943. *Absorption of Electrolytes by Ion-exchange Materials.*

By F. L. Tye.

A modified thermodynamic treatment of electrolyte absorption by an ion-exchange resin is presented which takes account of the potential gradient existing in the resin. As a result, the decrease of the mean activity coefficient of the absorbed electrolyte to low values in dilute solution is explained. An equation, which relates the concentrations of absorbed and external electrolyte, is deduced and shown to agree with experimental results over a wide range of crosslinking and concentration by appropriate choice of a single parameter.

A NUMBER of studies [1-5] have been made on the concentration of electrolyte absorbed by an ion-exchange resin in contact with an electrolyte. The remarkable feature of all these investigations is that in dilute solution the concentration of electrolyte absorbed in the resin phase is much greater than would be expected from simple electrolyte theory. An equivalent way of expressing this behaviour is to state that in dilute solutions the mean activity coefficient of the absorbed electrolyte tends to very low values. This is in sharp contrast to the tendency for the mean activity coefficient of simple electrolyte solutions to approach unity at low concentrations. The decrease of the mean activity coefficient of simple electrolytes to low values at low electrolyte concentrations is not confined to ion-exchange resins but is common to all systems in which fixed charges are present, *e.g.*, soluble polyelectrolytes. The phenomenon is obviously connected with the fixed charges, but the precise explanation has not yet been given. It is the purpose of this paper to present an explanation and to deduce an equation relating the concentration of electrolyte absorbed by the resin phase to the external concentration.

Freeman [6] attempted to prove that the phenomenon of low mean activity coefficients at low concentrations is unreal and merely due to incomplete separation of the ion-exchange resin from the external electrolyte in the experimental technique. The original workers [1,5] rejected this possibility. One difficulty in Freeman's approach is that the amount of external solution not separated from the resin is not constant for one experimental technique. Thus, using Davies and Yeoman's results [5] on a 5·5% divinylbenzene resin, Freeman [6] has to assume that the ratio of external to internal water for the separated resin is 0·036 for hydrochloric acid but 0·087 for potassium chloride. If Freeman's procedure is applied to lightly crosslinked resins the position becomes absurd. For ammonium chloride and a 2% divinylbenzene resin,[1] for example, it is necessary to assume a ratio of external to internal water of 0·6 to avoid low mean activity coefficients at low concentrations. For ammonium chloride and a 0·4% divinylbenzene resin [3] an even larger amount of external water has to be assumed. Further evidence of the reality of the low mean activity coefficients can be obtained from the work of Mackie and Meares [7] who used a single piece of ion-exchange material and so diminished the possibility of separation errors. Finally, as already mentioned, low mean activity coefficients are obtained with soluble polyelectrolytes and in this case phase separations are not involved.

Symbols.—A Concentration of fixed charges (g. equiv./l.), appropriate to the external concentration.

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[1] Gregor, Gutoff, and Bregman, *J. Colloid Sci.*, 1951, **6**, 245.
[2] Gregor and Gottlieb, *J. Amer. Chem. Soc.*, 1953, **75**, 3539.
[3] Gottlieb, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1953.
[4] Pepper, Reichenberg, and Hale, *J.*, 1952, 3129.
[5] Davies and Yeoman, *Trans. Faraday Soc.*, 1953, **49**, 968.
[6] Freeman, *J. Phys. Chem.*, 1960, **64**, 1048.
[7] Mackie and Meares, *Proc. Roy. Soc.*, 1955, *A*, **232**, 485.

a Activity.
c Concentration (g. equiv./l.).
e Electron charge.
f Activity coefficient.
$\mathbf{k}$ Boltzmann's constant.
P Pressure.
$\mathbf{R}$ Gas constant.
T Absolute temperature.
V Partial molar volume.
z Valency.
β Fraction of pore space at zero electrical potential.
$\mathbf{F}$ The Faraday
μ° Chemical potential in standard state.
ν Moles of ion from 1 mole of electrolyte.
ψ Electrical potential.

Unbarred synbols refer to the external electrolyte and barred ones to the resin phase. Subscripts c and o refer to counter- and co-ions, respectively, + and — to positive and negative ions respectively, and $\pm$ to mean values. Where c or $\bar{c}$ appears with no subscript it refers to concentration of external or absorbed electrolyte, respectively.

Classical Theory.—In the classical thermodynamic treatment the electrochemical potentials of the cations and of the anions in an ion-exchange material and external electrolyte are respectively set equal at equilibrium. Thus,

$$\mu^\circ_+ + \mathbf{R}T\ln a_+ + z_+\psi\mathbf{F} + PV_+ = \bar{\mu}^\circ_+ + \mathbf{R}T\ln \bar{a}_+ + z_+\bar{\psi}\mathbf{F} + \bar{P}\bar{V}_+ \qquad (1)$$

and

$$\mu^\circ_- + \mathbf{R}T\ln a_- + z_-\psi\mathbf{F} + PV_- = \bar{\mu}^\circ_- + \mathbf{R}T\ln \bar{a}_- + z\bar{\psi}\mathbf{F} + \bar{P}\bar{V}_- \qquad (2)$$

If $PV^+ - \bar{P}\bar{V}_+$ and $PV_- - \bar{P}\bar{V}_-$ are assumed to be negligible, as is permissible for small ions, the standard state of the resin phase is made the same as that of the external solution, namely infinite dilution, so that $\mu^\circ_+ = \bar{\mu}^\circ_+$, and $\mu^\circ_- = \bar{\mu}^\circ_-$; and if the electrical potential in the external phase is taken as zero; then equations (1) and (2) reduce to

$$\mathbf{R}T\ln a_+ = \mathbf{R}T\ln \bar{a}_+ + z_+\bar{\psi}\mathbf{F} \qquad (3)$$

and

$$\mathbf{R}T\ln a_- = \mathbf{R}T\ln \bar{a}_- + z_-\bar{\psi}\mathbf{F}. \qquad (4)$$

By combining equations (3) and (4) with the relation

$$\nu_+z_+ + \nu_-z_- = 0, \qquad (5)$$

the usual Donnan expression is obtained

$$a_+^{\nu_+}a_-^{\nu_-} = \bar{a}_+^{\nu_+}\bar{a}_-^{\nu_-}. \qquad (6)$$

Equation (6) may be rewritten

$$(A + \bar{c})^{\nu_c}\bar{c}^{\nu_o} = c^{\nu_c+\nu_o}(f_\pm/\bar{f}_\pm)^{\nu_c+\nu_o} \qquad (7)$$

to give the relation used to calculate the mean activity coefficient in the resin phase from experimental results. This activity coefficient, $\bar{f}_\pm$, will be termed the Donnan mean activity coefficient to distinguish it from another which appears in the new treatment.

New Treatment.—To understand the reason for the unexpected behaviour of the Donnan mean activity coefficient, $\bar{f}_\pm$, consider equations (3) and (4) again. The final Donnan expression (6) is obtained from these, with the help of equation (5), by eliminating the electrical potential $\bar{\psi}$. This implies that $\bar{\psi}$ is constant throughout the resin phase. It is however firmly established [8,9] that, in the vicinity of fixed charges, electrical potential changes continuously, from a numerically high value adjacent to the charges to zero or a numerical minimum in more remote regions. A consequence of this is that, on average,

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[8] Corkill and Rosenhead, *Proc. Roy. Soc.*, 1939, *A*, **172**, 410.

[9] Verwey and Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Company, New York, 1948.

the cations in the resin phase are at a lower potential than the anions. Hence the $\bar{\psi}$ term in equations (3) and (4) must be replaced by two unequal terms $\bar{\psi}_+$ and $\bar{\psi}_-$.

Thus, $$\boldsymbol{R}T \ln a_+ = \boldsymbol{R}T \ln \bar{\bar{a}}_+ + z_+\bar{\psi}_+\boldsymbol{F} \tag{8}$$

and $$\boldsymbol{R}T \ln a_- = \boldsymbol{R}T \ln \bar{\bar{a}}_- + z_-\bar{\psi}_-\boldsymbol{F}. \tag{9}$$

The double bar is used in the resin phase to distinguish activities and activity coefficients arising in the present treatment from those which appear in the classical theory.

Combining equations (5), (8), and (9) we have

$$\ln a_+^{\nu_+}a_-^{\nu_-} = \ln \bar{\bar{a}}_+^{\nu_+}\bar{\bar{a}}_-^{\nu_-} + \boldsymbol{F}(z_+\nu_+\bar{\psi}_+ + z_-\nu_-\bar{\psi}_-)/\boldsymbol{R}T. \tag{10}$$

Now, by substitution from equation (6) and rearrangement

$$\bar{f}_\pm = f_\pm \exp\left[\frac{\boldsymbol{F}(z_+\nu_+\bar{\psi}_+ + z_-\nu_-\bar{\psi}_-)}{\boldsymbol{R}T(\nu_+ + \nu_-)}\right]. \tag{11}$$

It is now apparent that the Donnan mean activity coefficient, $\bar{f}_\pm$, contains a potential term, and it is this term which is responsible for the low values in dilute solutions. The other activity coefficient, $\bar{\bar{f}}_\pm$ is independent of potential terms arising from the presence of fixed charges and is therefore more akin to the activity coefficients of simple electrolyte solutions. It is convenient to call, $\bar{\bar{f}}_\pm$ the Debye–Hückel mean activity coefficient. Let us now consider the potential term. At high concentrations the fixed charges are screened and as a result the differences of potential within the resin are small. Thus $\bar{\psi}_+$ and $\bar{\psi}_-$ tend to equality, the exponential power term tends to zero and the value of $\bar{f}_\pm$ approaches that of $\bar{\bar{f}}_\pm$.

At low concentrations the fixed charges cause potential gradients in the pores of the ion-exchange resin. As a result, the centre of gravity of the cations is at a lower potential than the centre of gravity of the anions; the exponential power term in equation (11) is therefore negative and the exponential itself less than unity so that $\bar{f}_\pm$ is less than $\bar{\bar{f}}_\pm$. Thus, although the Debye–Hückel mean activity coefficient, $\bar{\bar{f}}_\pm$, may behave similarly to the activity coefficients of simple electrolyte solutions, the Donnan mean activity coefficient, $\bar{f}_\pm$, has a lower value, and, as the difference between $\bar{f}_\pm$ and $\bar{\bar{f}}_\pm$ increases as the concentration decreases, low values of the Donnan mean activity coefficient are to be expected in dilute solutions.

An Equation relating Internal and External Electrolyte Concentration.—It is apparent from the foregoing that any successful theoretical treatment of the concentration of absorbed electrolyte must take into account the varying electrical potential in the resin phase. One approach to the problem is to assume a model for the ion-exchange material, determine the electrical potential distribution by solving the Poisson–Boltzmann equation,[10] then to use the Boltzmann distribution law to calculate ionic distribution and finally integrate this to obtain the average concentration of absorbed electrolyte. This has been done by Lazare, Sundheim, and Gregor,[11] and by Klaarenbeek,[12] who used infinite parallel charged plates as the model for the ion-exchange material. Unfortunately the final expressions are complicated and therefore difficult to use in practice. A much simpler treatment is presented here. The variation of electrical potential is taken into account by averaging it into two levels, one of which is zero. Other than this, no particular model is assumed for the ion-exchange material.

The pore space in the ion-exchange material is divided into a fraction $1 - \beta$ at an

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[10] Booth, *J. Chem. Phys.*, 1951, **19**, 821.

[11] Lazare, Sundheim, and Gregor, *J. Phys. Chem.*, 1956, **60**, 641.

[12] Klaarenbeek, quoted by Overbeek in " Progress in Biophysics and Biophysical Chemistry " (Ed. Butler), Pergamon Press, London, 1956, Vol. 6, p. 57.

electrical potential $\bar{\psi}$ and a fraction β at zero electrical potential. The division of the pore space into the two regions is not considered to have physical reality and it is not suggested that there necessarily exists any portion of pore space at zero potential. The division is merely a mathematical device to introduce two potential levels which constitute a better representation than the single potential level of the classical treatment.

The concentrations of ions in each region are given by the Boltzmann distribution law. At potential $\bar{\psi}$, the concentration of cations is $c \exp(-z_+e\bar{\psi}/\boldsymbol{k}T)$ and the concentration of anions is $c \exp(-z_-e\bar{\psi}/\boldsymbol{k}T)$. In the pore space at zero potential the concentrations of cations and anions are, of course, both c. The two pore space fractions being taken together, the " average " concentrations of cations and anions are:

$$\bar{c}_+ = \beta c + (1 - \beta)c \exp(-z_+e\bar{\psi}/\boldsymbol{k}T) \tag{12}$$

and

$$\bar{c}_- = \beta c + (1 - \beta)c \exp(-z_-e\bar{\psi}/\boldsymbol{k}T). \tag{13}$$

Eliminating $\bar{\psi}$ from equations (12) and (13), we have

$$[(\bar{c}_+ - \beta c)/(1 - \beta)c]^{z_-} = [(\bar{c}_- - \beta c)/(1 - \beta)c]^{z_+} \tag{14}$$

or

$$[(\bar{c}_c - \beta c)/(1 - \beta)c]^{z_o} = [(\bar{c}_o - \beta c)/(1 - \beta)c]^{z_c}. \tag{15}$$

Substituting $A + \bar{c} = \bar{c}_c$ in equation (15) and rearranging gives

$$[\bar{c} - \beta c]^{1-z_c/z_o} + A[\bar{c} - \beta c]^{-z_c/z_o} - [(1 - \beta)c]^{1-z_c/z_o} = 0. \tag{16}$$

This is the general equation.

When $z_c + z_o = 0$, equation (16) reduces to a quadratic in $(\bar{c} - \beta c)$:

$$(\bar{c} - \beta c)^2 + A(\bar{c} - \beta c) - (1 - \beta)^2c^2 = 0, \tag{17}$$

the positive root of which is

$$\bar{c} = \beta c - A/2 + \sqrt{[A^2/4 + (1 - \beta)^2c^2]}. \tag{18}$$

Equation (18) applies to 1 : 1 and 2 : 2 electrolytes and relates the concentration of absorbed electrolyte to the external concentration . It contains one unknown parameter, β. In this sense it is not inferior to the more complex approach of Lazare, Sundheim, and Gregor,[9] and Klaarenbeek,[10] which also yields an equation containing an unknown parameter, namely the separation of the infinitely charged plates used as the model for the ion-exchange material.

To test whether equation (18) is of the right type, an expression for $\bar{f}_\pm/f_\pm$ is obtained by substituting equation (18) in equation (7), remembering that $\nu_c = \nu_o$.

Thus,

$$(\bar{f}_\pm/f_\pm)^2 = [1 + 2\beta\{\beta - 1 + \sqrt{[A^2/4c^2 + (1 - \beta)^2]}\}]^{-1}. \tag{19}$$

When $c \longrightarrow 0$, $A/2c \longrightarrow \infty$, and $\bar{f}_\pm/f_\pm \longrightarrow 0$; the requirement of $\bar{f}_\pm$ tending to low values at low concentration is therefore satisfied. When c is large, $(A/2c)^2 \ll (1 - \beta)^2$, and $\bar{f}_\pm/f_\pm \longrightarrow 1$; this also is in agreement with experiment.[2] One further comparison with experiment supports the general satisfactory nature of equation (18). As c tends to zero, equation (18) indicates that $\bar{c}/c$ tends to the constant value of β. The recent results of Freeman [6] show clearly that experimentally $\bar{c}/c$ does indeed tend to a constant value as c decreases.

Detailed Comparison with Experiment.—For detailed comparison of equation (18) with experiment, the studies on the absorptions of hydrogen and alkali-metal chlorides by polystyrenesulphonate resins, crosslinked with various percentages of divinylbenzene, have been chosen, as these are the most comprehensive available.

The comparisons are shown in Figs. 1—4. The experimental results are in molalities and the terms c and $\bar{c}$ in equation (18) have been considered to be in these units also. The agreement with ammonium chloride is very good at all divinylbenzene contents. For the sake of clarity, comparisons for 0·4 and 17% divinylbenzene have been omitted from Fig. 1, although the agreement with these is equally good. There is reasonable agreement with potassium chloride. For lithium chloride the coincidence is good with 2% divinylbenzene resin but is not so satisfactory at the higher crosslinkages. With hydrochloric acid the agreement is again good at all crosslinkages when the results of Gregor *et al.*[2] are used. However, no choice of β is possible that will give any sort of agreement with the results of Pepper, Hale, and Reichenberg[4] on 5% and 10% divinylbenzene resins or with those of Davies and Yeoman [5] on a 5·5% divinylbenzene resin supplied by Pepper. The results of Pepper *et*

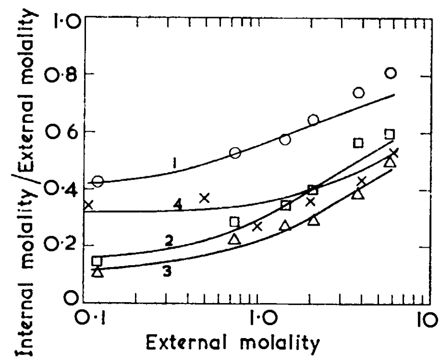


Fig. 1. Absorption of ammonium chloride.

2% DVB: ○ experimental, ref. 1; curve 1, calculated $\beta = 0·40$. 6% DVB: □ experimental, ref. 1; curve 2, calculated $\beta = 0·15$. 10% DVB: △ experimental, ref. 1; curve 3, calculated $\beta = 0·12$. 26% DVB: × experimental, ref. 3; curve 4, calculated $\beta = 0·31$.

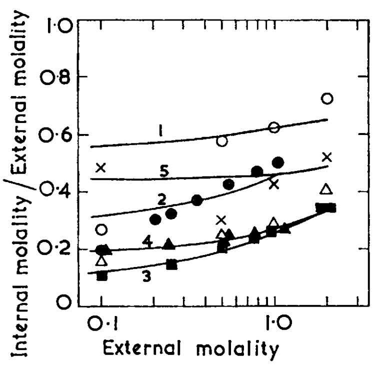


Fig. 2. Absorption of potassium chloride.

2% DVB: ○ experimental, ref. 2; curve 1, calculated $\beta = 0·55$. 2·25% DVB: ● experimental, ref. 5; curve 2, calculated $\beta = 0·29$. 5·5% DVB: ■ experimental, ref. 5; curve 3, calculated $\beta = 0·12$. 10% DVB: △ experimental, ref. 2; ▼ experimental, ref. 5; curve 4, calculated $\beta = 0·19$. 26% DVB: × experimental, ref. 2; curve 5, calculated $\beta = 0·45$.

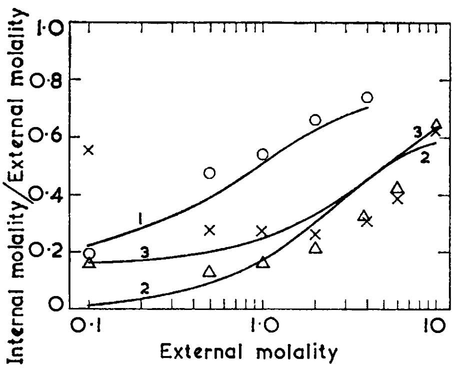


Fig. 3. Absorption of lithium chloride.

2% DVB: ○ experimental, ref. 3; curve 1, calculated $\beta = 0·17$. 10% DVB: △ experimental, ref. 3; curve 2, calculated $\beta = 0$. 26% DVB: × experimental, ref. 3; curve 3, calculated $\beta = 0·15$.

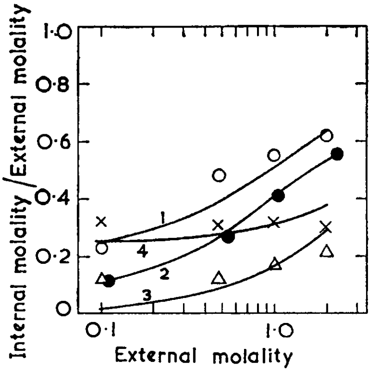


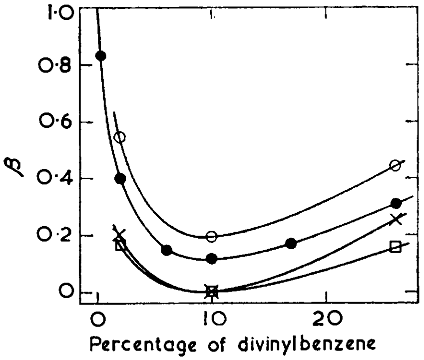
Fig. 4. Absorption of hydrochloric acid.

2% DVB: ○ experimental, ref. 2; curve 1, calculated $\beta = 0·20$. 2% DVB: ● experimental, ref. 4; curve 2, calculated $\beta = 0·06$. 10% DVB: △ experimental, ref. 2; curve 3, calculated $\beta = 0$. 26% DVB: × experimental, ref. 2; curve 4, calculated $\beta = 0·25$.

al.[4] do, however, agree with equation (18) for a 2% divinylbenzene resin. The disagreement between Gregor *et al.* and Pepper *et al.* for hydrochloric acid at all cross-linkages and between the former workers [3] and Davies and Yeoman [5] for potassium chloride at 2—2·5% crosslinking is far outside experimental error and further clarification is necessary. The results of Gregor *et al.*[1-3] with 26% divinylbenzene resins are also surprising in that they all show electrolyte absorptions greater than those obtained with some of the resins of lower crosslinking.

Gregor and his co-workers [1-3] also give some figures for absorption from external solutions less than 0·1M which suggest that equation (18) fails at external concentrations below 0·1M. Many of the experimental results in this region are difficult to understand, however, and it is possible that the data, and not the equation are at fault. Thus, the steady downward trend of $\bar{c}/c$ as the external concentration is decreased is suddenly reversed below 0·1M, and in some cases the value of $\bar{c}/c$ in the region of 0·01M is three or four times as great as that at about 0·1M. In one instance, that of 0·01M-lithium chloride in equilibrium with a 26% divinylbenzene resin,[3] the concentration of absorbed electrolyte is actually given as greater than the external concentration. Freeman [6] has suggested that this effect is due to absorption by impurities in the resin.

FIG. 5. β Values.
● NH_4Cl. ○ KCl. □ LiCl. × HCl.



In spite of the minor disagreements noted, and the extreme simplicity of the theoretical treatment being considered, equation (18) gives good agreement at all divinylbenzene contents and over a wide range of concentration. It is, perhaps, surprising that the use of a constant value of β at all concentrations should be satisfactory. To some extent this is due to the form of equation (18) which is such that at high concentrations the value calculated for $\bar{c}$ is not very sensitive to the value assigned to β. The value of β can therefore be chosen to match the experimental results at the lower concentrations.

In Fig. 5 the values of β which give the best agreement with the results of Gregor and his co-workers [1-3] are plotted against the percentage of divinylbenzene in the resin. The values for ammonium chloride, which are the most extensive, fall on a smooth curve. It is satisfying that extrapolation of this curve indicates that at zero crosslinking β is unity. The β values for the other electrolytes fall on curves of similar shape. The decrease of β in the range of crosslinking 0—10% is understandable. As crosslinking increases, the concentration of fixed charges increases so that the potential in the resin is higher and hence the fraction β of pore space which is considered mathematically as being at zero potential, must decrease. The rise of β above 10% crosslinking is due to the surprising fact, already mentioned, that higher electrolyte absorptions were found experimentally for the 26% divinylbenzene resin than for the 10% divinylbenzene material.

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