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A Lattice Model for Ion Exchangers

Monte Carlo Computations for Salt Sorption in a Simplified Model

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The thermodynamic properties of a simplified lattice model of an ion exchanger consisting of a number of independent subsystems are described. The free energies of the subsystems are computed by a Monte Carlo method, and the chemical potential of salt in the model is calculated statistically. The predicted limiting sorption of salt is found to agree with some general experimental observations.

The great variety of models which have been proposed for ion exchangers may tentatively be divided into two main types, the "quasi solution" (q.s.) models and the "structural electrostatic" (s.e.) models.[1] A preliminary report on a third type, a lattice model, is given in this paper.

Many properties of polyelectrolyte gels are not radically different from corresponding properties of concentrated electrolyte solutions. In the q.s. models this similarity is acknowledged by treating the gel as a solution in an elastic bag. The bag is permeable to the solvent, to counter ions and co-ions, but impermeable to the "fixed" ions. These correspond to the fixed ionic groups in the gel, and usually they are represented by uni- or poly-valent organic ions, approximating bits of the real crosslinked structure. The salt sorption can then be treated as a "Donnan equilibrium" between the external solution and the model solution. All reasonable q.s. models show the same limiting sorption behaviour in a dilute solution of a 1,1-electrolyte (or n,n-electrolyte)

$$\mathrm{m} = K_{\mathrm{A}}(a_{\pm}')^2 \tag{1}$$

where m is the molality of sorbed salt, $a_{\pm}'$ is the mean ionic activity in the external solution with molality m′ and K_{A} is a temperature-dependent coefficient which is determined mainly by the molality of fixed charges in the swollen resin.

In extremely high dilution

$$\mathrm{m} = K_{\mathrm{A}}(\mathrm{m}')^2 \tag{2}$$

which may be called an ideal Donnan sorption isotherm.

For some ion exchanger/salt solution systems the sorption behaviour have indeed been reported to be adequately represented by simple model solutions.[2] The majority of investigations have, however, led to isotherms which deviate significantly from eqn. (1) in dilute solutions.[3] In many cases the isotherm (for 1,1-electrolytes) may approximately be represented by [4]

$$m = K_B(a_\pm')^\alpha \tag{3}$$

with α in the range 1.4 to 1.7 for dilute solutions. The internal mean activity coefficient $\gamma_\pm$ as defined by

$$\gamma_\pm^2 m_+ m_- = (\gamma_\pm')(m')^2 \tag{4}$$

will then tend to zero with decreasing m'. (For a cation exchanger, $m_- = m$ and $m_+ = m + m_F$, where m_F is the molality of univalent fixed ions.)

In constructing the q.s. model it has not been taken into account that the bulky network of organic groups must to some extent restrict the possible configurations of ions and ionic groups relative to a free solution. Probably the most important consequence is that the fixed ions are approachable from one side only, and one gets an enhanced probability of ionic distributions of the type

matrix-X···C···C···X-matrix

where X represents a fixed ion and C a counter ion.

Different structural restrictions are accounted for in the various "structural electrostatic" models. This term is introduced here because the models referred to derive their special properties from the ionic distributions which are determined by the electrostatic forces and the postulated structural restrictions.

Swelling, selectivity, and to some extent sorption behaviour have been semiquantitatively described by models of this type. Even for severely simplified structures, however, the mathematical derivations become prohibitively complex. Hence it is necessary to introduce approximations with somewhat unpredictable effects, particularly on limiting laws like eqn. (2). The lattice model, as developed below, may be better suited for predicting the effect of various physical simplifications without introducing any serious mathematical approximations, at least in the case of limiting sorption behaviour.

THE LATTICE MODEL

The lattice model is an assembly of M non-interacting and distinguishable subsystems. The whole system may be pictured as a three-dimensional lattice. Each subsystem, or lattice site, is constructed as a simplified model of a microscopic part of a poly-electrolyte gel. This submodel must retain some essential structural properties of the complete resin network. It is assumed that counterions, co-ions, and neutral molecules may diffuse between a subsystem and its surroundings. The number of mobile ions and neutral molecules of different kinds in a subsystem may then be used to define different "subsystem states." If all subsystems are equal, each containing F univalent fixed ionic groups and each with a number s of possible states denoted by $j = 0,..., s-1$, then the canonical partition function for the whole assembly may be written as

$$Q = \sum_{g} M! \prod_{j=0}^{s-1} \frac{q_j^{K_j}}{K_j!} \tag{5}$$

Here q_j is the partition function for a subsystem in state No. j and K_j is the number of subsystems in this state for a given assembly configuration. The sum is to be taken over all possible assembly configurations $g = \{K_0, ..., K_{s-1}\}$ consistent with given total numbers N_i of mobile ions or neutral molecules of each kind and a constant number M of subsystems.

A SPECIAL CASE OF THE LATTICE MODEL

The present discussion will be restricted to a very simplified example of the general lattice model. First, the subsystem is pictured as a spherical cavity with a diameter approximately equal to the estimated pore diameter of a typical ion exchanger. F negative ionic groups are represented by a constant charge density on the cavity surface. The well-known "primitive model" is used for the internal solution of counter-ions and co-ions, *i.e.* these ions are represented by hard, charged spheres in a continuous medium. Both types of mobile ions are assumed to be uni-valent with equal radii. Secondly, only four states are considered important:

0. A "reference" state with F counter-ions and no co-ions.
1. A state with $F+1$ counter-ions and no co-ions.
2. A state with F counter-ions and one co-ion.
3. A state with $F+1$ counter-ions and one co-ion.

Thus relative to state 0, states 1, 2, and 3 have an extra cation, anion, and pair of ions, respectively.

The main purpose of the simplified model is the prediction of limiting sorption behaviour, in the present case for 1,1-electrolytes. Some approximations which are implied by the simplifying assumptions must be discussed from this viewpoint.

Constant subsystem dimensions imply constant swelling. Experimentally this is always observed in sufficiently dilute solutions, but the upper concentration limit for effectively complete swelling depends on the rigidity of the resin matrix.

Adoption of the "primitive electrolyte model" implies that the thermodynamic properties of the system are determined essentially by the available ionic configurations. Thus, the number of solvent molecules is not an explicit model parameter and must if necessary be introduced by a separate assumption.

Finally, the main reason for restricting the allowed subsystem states to only four ionic combinations is the ensuing simplification of the statistical formulae which permits a complete numerical characterization of the model. At low concentrations, the most probable ionic combinations omitted in the specialized model would be those with a small deficit of counter-ions relative to the reference state. Preliminary calculations indicate, however, that inclusion of these states would not have any important effects on the predicted sorption behaviour.

Utilizing eqn. (5), the partition function for the specialized lattice model may now be written as:

$$Q(M,N,T) = \sum_{g} M! \frac{q_0^{K_0} q_1^{K_1} q_2^{K_2} q_3^{K_3}}{K_0! K_1! K_2! K_3!} = \sum_{g} Q_g \tag{6}$$

The sum is to be taken over all configurations $g = \{K_0, K_1, K_2, K_3\}$ satisfying the restrictions

$$K_0 + K_1 + K_2 + K_3 = M \tag{7}$$

$$K_1 = K_2 \tag{8}$$

$$K_2 + K_3 = N \tag{9}$$

Here, eqn. (8) is the condition of electroneutrality for the whole assembly, while N in eqn. (9) is the total number of sorbed "salt molecules" in the lattice.

The largest term Q_{g*} in the expression for Q may in the thermodynamic limit, $M \to \infty$, be found from

$$\left(\frac{\partial \ln Q_g}{\partial K_1}\right)_{M,N,T} = 0 \tag{10}$$

because the eqns. (7)–(9) define three of the K's in terms of the fourth, and this may be chosen as K_1. When Q_g from eqn. (6) is inserted in eqn. (10) and eqn. (10) is solved, one obtains an "equilibrium equation":

$$\frac{K_1 K_2}{K_0 K_3} = \frac{q_1 q_2}{q_0 q_3} \overset{\text{def}}{=} b \tag{11}$$

This equation together with eqns. (7)–(9) define the configuration $g^* = \{K_0^*, K_1^*, K_2^*, K_3^*\}$ which maximize Q_g.

When solved, these equations yield:

$$K_1^* = K_2^* = \frac{-M + \sqrt{M^2 + 4(b^{-1}-1)N(M-N)}}{2(b^{-1}-1)} \tag{12}$$

$$K_0^* = M - N - K_1^* \tag{13}$$

$$K_3^* = N - K_1^* \tag{14}$$

These values may be inserted in the expression for Q_g (eqn. 6), and all thermodynamic properties of the lattice model can then be derived from the corresponding Helmholtz free energy function

$$A = -kT \ln Q_{g*}(M,N,T) \tag{15}$$

where Q_{g*} has been substituted for the whole sum in eqn. (6). The equilibrium salt sorption, for instance, is determined by

$$\mu(\mathrm{m}) = \left(\frac{\partial \mathrm{A}}{\partial N}\right)_{M,T} = \mu'(\mathrm{m}') \tag{16}$$

where $\mu(\mathrm{m})$ is the chemical potential of salt in the model at molality m and $\mu'(\mathrm{m}')$ is the corresponding potential in the external solution.*

The derivative in eqn. (16) may conveniently be calculated from an expression derived from eqn. (6):

$$\ln Q_{g*} = M \ln M - \sum_{i=0}^{3} K_i^*(\ln q_i - \ln K_i^*) \tag{17}$$

by using $K_i^*(M,N)$, defined by eqns. (12)–(14), as parameters. This leads to the simple relation:

$$\mu/kT = \ln \frac{{q_0}^2}{q_1 q_2} + \ln \frac{K_1^* K_2}{(K_0^*)^2} \tag{18}$$

which may be shown to be a special case of a formula valid for more general lattice models.

When the expressions for K_i^* from eqns. (12) and (13) are inserted in eqn. (18) together with the abbrevations

$$\frac{q_1 q_2}{{q_0}^2} = w^2 \tag{19}$$

$$2(b^{-1} - 1) = p(T) \tag{20}$$

$$N/M = \theta \tag{21}$$

one gets

$$\mu(\theta,T) = -2kT \ln w + 2kT \ln \frac{2\theta - 1 + \sqrt{1 + 2p\theta(1-\theta)}}{(p+2)(1-\theta)} \tag{22}$$

This equation defines μ as a function of the internal salt concentration because the latter is related to θ by

$$c = \frac{\theta}{N_A v} \tag{23}$$

Here, N_A is Avogadro's constant and v is the subsystem volume $v = \pi d^3/6$. In the following, c rather than m will be used as concentration variable, because c is more directly related to the statistical formulae. The internal salt

* $\mu(\mathrm{m})$ as defined by eqn. (16) does not correspond strictly to the ordinary chemical potential of salt in a real gel as defined by

$$\mu_s \overset{\text{def}}{=} \left(\frac{\partial A_{gel}}{\partial N}\right)_{V,T,N_r,N_w} \tag{16a}$$

where both the amount of resin (N_r) and the amount of water (N_w) are kept constant, but rather to

$$\mu_{s,\varepsilon} \overset{\text{def}}{=} \left(\frac{\partial A_{gel}}{\partial N}\right)_{V,T,N_r,\varepsilon} \tag{16b}$$

where ε is some measurable dielectric coefficient of the gel. In the lattice model, ε is the effective DE-coefficient of the medium between two ions. The physical interpretation of this quantity in a real system is somewhat ambiguous, but for all reasonable interpretations the difference between (16b) and (16a) will be insignificant for the present purpose. μ as defined by eqn. (16) may thus be regarded as corresponding to the ordinary potential defined by eqn. (16a).

molality m is not explicitly defined by the model parameters but is related to c by

$$\mathrm{m} = c/\varrho_{\mathrm{w}} \tag{24}$$

where ϱ_{w} is the mean density of water in the subsystems (pores). At low concentrations, ϱ_{w} is a constant, and thus will not alter the form of the limiting sorption behaviour.

For sufficiently small values of θ, eqn. (22) may be rewritten by expanding the square root in a power series and putting $-2kT \ln w = \eta(T)$.

$$\mu = \eta(T) + 2kT \ln \frac{\theta}{1-\theta}\left(1 - \frac{p}{2}\theta + \frac{p^2}{2}\theta^2 + \cdots\right) \tag{25}$$

Numerical evaluation of the parameter p from realistic model properties indicates that this expansion is valid up to θ-values which correspond to high internal concentrations. In a hypothetical ideal case with "indifferent internal equilibrium", b in eqn. (11) has the value 1, and $p = 0$ (eqn. 20). Then eqn. (25) is reduced to

$$\mu = \mu_{\mathrm{ideal}} = \eta(T) + 2kT \ln \frac{\theta}{1-\theta} \tag{26}$$

which differs from a Langmuir isotherm only by the factor 2.

In the general, non-ideal case, the equilibrium salt sorption is determined by eqn. (16). As quantum effects are neglected in the primitive model, only the configurational parts of chemical potentials, partition functions *etc.* are relevant. The relevant expression for the chemical potential of salt in the external solution is then

$$\mu' = 2kT \ln \frac{N'}{V'} y_{\pm}' \tag{27}$$

or

$$\mu' = 2kT \ln N_{\mathrm{A}} a_{\pm}' \tag{28}$$

where $a_{\pm}' = c' y_{\pm}'$ now is the mean ionic activity on a molarity basis.

Eqns. (22) and (28) may be inserted in eqn. (16), giving an explicit sorption equation

$$\frac{2\theta - 1 + \sqrt{1 + 2p\theta(1-\theta)}}{(p+2)(1-\theta)} = N_{\mathrm{A}} w a_{\pm}' \tag{29}$$

Expansion of the left-hand expression in a power series, followed by inversion and introduction of c from eqn. (23) finally gives an explicit expression for the internal salt concentration

$$c = \frac{w}{v} a_{\pm}' - \frac{w}{v}\left(1 - \frac{p}{2}\right) N_{\mathrm{A}} w (a_{\pm}')^2 + \frac{w}{v}\, 3\left(1 - \frac{p}{2}\right) N_{\mathrm{A}}^2 w^2 (a_{\pm}')^3 + \cdots \tag{30}$$

This equation will be discussed in connection with the evaluation of its parameters.

THE CHARGING PROCESS

The thermodynamic properties of the present model are determined by the partition functions q_i through their combinations in parameters like w and p. From the expressions for these parameters it may be seen that only ratios between partition functions are required, corresponding to differences between free energies $A_i = -kT \ln q_i$. For the present model it was found feasible to compute these differences by numerical evaluation of a "Güntelberg" charging process.

In this process, a system is brought from a state "i" to a state "j" with one more ion by introducing the extra ion in two steps:

1. An "uncharged ion" is added in the form of a hard sphere (with ε equal to the surrounding medium).
2. This ion is given full charge by increasing a charging parameter λ from 0 to 1 in small steps.

If A_i and q_i are interpreted as configurational properties, the free energy of a subsystem with a partially charged extra ion can be expressed by

$$A_j(\lambda) = -kT \ln q_j(\lambda) = -kT \ln f_j \int_v \cdots \int e^{-U(\lambda)/kT} \, d\vec{r}_1 \cdots d\vec{r}_{L_j} \tag{31}$$

Here v is the volume of the subsystem, $U(\lambda)$ is the potential energy of the ionic configuration $\{\vec{r}_1, \cdots, \vec{r}_{L_j}\}$, and L_j is the total number of mobile ions in a subsystem in state "j". The statistical factor f_j which accounts for the indistinguishability of ions of the same type is determined by the number L_{jk} of ions of each type "k":

$$f_j = 1/\prod_k L_{jk}! \tag{32}$$

For simplicity this factor has been omitted in the following equations, but will be reintroduced in the final numerical evaluations.

The change in free energy in the two steps indicated above may now be discussed separately:

$$A_j - A_i = [A_j(\lambda=0) - A_i] + [A_j(\lambda=1) - A_j(\lambda=0)] \tag{33}$$

The first bracket corresponds to the loss of free energy when an uncharged particle is introduced into a cavity in state "i". It may be interpreted by means of the "free volume" for such a particle in state "i":

$$(\Delta A_j)_1 = A_j(\lambda=0) - A_i \overset{\text{def}}{=} -kT \ln V_j^f \tag{34}$$

For a dimensionless particle, $V_j^f = V_j^0$ would be that part of the cavity volume which is not occupied by ions. For a hard, uncharged sphere with the same diameter d as the ions, V_j^f may be approximated by

$$V_j^f = v - (L_j - 1)\frac{4\pi}{3} d^2 \tag{35}$$

if the cavity is not too crowded by free ions and these do not form stable aggregates.*

The second bracket in eqn. (33) corresponds to an electrostatic charging process:

$$(\Delta A_j)_2 = A_j(\lambda=1) - A(\lambda=0) = \int_0^1 \frac{\partial A_j(\lambda)}{\partial \lambda}\,\mathrm{d}\lambda \tag{36}$$

Eqn. (31) gives

$$\frac{\partial A_j(\lambda)}{\partial \lambda} = \frac{\int \cdots \int_v \frac{\partial U(\lambda)}{\partial \lambda} \mathrm{e}^{-U(\lambda)/kT} (\mathrm{d}\vec{r})^L}{q_j'} = \left\langle \frac{U(\lambda)}{\partial \lambda} \right\rangle \tag{37}$$

where the brackets indicate an ensemble average and the index in L_j has been dropped. The expression above has a simple interpretation because the energy $U(\lambda)$ is a sum of ionic pair potentials:

$$U(\lambda) = \sum_{i<k<L} u_{ik} + \sum_{i=1}^{L-1} u_{iL} \tag{38}$$

Only the last sum, which involves the extra ion with number L, contains the charging parameter λ, and has the form

$$u(\lambda) = \sum_{i=1}^{L-1} \frac{z_i z_L \mathrm{e}^2 \lambda}{4\pi\varepsilon r_{iL}} \tag{39}$$

Hence

$$\frac{\partial U(\lambda)}{\partial \lambda} = \frac{u(\lambda)}{\lambda} \tag{40}$$

and eqn. (36) becomes

$$(\Delta A_j)_2 = \int_0^1 u(\lambda)\,\frac{\mathrm{d}\lambda}{\lambda} \tag{41}$$

where $u(\lambda)$ is that part of the potential energy which involves the extra, partially charged ion. Eqn. (41) is analogous to the wellknown expression by Güntelberg,[5] but has a different interpretation because of the limited number of ions in the present case.

Eqns. (34) and (41) may be generalized to subsystems differing in ionic content by two or more ions. The extra energy $u(\lambda)$ will then be a sum of expressions similar to eqn. (39), one for each extra ion, and V_j^f will be a product of free volumes for each extra uncharged sphere.

MONTE CARLO PROCEDURE

For the present model it was found expedient to perform all charging processes from the reference state, *i.e.* from state 0 to states 1, 2, and 3, using the generalized versions of eqns. (34) and (41) for state 3.

*Eqn. (31) or even $V^f = v$ should be sufficiently accurate with the present model parameters and for the present purpose. If necessary, however, V^f/V_0^0 may be computed numerically in a fashion similar to that for step 2 by increasing the diameter d gradually from zero to its final value.

In each case the average extra energy $u(\lambda)$ was computed for small increments in λ by Metropolis's Monte Carlo procedure.[6] This method has been widely used in investigations on models for various thermodynamic systems.[7] Successive configurations of the given model system are generated on a computer in such a pseudo-random manner as to constitute a Markov chain with a Boltzmann limiting distribution of configurations. The average ensemble value of a configuration property such as $u(\lambda)$ may then be evaluated by arithmetic averaging over the generated chain of configurations.

The system to be considered in the present case is a cavity with $F+1$ or $F+2$ mobile ions. Such a system is particularly well suited for the Monte Carlo evaluation because the small number of free particles makes artificial boundary conditions unnecessary.

In the start-configuration all ions are given random, non-overlapping positions. Successive configurations are then generated in the usual way [8] by random displacement of one ion at a time, taking the mobile ions in a given sequence and accepting each new, tentative configuration with probability $\exp(-\Delta U/kT)$. It was found unprofitable to limit the extent of each attempted move, *i.e.* the new position was chosen randomly within the cavity. Computations on systems with higher charge on the extra ions, however, gave increasingly poor accuracy, confirming the view that limits on particle displacements are essential in systems with strong interactions or high particle density.

Pseudo-random numbers for new coordinates and for stochastic selection are generated by a standard residue method.[9] Current values of U and $u(\lambda)$ for each new configuration are updated and accumulated by computing only those pair potentials which involve the displaced ion. This procedure saves computing time, and at given intervals, U and $u(\lambda)$ are computed *ab initio* in order to avoid accumulated errors in the updating. The generated chain of configurations is divided into equal parts or fragments, and averages for U and $u(\lambda)$ are computed for each fragment. The behaviour of these averages indicates the duration of the initial relaxation period, and total averages are then taken over the remaining equilibrium period.

The statistical independence of the partial averages can be checked by varying the size of the chain fragments, and the uncertainty in the total averages are then estimated from the mean deviation of the partial averages.

RESULTS AND DISCUSSION

The model properties were chosen to simulate a typical strong-acid ion exchange resin. Thus, the subsystem diameter D, corresponding to a mean pore diameter, was put equal to 30 Å. The number F of fixed ionic groups in a cavity was taken to be 12, giving a fixed-ion concentration of 1.4 mol/l in terms of pore-liquid volume. This corresponds roughly to a fully swelled, monosulfonated styrene-type cation-exchanger with 4 % DVB crosslinking. All ionic diameters d were put equal to 3.2 Å, which is a fairly typical Debye-Hückel diameter for simple 1,1-electrolytes, *e.g.* KCl. The temperature T was chosen as 298.15 K and the relative dielectric coefficient $\varepsilon_{rel} = \varepsilon/\varepsilon_0$ as 78.3.

The effects on the model behaviour of ε and T and the size of the common ionic charge e are not independent, however, but are connected through their effects on the "Bjerrum length"

$$r_B = \frac{e^2}{4\pi\varepsilon kT} \tag{42}$$

This connection arises because an explicit expression for $\langle u(\lambda)\rangle$ has the functional form

$$\langle u(\lambda)\rangle = kT\, f\,(D/r_B, d/r_B) \tag{43}$$

In the present case, e is simply the positive electronic charge, and hence is regarded as a constant.

For each of the three charging processes, $\langle u(\lambda)\rangle$ was calculated for $\lambda = 0.1$, $0.2, \cdots, 1.0$. Thirty Markov chains, each comprising 10 920 or 11 740 configurations, were generated for this purpose, using a simple Fortran program and an IBM 360/50H computer.

The initial relaxation period was roughly estimated to 40 configurations, corresponding to three or four moves per ion, but in the calculation of total averages, the first 520 or 560 configurations were removed.

The charging processes which yield $(\Delta A_j)_2$ according to eqn. (41) were evaluated by numerical integration. All relevant results of calculations are given in Table 1, and a graphic illustration of the three charging processes is shown in Fig. 1.

Table 1. Calculated parameters for lattice model.

I. Mean "extra potentials", $\langle u_j(\lambda)\rangle/\lambda = \psi_j$ (eqn. 39).

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
ψ_1/kT	1.21	1.09	1.05	0.86	0.85	0.76	0.80	0.68	0.60	0.51
$-\psi_2/kT$	1.39	1.38	1.52	1.57	1.70	1.72	1.92	2.00	2.03	2.19
$-\psi_3/kT$	0.25	0.59	0.89	1.14	1.41	1.78	2.03	2.27	2.56	2.91

II. Free energies in charging process, $(\Delta A_j)_2$ (eqn. 36).

j	1	2	3
$(\Delta A_j)_2/kT$	0.877 ± 0.033	-1.693 ± 0.029	-1.437 ± 0.023

(With estimated probable errors).

III. Characteristic parameters.

Volume of cavity	$v = 14\,140$ Å^3	
Free volume	$V_1^* = 12\,490$ Å^3	(eqn. 35)
"Equilibrium constant"	$b = 0.516$	(eqn. 11)
Sorption parameter	$p = 1.887$	(eqn. 20)
Sorption parameter	$w = 5257$ Å^3	(eqn. 19)

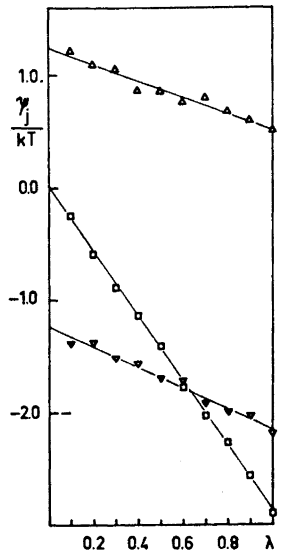

Fig. 1. Mean potentials $\psi_j = \langle u_j(\lambda) \rangle / \lambda$ on extra ions with fractional charge λ in a spherical cavity with twelve univalent, mobile cations. △, extra cation. ▽, extra anion. □, pair of extra cation and anion.

As the behaviour of the primitive model for small ionic systems may be of some general interest, a comment on the variation of $\partial A_j/\partial\lambda = \langle u(\lambda) \rangle / \lambda$ with λ will be made here.

$\partial A_j/\partial\lambda$, which can be interpreted as a mean electrostatic potential at the position of the extra ion(s), is in each case nearly a linear function of λ. This indicates that the mean potential at the position of each extra ion, caused by the remaining mobile ions, is proportional to the charge on this extra ion. (The fixed ions in the present model make a constant contribution.) This is in accordance with a fundamental assumption in the Debye-Hückel theory, but the linear dependence must break down at higher ionic charges. Simple electrostatic considerations indicate that for high λ-values $\partial A_1/\partial\lambda$, $\partial A_2/\partial\lambda$ and $(1/\lambda)\partial A_3/\partial\lambda$ must all approach constant values because the highly charged "extra" ions will immobilize the other ions. Such trends were indeed confirmed by rough Monte Carlo-computations, but as explained above, the chain convergence of $\langle u(\lambda) \rangle$ then became slower as λ is increased to high values.

An internal check on the linear functions in Fig. 1 is furnished by a demand that the functions $(1/\lambda)\, u_1(\lambda)$ and $(1/\lambda)\, u_2(\lambda)$ can be made co-linear by changing the sign on λ in the last function. This is necessary because the dis-charging of one anion and the charging of one cation can be performed by a single charging parameter running from -1 to $+1$. A further check is given by the physical interpretation of $(1/\lambda)\ \langle u_3(\lambda) \rangle$ which requires this function to go to zero with λ, as is indeed the case.

Finally, V_j^f is calculated from eqn. (35) (generalized in the case of V_3^f) which gives

$$V_1^f = V_2^f \simeq (V_3^f)^{\frac{1}{3}} \simeq v - 12\,\frac{4\pi}{3}\,d^3 \tag{44}$$

When these values are used, and the correct statistical factors from eqn. (32) are introduced, the following expressions for the characteristic parameters b and w are obtained:

$$b = e^{[(\Delta A_3)_2 - (\Delta A_1)_2 - \Delta A_2)_2]/kT} \tag{45}$$

$$w = \frac{V_1^f}{\sqrt{13}} e^{[-(\Delta A_1)_2 - (A_2)_2]/2kT} \tag{46}$$

Numerical values for w and p are thus obtained (Table 1) and give numerical values for the predicted salt sorption:

$$c = 0.37 a_\pm' - 0.072 \text{ l mol}^{-1} (a_\pm')^2 + 0.68 \text{ l}^2 \text{ mol}^{-2} (a_\pm')^3 + \cdots \tag{47}$$

For sufficiently small concentrations a limiting sorption equation is obtained:

$$\text{m} = K\text{m}' \tag{48}$$

where K may be estimated from eqns. (24) and (47) as $K \simeq 0.4$.

The limiting sorption behaviour of the present model is seen to deviate from both ideal Donnan sorption (eqn. 2) and the empirical eqn. (3).

It does, however, agree with the general observation for "normal" ion exchangers, that for sorption from very dilute solutions, the experimental molality of sorbed salt is of the same order as the external molality.[3] A decrease in the sorption coefficient m'/m at somewhat larger concentrations, corresponding to a negative second coefficient in eqn. (47), has also been reported.[10]

The lattice model seems to merit further investigation. Two extensions of the present, specialized model suggest themselves. A larger number of subsystem states may be included in the statistical treatment, thus removing the restriction to low external concentrations. Secondly, different kinds of subsystems may be tried by introducing structural features which are important for selecting between different counter-ions. Synthetic zeolites with known structures may be a promising field of application for an extended lattice model.

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