation determined.

The system sodium chloride–hydrochloric acid was chosen for study since the mean ionic activity coefficients of the electrolytes, and hence the activity of water, in the mixed solutions are known.[5]

[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, pp. 459–467, 547, 557.

Activity coefficients for each of the binary solutions are also available.[5]

Experimentally, the total sodium and/or hydrogen content of the resin, the sorbed sodium chloride and/or hydrochloric acid, the sorbed water, and the composition of the outside solution had to be determined. Measurements were made on two different kinds of systems: one which consisted of pure sodium resin or hydrogen resin in a solution of sodium chloride or hydrochloric acid at different molalities, and the other of sodium–hydrogen resin in equilibrium with sodium chloride–hydrochloric acid solutions at several molalities of the external solution. The first kind of system furnishes the data (N_A, N_X, N_w or N_B, N_X, N_w) required for the determination (by means of equation 8) of the activity coefficients of the pure resins in solutions of the corresponding chlorides. The second kind of system furnishes the data (N_A, N_B, N_X, N_w) required for the evaluation (by means of equation 6) of the equilibrium constant for the exchange.

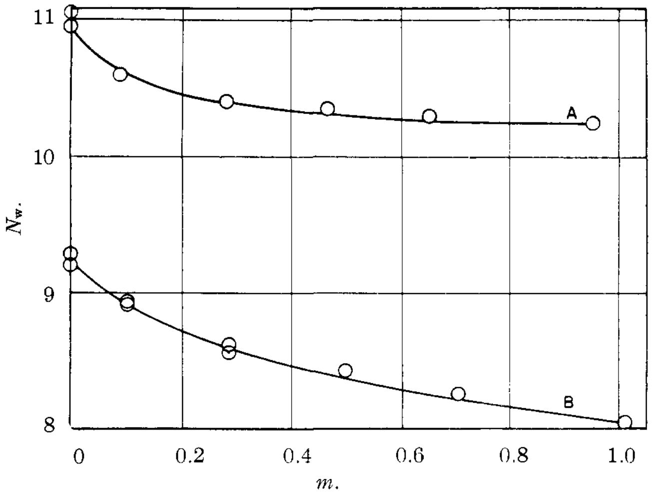

Fig. 1.—Water uptake (N_w, moles of water per equivalent of resin) by pure Dowex 50 resins in corresponding chloride solutions of molality m: curve A, HRes in HCl; curve B, NaRes in NaCl.

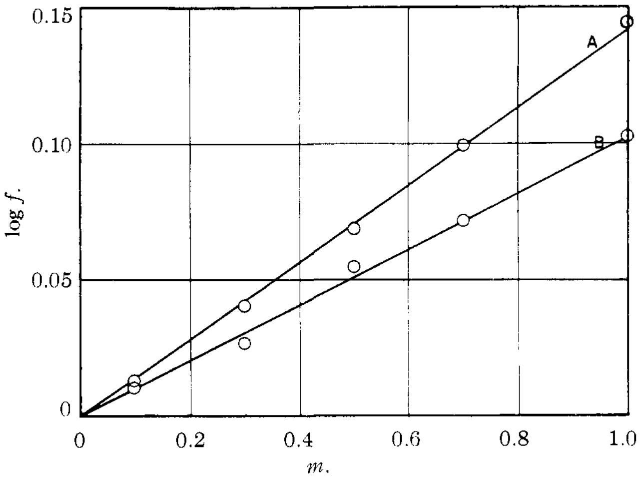

Fig. 2.—Calculated activity coefficients of pure resins in their corresponding chloride solutions, determined from the complete equation 8: curve A, HRes in HCl; curve B, NaRes in NaCl.

Experimental Methods

The resin used was Dowex 50, which contained 8% DVB. Only those particles which in the sodium form (air-dried) were larger than No. 30 Sieve, U. S. Standard Sieve Series, were used.

Resin and solution were placed in a glass-stoppered flask and allowed to stand overnight, with occasional shaking, in a water-bath maintained at 25°. The resin was separated from the solution by means of filtration. It was "wiped dry" with successive pads of dry filter paper, and portions were weighed out immediately for the determination of total cation and of sorbed electrolyte. The resin was washed free from sorbed cation with several portions of water, and these washings were analyzed.

To determine sorbed sodium chloride, the washings were evaporated to dryness and baked. The residues were dissolved either in a small amount of water or in 5 ml. of 0.01 N sodium chloride solution, depending on chloride concentration. The solutions were titrated with 0.01 N silver nitrate solution, dichlorofluorescein being used as indicator. When sodium chloride was added, the solvent solution was separately analyzed and the sorbed sodium chloride obtained by difference. To determine sorbed hydrogen chloride, the washings were titrated with 0.01 N sodium hydroxide solution.

To determine total sodium the unwashed resin was exhaustively exchanged with 5 N hydrochloric acid in a column and the eluate evaporated to dryness. The residue was baked in an oven at 110°, and the chloride (assumed to be present only as sodium chloride) was dissolved and titrated potentiometrically with silver nitrate solution. The total hydrogen in the resin was determined by direct titration of "wiped dry" unwashed resin samples with standard sodium hydroxide solution.

Known volumes of solution at 25° were taken for analysis. Portions of the solution were titrated potentiometrically with silver nitrate solution for the determination of total chloride. Other portions of the solution were titrated with sodium hydroxide solution for the determination of total hydrogen ion. The sodium chloride content was calculated as the difference between the total chloride ion and the hydrogen ion content. Density determinations at 25° were made on each solution in order to convert normality into molality.

In the exchanges at 1.0 and 0.5 m ionic strength, the resin was analyzed for total hydrogen ion, total sodium ion, sorbed hydrogen ion, and sorbed chloride ion and the water content was calculated by difference. In the case of the exchange at 0.1 m ionic strength, the resin was analyzed merely for total hydrogen ion and total sodium ion, for the amount of sorbed electrolyte was too small to be measured accurately.

Results

Sodium Resin in Sodium Chloride Solution and Hydrogen Resin in Hydrochloric Acid.

—The experimentally determined values of N_{Cl}, the number of moles of anion, or adsorbed electrolyte, per equivalent of resin, and of N_w, the number of moles of water per equivalent of resin, are shown in Table I for sodium resin in sodium chloride and for hydrogen resin in hydrochloric acid.

Table I

Takeup of Water and Electrolyte by Sodium and Hydrogen Resins in Corresponding Chloride Solutions of Various Molalities

m_{NaCl}	Sodium N_{Cl}	N_w	m_{HCl}	Hydrogen N_{Cl}	N_w
0	0	9.26	0	0	11.03
.105	.0015	8.93	.099	.0029	10.61
.292	.0055	8.60	.285	.0047	10.42
.504	.0095	8.43	.468	.0065	10.36
.708	.0152	8.26	.652	.0093	10.31
1.013	.0227	8.06	.956	.0170	10.26

In Fig. 1 the water uptake is seen to decrease with increasing molality of external solution for both resins. At any given molality, more water is taken up by hydrogen resin than by sodium resin.

Table II gives the activity coefficients for each pure resin as calculated from equation 8. They are seen to deviate significantly from unity at molalities as high as 1.0. In Fig. 2, $\log f$ is shown to be a linear function of the external molality, a convenient result not generally to be expected except over a limited concentration range at low molality.

TABLE II

ACTIVITY COEFFICIENTS OF PURE RESINS IN SOLUTIONS OF VARIOUS MOLALITIES

	NaRes in NaCl $\log f_{Na}$		HRes in HCl $\log f_H$	
m	Eq. 8	Eq. 10	Eq. 8	Eq. 10
0	0	0	0	0
.1	.0108	.0135	.0133	.0148
.3	.0269	.0379	.0408	.0454
.5	.0551	.0793	.0692	.0671
.7	.0723	.1069	.0993	.1101
1.0	.1026	.1564	.1450	.1614

Table II also includes the values of $\log f$ calculated from equation 10, in which the sorption of electrolyte is ignored. The fact that these values are quite different from those obtained from equation 8 indicates that for the pure resin, at least, the sorption of electrolyte does contribute significantly to the value of the activity coefficient.

Sodium–Hydrogen Exchange.—The pertinent exchange data at each ionic strength consist of the solution composition and the total number of moles, per equivalent of resin, of each component, sodium, hydrogen, chloride and water. The actual experimental data for the exchange measurements at 1.0, 0.5 and 0.1 *m* ionic strength are not reported here. Rather in Tables III, IV and V are reported the values obtained when the experimentally determined quantities were plotted against mole fraction of sodium resin, a smooth curve drawn, and the "smoothed values" read off at mole fractions of 0, 0.2, 0.4, 0.6, 0.8 and 1.0. Such a procedure was necessary in order to permit calculation of values for $\log f_{Na}$ and $\log f_H$ which would be comparable at the three molalities.

Figure 3 shows the experimental values of water uptake N_w plotted against mole fraction of sodium resin at each molality. Least square straight lines have been drawn through each set of points. The fact that the slopes of the three curves are very nearly the same lends credence to the assumption made by Davidson and Argersinger that $(n_A - n_B)$ is independent of ionic strength.

Discussion

The values of K for the exchange, calculated by equation 6, are 1.52, 1.55 and 1.57 for the 1.0, 0.5 and 0.1 *m* ionic strength exchanges, respectively. The slight increase of K with decreasing molality is not of much significance, for the over-all accuracy of the experiments may not be better than 2–3%.

TABLE III

SODIUM–HYDROGEN EXCHANGE AT 1.0 MOLAL IONIC STRENGTH (INTERPOLATED VALUES)

N_{NaRes}	m_{Na}/m	N_{Na}	N_H	N_X	N_w	$\log K_a$
0	0	0	1.017	0.0170	10.12	0.167
.2	.153	.205	0.813	.0179	9.64	.219
.4	.315	.407	.610	.0189	9.21	.240
.6	.520	.613	.405	.0200	8.76	.235
.8	.760	.820	.200	.0212	8.32	.185
1.0	1.000	1.023	0	.0225	7.88	.099

TABLE IV

SODIUM–HYDROGEN EXCHANGE AT 0.5 MOLAL IONIC STRENGTH (INTERPOLATED VALUES)

N_{NaRes}	m_{Na}/m	N_{Na}	N_H	N_X	N_w	$\log K_a$
0	0	0	1.007	0.0068	10.25	0.180
.2	.140	.200	0.803	.0072	9.86	.212
.4	.295	.400	.600	.0076	9.48	.229
.6	.500	.605	.403	.0082	9.10	.218
.8	.742	.805	.200	.0087	8.72	.173
1.0	1.000	1.005	0	.0093	8.32	.024

TABLE V

SODIUM–HYDROGEN EXCHANGE AT 0.1 MOLAL IONIC STRENGTH (INTERPOLATED VALUES)

N_{NaRes}	m_{Na}/m	N_w	Log K_a
0	0	10.34	0.152
.2	.145	10.06	.196
.4	.304	9.76	.226
.6	.487	9.46	.226
.8	.725	9.16	.184
1.0	1.000	8.88	.065

If electrolyte sorption is taken into account in the evaluation of $\log f_A(Q)/f_B(S)$ for the pure resins by the use of equation 8 as given, but is ignored in the exchange process by the elimination from equation 6 of those terms explicitly involving N_X, then for the sodium–hydrogen system the value of K is found to be essentially unchanged even at 1.0

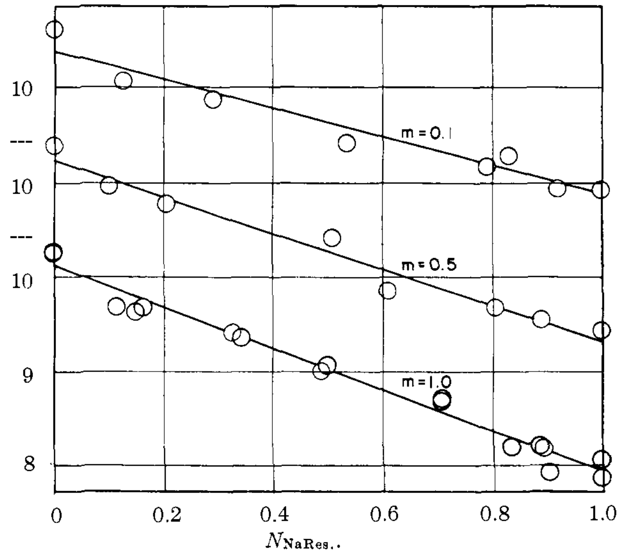

Fig. 3.—Water uptake (N_w moles of water per equivalent of resin) by mixed sodium and hydrogen forms of Dowex 50, as a function of resin composition, in their exchange equilibrium at three different total solution molalities. The lines for 0.1 and 0.5 *m* total molality have been vertically displaced as indicated.

m ionic strength, where the sorption terms would be expected to make a more significant contribution than at the lower molalities. Thus the sorption correction in the exchange itself is negligible for the sodium–hydrogen case; this result may be due to the fact that the actual N_X values in this system are small for the moderately stiffly cross-linked resin here used. Furthermore in this particular system the differences not only between $N_X(Q)$ and $N_X(S)$ but also between $\log K_A(Q)$ and $\log K_B(S)$ are quite small, so that the electrolyte sorption terms in equation 6 are necessarily small also. The electrolyte sorption terms in equation 8, on the other hand, do not so readily tend to cancel out, since they in addition involve the difference between solvent activities in the two pure solutions.

Since it is the difference $\log f_{Na}(Q) - \log f_H(S)$, rather than their separate values, which contributes to the calculated value of the equilibrium constant, it is of interest to compare the values of this difference, when the $\log f$'s are computed in the following ways: (1) from equation 8, in which electrolyte sorption is taken into account; (2) from equation 10, in which electrolyte sorption is ignored; (3) from equation 5, in which electrolyte sorption is ignored, $\log f_A(Q)$ is identified with $-(n_A \log a_w)_{N_{ARes}=1}$, and the change of n_A with external molality is taken into account. From Table VI it can be seen that for Cases (1) and (3) the results are very similar. They might be used interchangeably in the equilibrium constant expression without affecting its value to an extent greater than the experimental error. Case (2), however, in which as in Case (3) electrolyte uptake is ignored, gives values greatly different from the others. It may be concluded that the further simplification introduced in Case (3) to some extent compensates for the neglect of electrolyte uptake.

TABLE VI

LOG f_H $(S)/f_{NA}$ (Q) CALCULATED IN THREE WAYS

m	From eq. 8	From eq. 10	From eq. 5
0	0	0	0
.1	.0025	.0013	.0042
.3	.0139	.0075	.0169
.5	.0141	.0122	.0149
.7	.0270	.0032	.0264
1.0	.0424	.0050	.0398

Thus in the case of sodium–hydrogen exchange, at least, the inclusion of water transfer in the equilibrium by the approximate Davidson–Argersinger method gives a value of *K* not much different from that calculated when sorption of the electrolyte is included. The agreement between these two methods may be fortuitous, however, and it should not be assumed that a similar statement would be valid for all pairs of cations. In the sodium–hydrogen exchange there is no great preference by the resin for one ion over the other, and each resin type behaves quite similarly with respect to both water and electrolyte uptake.

In the calculation of exchange equilibrium constants, it may be sufficient as a first approximation to identify the logarithms of the resin activity coefficients in their pure solutions with the negative product of their water uptake (N_w, the number of moles of water per equivalent of resin), and the logarithm of the activity of water in the binary solution. This has the obvious advantage of experimental simplicity. For two ions whose behavior toward the resin is similar this would probably be adequate, but a discrepancy would doubtless appear for an exchange which involves two cations one of which is sorbed much more strongly than the other. In the latter instance, the inclusion of the N_X terms in the equilibrium constant expression would probably also be necessary.

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