A Theoretical Treatment of Activity Coefficients in Resin Phase

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Introduction

The phenomena of ionic exchange have been studied from the statistical point of view by several investigators. Hamada[1] and Davis[2] independently applied a statistical model to the ion exchange equilibria. Hamada derived the equation of the simple mass action type by assuming a lattice model as ion exchange equilibria, while Davis dealt with ion exchange equilibria, assuming a regular model for ionic exchange, by a modification of a statistical theory of a localized monolayers derived from Fowler and Guggenheim[3]. The latter author first applied the theory to an uni-uni-valent exchange and showed that the resultant equation is of the simple mass action type, ignoring the interaction energy between ion pairs in the exchanger phase. Afterwards he studied two types of irregular models of ionic exchange systems. Seiyama, Sakaki and Nagamatsu[4] developed the statistical theory of Hamada and Davis, by applying "a quasi-chemical method" of Guggenheim[5], and they discussed in detail the ion exchange equilibria involving uni-uni-valent and uni-di-valent exchange.

According to the experimental results of Argersinger, Davidson[6] as well as the present authors[7], it can be expected that the activity coefficients in any exchange ratio will be affected markedly by the interaction energy of each ion pair in the solid phase. Generally the interaction of each pair presumably involves the following forces: ion-dipole, van der Waals and covalent bond forces as short range forces, and electrostatic forces (Coulomb force) as long range forces.

Accordingly ion exchange phenomena should be investigated under consideration of all these forces. Above all, the anomaly in the activity coefficients in the resin phase will principally depend on the interaction forces described above.

Davis[2] and Hamada[1] ignored the interaction energy between ion pairs in the exchanger phase, while Seiyama, Sakai and Nagamatsu[4] gave a statistical explanation of the ion exchange equilibrium constants under consideration of the interaction energy between ion pairs in the resin phase. But they did not treat the activities in the exchanger phase extensively. The authors

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[3] R.H. Fowler and E.A. Guggenheim, "Statistical Thermodynamics" (1938).

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[5] E.A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948).

[6] W.J. Argersinger, Jr. and A.W. Davidson, *J. Phys. Chem.* **56**, 92 (1952).

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present here a theoretical treatment under several assumptions, in which it will be shown that the energy of mutual ionic-interaction has an important significance in the activity determination in the solid phase.

Theoretical

The following discussions are based on Guggenheim's theory which deals with "A Generalization of the Quasi-Chemical Method". In this treatment, the following conditions are assumed.

1) Ionic exchange systems have no empty sites.

2) A polyvalent ion will occupy a set of r adjacent sites, r being the number of sites occupied by an ion.

3) We may neglect interaction between pairs of ions that are not nearest neighbours, so that the total interaction energy of the ions can be expressed as the sum of contributions from each pair of nearest neighbours.

4) We treat ion exchange resins as slightly swollen gels so that the volume change of the system due to the exchange process is small.

5) It is assumed that the electrolyte solution involving the exchangeable ions is able to diffuse freely through the network of the exchange resin, so that there is no mechanical resistance associated with ionic size in the exchange process.

6) We also considered the case where the ionic concentration of the electrolyte solution in the exchange system is comparatively small, so that the effect of the presence of the free electrolytes (non-fixed electrolytes at the exchanging lattice points) in the resin phase at equilibrium will be small.

Let us consider a lattice model which has regular N sites as the ion exchange resin phase and in which one site has one negative charge.

Let N_A : Number of ions of any type of A.
r_A : Number of sites occupied by one ion of type A.
z : Number of sites which are nearest neighbours of any given site in regular array.
q_A : A function of z and r_A which determines the frequency with which a valence element of an ion of type A will occupy a site adjacent to another occupied site.

In a specific state having any exchange ratio, we have

$$N = r_A N_A + r_B N_B$$

Parameters q_A, q_B are defined by

$$z(r_A - q_A) = 2(r_A - 1)$$

$$z(r_B - q_B) = 2(r_B - 1)$$

zq_A is the so-called corrected co-ordination number, i.e., the number of sites, neighbours of the r_A sites occupied by an ion A, excluding those neighbours of each site occupied by the next element of the same ion. The physical meaning of q_B is similar to q_A. It is assumed that in any given configurations of the system, inter-ionic (inter-ionic of hydrogen ion and metallic ions) potential energy consists of a sum of the following terms ϕ_{AA}, ϕ_{BB} and ϕ_{AB}. ϕ_{AA}, ϕ_{BB} and ϕ_{AB} denote the contribution to the internal energy by a pair of sites occupied both by A ions, botn by B ions, and one occupied by A and the other occupied by B respectively.

Let the number of pairs of neighbouring sites in which one site is occupied by an ion A and the other by an ion B be denoted by zX. The partition function Q of the system is written in the form

$$Q = \sum_x g(N_A, N_B, X) \exp(zX\phi/2kT),$$

where $\phi = \phi_{AA} + \phi_{BB} - 2\phi_{AB}$ and $g(N_A, N_B, X)$ denotes the number of distinguishable configurations of all the N_A ions of A and N_B ions of B for a given value of X. This combinatory factor $g(N_A, N_B, X)$ is expressible as an explicit function of N_A, N_B, X, involving z, r_A, r_B, q_A, q_B as parameters. In a real exchange system, each ion in an exchangeable point (lattice point) will exist in a hydrated state according to the size of the framework and the kinds of the exchangeable ions.

The total free energy F' can be represented by the following equation,

$$F' = N_A \mu_A^{0'} + N_B \mu_B^{0'} + \Delta F_1 + \Delta F_2,$$

where ΔF_1 and ΔF_2 are the free energies of mixing, which contain the configurational term and the term due to the interaction energy respectively.

The terms of $\mu_A^{0'}$ and $\mu_B^{0'}$ in the total free energy F' should be expressed by the following equations.

$$\mu_A^{0'} = -\frac{q_A z}{2}\phi_{AA} + u_A^0 - kT \log v_{f_A} - kT \times \log\left(\frac{2\pi m_A kT}{h^2}\right)^{3/2}$$

$$\mu_B^{0'} = -\frac{q_B z}{2}\phi_{BB} + u_B^0 - kT \log v_{f_B} - kT \times \log\left(\frac{2\pi m_B kT}{h^2}\right)^{3/2}$$

In these expressions, u_A^0 and u_B^0 are the potential energies of ions A and B in an equilibrium state respectively. v_{f_A}, v_{f_B} are the free volumes and m_A, m_B the masses of the respective ions in the exchangeable point at constant temperature. If we consider free energy due to configuration only, the free energy F can be expressed by the following equation,

$$F=N_A\mu_A^0+N_B\mu_B^0+\Delta F_1+\Delta F_2=kT\log Q.$$

In this expression, μ_A^0 and μ_B^0 are respectively the chemical potentials of each pure resin. The quantity which has the most important meaning in the problem treated here is free energy of mixing $\Delta F=\Delta F_1+\Delta F_2$. If we use Flory's approximation for ΔF_1,

$$\Delta F_1/kT=\left(1-\frac{1}{2}z\right)r_AN_A\log r_AN_A$$
$$+\left(1-\frac{1}{2}z\right)r_BN_B\log r_BN_B-\left(1-\frac{1}{2}z\right)$$
$$\times(r_AN_A+r_BN_B)\log(r_AN_A+r_BN_B)$$
$$+\frac{1}{2}z\Big\{q_AN_A\log q_AN_A+q_BN_B\log q_BN_B$$
$$-(q_AN_A+q_BN_B)\log(q_AN_A+q_BN_B)\Big\}.$$

ΔF_2 which contains the term of the interaction energy can be expressed as,

$$\Delta F_2/kT=\frac{1}{2}z(q_AN_A+q_BN_B)\Big\{\theta\log\frac{\beta-1+2\theta}{\theta(\beta+1)}$$
$$+(1-\theta)\log\frac{\beta+1-2\theta}{(1-\theta)(\beta+1)}\Big\}.$$

In this expression β and θ are represented as follows,

$$\beta=\left\{(1-2\theta)^2+4\theta(1-\theta)e^{\frac{\phi}{kT}}\right\}^{1/2}$$

$$\theta=\frac{q_AN_A}{q_AN_A+q_BN_B},\quad 1-\theta=\frac{q_BN_B}{q_AN_A+q_BN_B}.$$

Therefore by using the above equations the chemical potentials of ions A and B are given as the differential forms of the corresponding free energies:

$$\mu_A=\frac{\delta F}{\delta N_A}=\mu_A^0+kT\Big\{(1-\frac{1}{2}z)r_A$$
$$\log\frac{r_AN_A}{r_AN_A+r_BN_B}+\frac{1}{2}zq_A\log\frac{q_AN_A}{q_AN_A+q_AN_B}$$
$$+\frac{1}{2}zq_A\log\frac{\beta-1+2\theta}{(\beta+1)\theta}\Big\}$$

$$\mu_B=\frac{\delta F}{\delta N_B}=\mu_B^0+kT\Big\{(1-\frac{1}{2}z)r_B\log$$
$$\times\frac{r_BN_B}{r_AN_A+q_BN_B}+\frac{1}{2}zq_B\log\frac{q_BN_B}{q_AN_A+q_BN_B}$$
$$+\frac{1}{2}zq_B\log\frac{\beta+1-2\theta}{(\beta+1)(1-\theta)}\Big\}$$

The relation between the activity and the chemical potential is expressed by the following equations,

$$\mu_A=\mu_A^0+kT\log a_A$$
$$\mu_B=\mu_B^0+kT\log a_B$$

where a_A, a_B are activities of A and B ions in the resin phase respectively, therefore the activity coefficients are given by the following expressions,

$$\frac{N_A}{N_A+N_B}f_A=e^{\frac{\mu_A-\mu_A^0}{kT}}$$

$$\frac{N_B}{N_A+N_B}f_B=e^{\frac{\mu_B-\mu_B^0}{kT}}$$

Then we can calculate the activity coefficients in the ion exchange resin phase from the above equations. The results obtained by calculation using the above equations are shown in Figs. 1, 2 and 3.

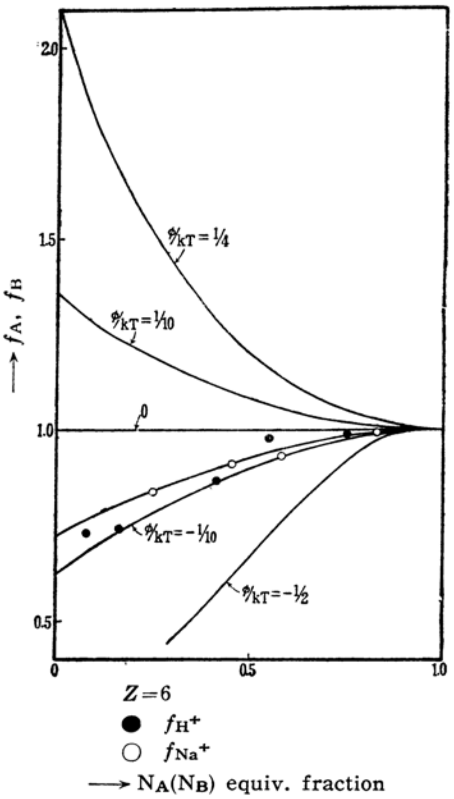
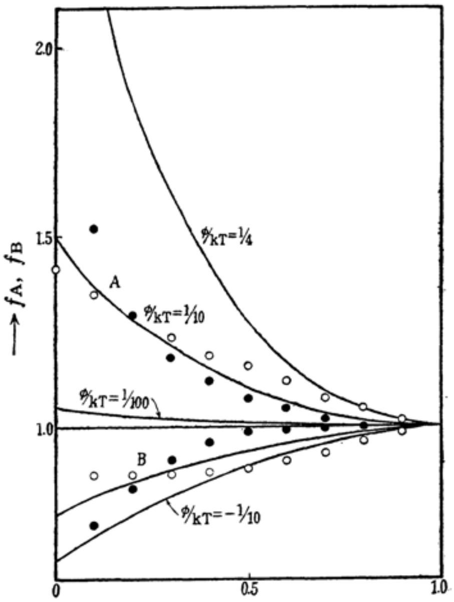


Fig. 1. Relationship between activity coefficients and exchange ratios in the resin phase of uni-uni-valent exchange system. (The dots show the experimental values).



$Z=8$
● f_{H^+}
○ f_{Na^+}, f_{Ag^+}
→ $N_A(N_B)$ equiv. fraction

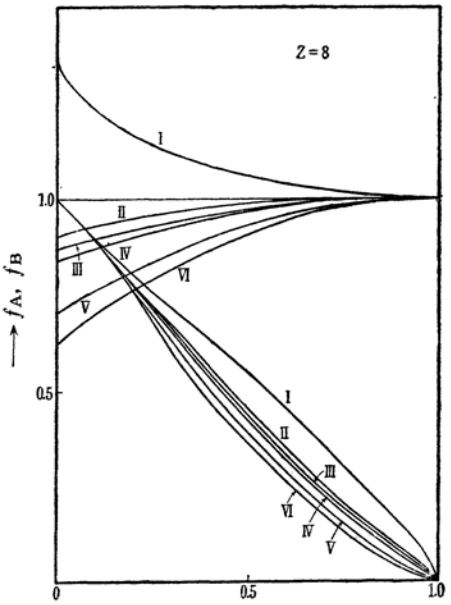
Fig. 2. Relationship between activity coefficients and exchange ratios in the resin phase of uni-uni-valent exchange system. (The dots show the experimental values of Argersinger and Davidson).

Experimental

A film of carboxymethylcellulose (ion exchange capacity 3.29 meq./g. for dry sample) was used as the cation exchanger. The film (acid form), which was about $2.5\times2.5\ \text{cm}^2$ and about10 μ thick, was used as the sample. Equilibrium studies of the H–Na, H–NH_4 and H–Ca exchanges were made while maintaining Na, NH_4 and Ca concentrations constant at various hydrogen ion concentrations in the solution phase.

In each exchange experiment, the sample was placed in a ground glass stopperd flask in contact with an aqueous solution of the appropiate salts of the cations. The volume of the electrolyte solution was 100 ml. Initial and equilibrium concentrations of hydrogen ions were determined by the glass electrode in the solution phase. The films, which reached equilibrium, were washed with sufficient 70% alcoholic solution in the uni-uni-valent case (H–Na exchange), and with distilled water in the uni-di-valent case (H–Ca exchange). The equilibrium temperature was maintained at 15±1°C. The infrared spectra of the exchanger film were measured with a double beam system spectrometer of Baird Co. with a rock salt prism*.

As described in the previous paper⁷⁾, several precautions were necessary to minimize errer in measurements of the infrared spectra. The apparent equilibrium constants were calculated by the following equation, using the spectrophotometric method,



→ N_A equiv. fraction

Fig. 3. Relationship between activity coefficients and exchange ratios in the resin phase of uni-di-valent system.

I. .... $\dfrac{\phi}{kT}=1/10$
II. I/100
III..0
IV. ....–1/100
V..–2/100
VI. ....–1/10

$$pKa=r_B\log\varepsilon_a-r_A\log k\varepsilon_b-(r_B-r_A)\log(\varepsilon_a+k\varepsilon_b)$$
$$+r_A\log B^{+r_B}-r_B\log A^{+r_A}+\log\frac{\gamma_B{}^{r_A}}{\gamma_A{}^{r_B}}$$

where A and B are the concentrations of the two exchangeable ions respectively, r_A is the valence of the A ion, γ_A is the activity coefficient of the A ion in the electrolyte solution, ε_a is the absorption intensity of carbonyl band (5.6 μ or 6.3 μ) of carboxyradical fixing the A ion in an exchanger, when the C–H stretching vibration in 3.4 μ was selected as the reference band, and k is a constant. In the calculation of pKa, the mean activity coefficients of the electrolyte from "Lewis, Table" were used.

Evaluation of the Activity Coefficients

For an ion exchange system we could consider the true equilibrium constant K as

$$K=Ka\frac{f_B{}^{r_A}}{f_A{}^{r_B}}$$

In the above equation, f expresses the activity coefficient of resin component on mole fraction basis, with pure resin as the standard state. The following equation is given from the Gibbs-Duhem relation,

$$m_A\mathrm{d}\mu_A+m_B\mathrm{d}\mu_B=(n_A/r_A)\mathrm{d}\mu_A+(n_B/r_B)\mathrm{d}\mu_B=0,$$

where m and n represent a mole fraction and an equivalent fraction of the respective ion in the solid exchanger phase respectively, and μ the chemical potential of the exchangeable ions in the resin phase. We can obtain the differential form of the logarithmic relation between K and Ka from the Gibbs-Duhem equation at constant temperature and pressure for the solid solution phase.

$$\left(\frac{n_A}{r_A}\right) d \log f_A + \left(\frac{n_B}{r_B}\right) d \log f_B = 0$$

On the other hand, the following equation is obtained from the above equation.

$$r_A \, d \log f_B - r_B \, d \log f_A = - d \log Ka$$

Now, we calculate the activity coefficient f from these equations. We carried out the calculation of the activity coefficients of salts in the three exchange systems of Na–H, NH_4–H and Ca–H at 0.02 N ionic concentration. The results are shown in Fig. 1. and Table I.

TABLE I

ACTIVITY COEFFICIENTS IN RESIN PHASE

Activity coefficients of Na^+ and H^+ in Na–H exchange system

n Equivalent fraction of Na^+	pKa Apparent equil. const.	f_A Activity coeff. of Na^+	f_B Activity coeff. of H^+
1.0	2.72*	1.000	0.79*
0.9	2.71	0.998	0.790
0.8	2.70	0.995	0.795
0.7	2.69	0.990	0.800
0.6	2.66	0.987	0.818
0.5	2.62	0.948	0.860
0.4	2.57	0.860	0.926
0.3	2.53	0.796	0.968
0.2	2.48	0.757	0.988
0.1	2.46	0.737	0.933
0	2.44*	0.72*	1.000

Activity coefficients of Ca^{++} and H^+ in Ca–H exchange system

n Equivalent fraction of Ca^{++}	pKa Apparent equil. const.	f_A Activity coeff. of Na^+	f_B Activity coeff. of H^+
1.0	2.97*	1.000	0.69*
0.9	2.96	1.000	0.697
0.8	2.95	0.988	0.705
0.7	2.93		0.719
0.6	2.88	0.953	0.747
0.5	2.80	0.871	0.783
0.4	2.66	0.731	0.842
0.3	2.50	0.582	0.904
0.2	2.30	0.412	0.957
0.1	2.10	0.278	0.990
0	1.88*	0.13*	1.000

Extrapolated Values

These experimental results obtained by the authors and the results obtained by Argersinger and Davidson have been compared with the theoretical values.

Discussion

Activity coefficients vary with the exchange ratio (fraction n in the resin phase) for constant co-ordination number z and inter-ionic interaction energy ϕ. In case of an uni-uni-valent system, both activity coefficients vary symmetrically, but in the case of an uni-di-valent system the activity coefficient of the di-valent ion varies more intensively than the uni-valent ion, with the increase of the exchange ratio.

In this derivation, the authors wish to emphasize that the activity coefficients are predominantly affected by the interaction energy.

In the uni-uni-valent case, corresponding to $\phi<0$, $\phi=0$, or $\phi<0$, the activity ceofficients are found to be smaller than unity, equal to unity, or greater than unity, respectively. According to the experimental results obtained by the authors and Argersinger and Davidson, the resin activity coefficients in Na–H and NH_4–H systems were found to be smaller than unity, therefore $\phi<0$. But in the Ag–H exchange system, both activity coefficients were found to be larger than unity.

Argersinger and Davidson[6] have explained that the difference in both cases may be due to the greater dissimilarity between the silver and hydrogen resins, as compared with the sodium and hydrogen resins. According to the theory derived here, this difference may be explained as due to the inter-ionic interaction in the resin phase, which plays an extremely important role.

From the above statements, it is evident that an activity coefficient larger than unity corresponds to one case only, that is $\phi>0$. Accordingly the activity coefficients generally may be explained as a function of the ionic interaction energy between each ion pair. In Na-H and NH_4–H exchange systems of carboxymethylcellulose the interaction energies ϕ/kT of each system are about -0.1 and -0.7–0.8 respectively.

In the case of the uni-di-valent exchange, when $\phi=0$, the activity coefficients are not unity owing to the contribution due to the configurational term. The activity coefficients of the di-valent ion, as compared with those of the uni-valent ion, vary extremely depending on the exchange ratio, but are always

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* After the samples were dried at 70-80°C for ten hours under reduced pressure, the measurements of the infrared spectra were carried out in the room of approximately constant relative humidity (35-40%) and constant temperature (20°C) during twenty minutes. Under such experimental rircumstances, the authors confirmed that the quantity of water contained in the film was quite small and the relative optical density of ν(CO) was affected to an extremely small extent by the contained water.

smaller than unity. On the other hand, the coefficients of the uni-valent ion in the uni-di-valent system have a trend similar to the uni-uni-valent case.

According to the experimental results by Argersinger and Davidson, the activity coefficients in the solid phase are affected only to an extremely small extent by the concentration of the electrolyt solutions. On the other hand, the activity coefficients are shown to be independent of the concentration of the electrolyte solutions and are denoted only as a function of n (equivalent fraction) in the resin phase. Thus the results obtained by the theoretical consideration coincide with experimental ones.

In real exchange phenomena, the experimental results would deviate more of less from the theory due to the following reasons:

1) The effect of the free ions which exist in the resin phase.

2) The swelling of the ion exchange resin actually does vary the exchange ratio, although it was assumed that the resin maintained a constant structure, independent of the exchange ratio.

3) The hydrated ions of Na and Ca have approximately the same volume under the same conditions. The ions of Na and Ca exist in the hydrated state in the resin phase. Therefore the size of each hydrated ion will also be nearly equal in the resin phase. Then the di-valent ion such as Ca would not be able to occupy the two ajacent sites completely, as was assumed in this theory.

In future work, it will be possible to predict and analyse the phenomena of both the " relative selectivity " of the ions in the exchanger and the separation efficiency, from the concept of the inter-ionic interraction involving ϕ. Of course, the size of the ions and the degree of hydration must be taken into consideration.

Conclusion

A theoretical treatment of activity coefficients in the resin phase of cation exchangers is given by using Guggenheim's theory which deals with " A Generalization of the Quasi-Chemical Method ".

The results indicate that the activities in the resin phase are markedly affected by the interaction energy ϕ between ion pairs and they are expressed as a function of ϕ, z, r and n.

Experimental evidence indicates that this conclusion is useful in several cases to explain the activity behavior of ions in the resin phase.

As a result, it is pointed out that the activity behavior in the resin phase of cation exchanger would be generally explained fairly well by considerations of the concept of the interaction energy.

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