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An Equation for Selectivity Coefficient of Ion Exchange in Mixed Solvent System

Hitoshi Ohtaki

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku Nagoya

and Hidetake Kakihana

Laboratory of Nuclear Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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Based on thermodynamic considerations an equation was derived for ion exchange equilibria in mixed solvent systems. In mixtures of water, W, and non-aqueous solvent, S, a selectivity coefficient of ion exchange of A and B ions, $K_A{}^B$, was expressed in terms of partial molal volumes of ions, $\bar{v}_A$ and $\bar{v}_B$, partial molal volumes of solvents, $\bar{v}_W$ and $\bar{v}_S$, and distribution coefficient of the solvents, D, between the external and the resin phases, thus

$$\ln K_A{}^B = [(\bar{v}_A - \bar{v}_B) + (\bar{h}_{WA} - \bar{h}_{WB})\bar{v}_{WA}] \ln D/(\bar{v}_S - \bar{v}_W)$$

where $\bar{h}_{WA}$ and $\bar{h}_{WB}$ represent hydration numbers of A and B ions and $\bar{v}_{WA}$ is partial molal volume of hydrated water. Symbols with bar denote quantities in the resin phase. Using the above equation and values from literatures, selectivity coefficients for sodium-potassium ion exchange in water-ethanol mixtures were calculated and compared with those experimentally obtained for examination of the validity of the equation.

Theremodynamic treatments of ion exchange equilibria in aqueous solution have been studied extensively by a number of authors and were critically reviewed by Kakihana, Ohtaki and Nomura.1) On the other hand, ion exchange equilibria in aqueous mixed solvents have been explored2-4) to a less extent and the variation of selectivity coefficients by addition of a miscible non-aqueous solvent has not been successfully interpreted even in a qualitative point of view. Sakaki4) explained the results in terms of the decrease of the bulk dielectric constant of the external solution. However, sufficient account was not made for *decrease* of the selectivity coefficient at the region of low values of ε. Kakihana and Kojima5) derived some fundamental equations for the ion exchange equilibria in mixed solvent systems as an extension of treatments in aqueous solution systems.

In the present paper a modified equation was derived from equations given by Kakihana and Kojima5) and the selectivity coefficient was estimated for a sodium-potassium ion exchange system with some reasonable approximations.

Derivation of Equation

Since full derivation of equations has already been described in Ref. 5, only the final equations are given. As mentioned in Ref. 5, no thermodynamical assumptions have been made during derivation of the equations except that partial molal volumes of species are assumed to be independent of pressure. In the present paper the equations are described in terms of total water, total non-aqueous solvent and hydrated ions, according to the treatment given in the chapter 3 of Ref. 1. Symbols used are same as those in Refs.

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1) H. Kakihana, H. Ohtaki and T. Nomura, *Bull. Tokyo Inst. Tech., Series-B*, **1960**, 1; H. Kakihana, T. Nomura and H. Ohtaki, *ibid.*, 14.

2) O. D. Bonner and J. C. Moorefield, *J. Phys. Chem.*, **58**, 555 (1954).

3) R. W. Gable and H. A. Strobel, *ibid.*, **60**, 513 (1956).

4) T. Sakaki, This Bulletin, **28**, 217, 220 (1955).

5) H. Kakihana and T. Kojima, *Bull. Tokyo Inst. Tech.*, **1963**, 75.

1 and 5 except the use of subscript "S" for the non-aqueous solvent instead of "O". Thus, for the ion exchange equilibrium of AX_p with BX_q, the following equations result:

$$\ln a_A(a_X)^p - \ln \bar{a}_A(\bar{a}_X)^p = \pi\bar{v}_{AX_p}/\boldsymbol{RT} \tag{1}$$

$$\ln a_B(a_X)^q - \ln \bar{a}_B(\bar{a}_X)^q = \pi\bar{v}_{BX_q}/\boldsymbol{RT} \tag{2}$$

$$\ln a_W - \ln \bar{a}_W = \pi\bar{v}_W/\boldsymbol{RT} \tag{3}$$

$$\ln a_S - \ln \bar{a}_S = \pi\bar{v}_S/\boldsymbol{RT} \tag{4}$$

where X denotes a univalent anion. Equations (1), (2) and (3) are essentially the same as Eqs. (3, 21), (3, 22) and (3, 17) of Ref. 1. Equation (4) is a newly noticed one in the present paper, which was not clearly shown in Ref. 5. Combination of Eqs. (3) and (4) gives

$$\ln D = \ln \bar{a}_W a_S/a_W \bar{a}_S = (\bar{v}_S - \bar{v}_W)\pi/\boldsymbol{RT} \tag{5}$$

or

$$\pi = \boldsymbol{RT} \ln D/(\bar{v}_S - \bar{v}_W) \tag{6}$$

where D is the distribution coefficient of the solvents between external solution and the resin phases.

Substituting Eq. (6), Eq. (7, 32) in Ref. 5 is rewritten as follows:

$$\begin{aligned}\ln K &= \ln (\bar{a}_B)^p(a_A)^q/(a_B)^p(\bar{a}_A)^q \\ &= [(q\bar{v}_A - p\bar{v}_B) + q(\bar{h}_{WA}\bar{v}_{WA} + \bar{h}_{SA}\bar{v}_{SA}) \\ &\quad - p(\bar{h}_{WB}\bar{v}_{WB} + \bar{h}_{SB}\bar{v}_{SB})] \ln D/(\bar{v}_S - \bar{v}_W) \\ &\quad + q(\bar{h}_{WA} \ln \bar{a}_{WA} - h_{WA} \ln a_{WA}) \\ &\quad - p(\bar{h}_{WB} \ln \bar{a}_{WB} - h_{WB} \ln a_{WB}) \\ &\quad + q(\bar{h}_{SA} \ln \bar{a}_{SA} - h_{SA} \ln a_{SA}) \\ &\quad - p(\bar{h}_{SB} \ln \bar{a}_{SB} - h_{SB} \ln a_{SB}) \\ &\quad + [q(h_{WA} - \bar{h}_{WA}) - p(h_{WB} - \bar{h}_{WB})] \ln a_W \\ &\quad + [q(h_{SA} - \bar{h}_{SA}) - p(h_{SB} - \bar{h}_{SB})] \ln a_S\end{aligned} \tag{7}$$

Although the above equation is thermodynamically rigorous, it is too complicated and contains many unknown parameters. The equation may be reduced to a simpler form with some reasonable assumptions which follows: 1) Activities of solvated water and solvated non-aqueous solvent with the ions in the external solution are same as those in the resin phase, respectively; thus $\bar{a}_{WA} = \bar{a}_{WB} = a_{WA} = a_{WB}$ and $\bar{a}_{SA} = \bar{a}_{SB} = a_{SA} = a_{SB}$.

2) Partial molal volume of water in the hydration sphere around A ion is same as that around B ion, $\bar{v}_{WA} = \bar{v}_{WB}$. The same assumption is available for the non-aqueous solvent, thus $\bar{v}_{SA} = \bar{v}_{SB}$.

3) In the region where the concentration of the non-aqueous solvent is not high, the solvation of the non-aqueous solvent is negligible and the hydration number remains unchanged.

For the sake of simplicity the case of $p = q$ will be considered. Then, Eq. (7) can be reduced to

$$\begin{aligned}\ln K &= \ln a_B a_A/\bar{a}_A a_B \\ &\simeq [(\bar{v}_A - \bar{v}_B) + (\bar{h}_{WA} - \bar{h}_{WB})\bar{v}_{WA}] \ln D/(\bar{v}_S - \bar{v}_W) \\ &\quad + [(\bar{h}_{WA} - h_{WA}) - (\bar{h}_{WB} - h_{WB})] \\ &\quad \times (\ln \bar{a}_{WA} - \ln a_W)\end{aligned} \tag{8}$$

or

$$\begin{aligned}\ln K_A{}^B &= \ln \overline{m}_B m_A/\overline{m}_A m_B \\ &\simeq [(\bar{v}_A - \bar{v}_B) + (\bar{h}_{WA} - \bar{h}_{WB})\bar{v}_{WA}] \ln D/(\bar{v}_S - \bar{v}_W) \\ &\quad + [(\bar{h}_{WA} - h_{WA}) - (\bar{h}_{WB} - h_{WB})] \\ &\quad \times (\ln \bar{a}_{WA} - \ln a_W) + \ln \bar{\gamma}_A \gamma_B/\bar{\gamma}_B \gamma_A\end{aligned} \tag{9}$$

where $K_A{}^B$ is the selectivity coefficient for the ion exchange of A ion with B ion. The second term of the right hand side of Eq. (9) may contribute to a small extent to the value of $\ln K_A{}^B$, because the term consists of the difference of two differences of small values. As briefly discussed by Sakaki,[4] the third term, the activity coefficient term, may not be large under ordinary experimental conditions. If we allow the above as sumptions, Eq. (9) may be written as a simpler form as follows:

$$\begin{aligned}\ln K_A{}^B &= [(\bar{v}_A - \bar{v}_B) + (\bar{h}_{WA} - \bar{h}_{WB})\bar{v}_{WA}] \\ &\quad \times \ln D/(\bar{v}_S - \bar{v}_W)\end{aligned} \tag{10}$$

Calculation of the Value of $K_{Na}{}^K$

In order to calculate the value of $K_A{}^B$, values on the right hand side of Eq. (10) were borrowed from literatures. Unfortunately studies on the distribution of solvents have been done with ion exchange resins containing only a sort of univalent ions, such as alkali metal[6], ammonium or quaternary ammonium ions.[7] Therefore, the value of D of an ion exchange resin containing two ionic components was assumed to be equal to an average value of D of ion exhange resins of A and B forms. Since most experiments of ion exchange equilibria in mixed solvents have been made between hydrogen and univalent ions,[2-5,8] the selectivity coefficient $K_A{}^B$ was calculated by the use of a relation:

$$K_A{}^B \simeq K_H{}^B/K_H{}^A \tag{11}$$

The sodium-potassium exchange system in water-ethanol mixture seems to be one of the most favorable systems for examination of validity of Eq. (10), because for this system all necessary data are available.

The partial molal volumes of sodium and potassium ions were reported to be -1.4 and 8.8 m*l*/mol, respectively, by Hepler.[9] The partial molal volumes of sodium salts and potassium salts together with their concentration dependence were summarized by Harned and Owen.[10] The difference

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[6] H. Ohtaki, H. Kakihana and K. Yamasaki, *Z. Phys. Chem., Neue Folge,* **21**, 224 (1959); H. Ohtaki, *ibid.,* **27**, 209 (1961).

[7] H. P. Gregor, D. Nobel and M. H. Gottlieb, *J. Phys. Chem.,* **59**, 10 (1955).

[8] O. D. Bonner, *J. Chem. Educ.,* **34**, 174 (1957).

[9] L. G. Hepler, *J. Phys. Chem.,* **61**, 1426 (1957).

[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd. Ed., Reinhold Publ. Corp., New York (1964), p. 361.

of the partial molal volumes of the corresponding halides of sodium and potassium at infinite dilution, $v^\circ_{\mathrm{NaX}}-v^\circ_{\mathrm{KX}}$, can be estimated as -10.2 ± 0.1 ml/mol and the partial molal volumes vary nearly in parallel with concentration for a given couple of halides. Thus the difference of the partial molal volumes of sodium and potassium ions in the resin phase, $\bar{v}_{\mathrm{Na}}-\bar{v}_{\mathrm{K}}$, might be assumed to be equal to that at the infinite dilution, -10.2 ml/mol.

The partial molal volumes of solvents, water and ethanol in this case, can be calculated from density data[11)] with the help of the following equation;

$$v_{\mathrm{S}} = (1/d) + (1-C_{\mathrm{S}})[\partial(1/d)/\partial C_{\mathrm{S}}] \qquad (12)$$

where d is density of the mixture and C_{S} is weight fraction of the non-aqueous solvent. With the prior assumption of the pressure independence of the partial molal volume of a solvent, values in the resin phase were assumed to be the same as those in ordinary two solvent mixtures, neglecting the effect of ions.

The partial molal volumes of hydrated water was assumed to be the same as that of water in pure state.

The hydration numbers in the resin phase, $\bar{h}_{\mathrm{WK}}$ and $\bar{h}_{\mathrm{WNa}}$, are less known. Glueckauf and Kitt[12)] have estimated hydration numbers of cations in sulfonated resins on the basis of data of water vapor adsorption. For sodium and potassium ions the hydration numbers were 1.5 and *ca.* 0.6, respectively. Hydration numbers of sodium, potassium and ammonium sulfonate resins of Dowex 50 were evaluated by Ohtaki, Gonda and Kakihana[13,14)] from isopiestic data of mixed solvent systems with variously cross-linked resins. Although their results showed that the hydration numbers of these ions varied with solvent composition for a given cross-linked resin, 8% DVB-resin or highly cross-linked resins have practically constant values of hydration number in a rather wide range of concentration of ethanol in the external solution. For Dowex 50-X8 of sodium and potassium forms, the hydration numbers were evaluated to be 4.1 and 2.7, respectively. Using these values the difference of the hydration numbers of sodium and potassium ions in the resin phase, $\bar{h}_{\mathrm{WNa}}-\bar{h}_{\mathrm{WK}}$, is thus assumed to be 1.4.

The distribution coefficient of the solvents, D, in a mixed form of ions of the ion exchange resin was calculated as an arithmetical mean of those in pure ionic forms,[14)] neglecting activity coefficients of the solvents in both phases.

Inserting these values evaluated above into Eq. (10), the selectivity coefficients for sodium-potassium ion exchange in water-ethanol mixtures were calculated. Experimental values were taken from Ref. 4. Selectivity coefficients at a specified composition of the solvents were estimated by interpolation and by using the relationship of Eq. (11). Results were tabulated in Table 1.

TABLE 1

wt% ethanol in solution	8.06	20.82	44.10
wt% ethanol in resin	4.6	10.7	21.0
$\bar{v}_{\mathrm{S}}$ (ml/mol)	53.9	53.1	53.6
$\bar{v}_{\mathrm{W}}$ (ml/mol)	18.1	18.1	18.1
$\log D$	0.27	0.35	0.47
$K_{\mathrm{Na}}{}^{\mathrm{K}}$ (Calc.)	1.30	1.42	1.59
$K_{\mathrm{Na}}{}^{\mathrm{K}}$ (from Ref. 4)	1.62	1.68	1.99

$\bar{v}_{\mathrm{WA}} = 18.1$ ml/mol, $\bar{h}_{\mathrm{WNa}}-\bar{h}_{\mathrm{WK}} = 1.4$

Despite the difference of the resin used by Sakaki from that in Ref. 14 and the approximations made in deriving Eq. (10), the calculated selectivity coefficients are fairly close to the experimental values. This will confirm the validity of Eq. (10).

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11) International Critical Tables, Vol. III, p. 115.

12) E. Glueckauf and G. P. Kitt, *Proc. Roy. Soc., A*, **228**, 322 (1955).

13) H. Ohtaki, K. Gonda and H. Kakihana, This Bulletin, **33**, 293 (1961).

14) H. Ohtaki, K. Gonda and H. Kakihana, *Ber. Bunsen Ges. phys. Chem.*, **67**, 87 (1963).