A Comparison of Methods for estimating Equilibrium Constants in Ion Exchange

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Four methods of estimating equilibrium constants in ion exchange have been compared. While three methods give results in good agreement, the fourth sometimes fails due to the fact that the location of an inflexion point does not always coincide with that corresponding to the equilibrium constant.

Recently Ruvarac and Petković[1] published a method for estimating equilibrium constants of ion-exchange reactions by transforming isotherm data to an expression with an inflexion point. The co-ordinates of the inflexion point are used to estimate the equilibrium constant. The method was first used by Ruvarac and Vesely[2] and extended to solvent extraction by Petković.[3]

In this paper the method is compared with three other methods of estimating equilibrium constants.

The Reaction

For simplicity the comparison will be limited to ion exchange with univalent ions, equation (1), where X = anion or cation

$$A^z + BX \rightleftharpoons AX + B^z \qquad (1)$$

framework of the ion exchanger. For cation exchange $z = +1$ and for anion exchange $z = -1$. The equilibrium quotient, κ, of reaction (1) is defined by equation (2), where $\bar{x}$ = mol fraction

$$\kappa = \frac{[AX]a_B}{[BX]a_A} = \frac{\bar{x}[B^z]}{(1-\bar{x})[A^z]}(y_1/y_2) \qquad (2)$$

of AX, a denotes activity, and [ ] molar concentration. The activity coefficient ratio y_1/y_2 in the aqueous phase can either be measured or estimated. In studies where the ionic strength is kept constant in the aqueous phase this ratio can be expected to be constant and included in κ.

The exchanger phase is treated as a binary mixture of BX and AX.[4] However, in most studies the water activity is nearly constant and little error is made by using the pseudo-binary approach outlined above.[4] It should be mentioned that the ternary system was treated in great detail by Gaines and Thomas.[5] Many workers have used this approach *neglecting* the water. For univalent–univalent ion exchange equation (3) below is obtained.

The Methods

(a) The Integration Method.—It was shown by Argersinger *et al.*[6] that by plotting log κ or ln κ *versus* $\bar{x}$ the equilibrium constant K of reaction (1) can be estimated from equation (3).

$$\log K = \int_0^1 \log \kappa(\bar{x})\,d\bar{x} \qquad (3)$$

This expression has often wrongly been attributed to Henry Thomas. An equivalent expression was given by Sillén and co-workers.[7] The integration can be performed either by graphical or numerical methods. It is important to carry out the experiments over as large a range of $\bar{x}$ values as possible in order to get good estimates of the limiting log κ values at $\bar{x} = 0$ [log κ(0)] and $\bar{x} = 1$ [log κ(1)].

(b) The Method of Ruvarac and Petković.—This method has been described in detail elsewhere.[1] Here a brief outline is given. The quantity y' is introduced and defined by equation (4a) or (4b). When plotted *versus* $\bar{x} = \bar{x}_{AX}$ an inflexion point with

$$y' = \log(a_B/a_A) \qquad (4a)$$

$$y' = \log([B]/[A]) \qquad (4b)$$

co-ordinates x^0, y'^0 is located. In order to find this point accurately y' is fitted by a third-degree polynomial in $\bar{x}$ using least-squares procedures. Then it is suggested that log K can be computed from equation (5).

$$\log K = y'^0 + \log[\bar{x}^0/(1-\bar{x}^0)] \qquad (5)$$

(c) The Polynomial $y' = a + b\bar{x} + c\bar{x}^2 + d\bar{x}^3$.—From equations (2)—(4), equation (6) can be derived where the

$$\log K = \int_0^1 y'\,d\bar{x} + \int_0^1 \log[\bar{x}/(1-\bar{x})]d\bar{x} = \int_0^1 y'\,d\bar{x} \qquad (6)$$

second integral is equal to zero. Then we obtain expression (7)

$$\log K = \int_0^1 (a + b\bar{x} + c\bar{x}^2 + d\bar{x}^3)d\bar{x} = a + \tfrac{1}{2}b + \tfrac{1}{3}c + \tfrac{1}{4}d \qquad (7)$$

(d) The Three-parameter Method.—Recently a simple three-parameter model was introduced to fit various kinds of ion-exchange data as illustrated in refs. 8—12. According to this method log κ of reaction (1) can be written as in equation (8)

$$\log\kappa = \log\kappa(1)\bar{x}^2 + \log\kappa(0)(1-\bar{x})^2 + 2\log\kappa_m\bar{x}(1-\bar{x}) \qquad (8)$$

where log κ (0) and log κ (1) are the limiting values mentioned earlier. In the literature most data are plotted versus $\bar{x}$, not $\bar{x}^2$. It is then useful to introduce equation (9). By least-squares fitting

$$\log\kappa = \log\kappa(1)\bar{x} + \log\kappa(0)(1-\bar{x}) + \bar{B}\bar{x}(1-\bar{x}) \qquad (9)$$

using equation (9) the parameters log κ (0) and log κ (1) are obtained together with the empirical constant $\bar{B}$. The third parameter, log κ_m, is now computed from equation (10). It is

Table. Estimates of log K at 298 K by the four methods

System	Ion exchanger	I/mol dm^{-3}	log K (*a*)	(*b*)	(*c*)	(*d*)	Ref.
(1) Ag^+–H^+	Wofatit KS	0.100	0.708	0.656	0.702	0.703	*a*
(2) Ag^+–H^+	Dowex 50	0.100	0.995	0.986	0.991	0.995	*a*
(3) SCN^-–Cl^-	Hydrous zirconia	0.100	0.188	0.128	0.182	0.180	*b*
(4) SCN^-–NO_3^-	Hydrous zirconia	0.100	0.288	0.299	0.293	0.293	*b*
(5) Cl^-–NO_3^-	Hydrous zirconia	0.100	0.017	−0.010	0.008	0.004	*b*
(6) Li^+–H^+	Semicrystalline zirconium phosphate	0.100	−1.367	−0.857	−1.631	−1.604	*c*
(7) Cs^+–H^+	Semicrystalline zirconium phosphate	0.100	0.281	−0.124	0.330	0.327	*c*
(8) K^+–H^+	Amorphous zirconium phosphate	0[d]	−0.224	−0.320	−0.217	−0.215	*e*

[a] E. Högfeldt, E. Ekedahl, and L. G. Sillén, *Acta Chem. Scand.*, 1950, **4**, 1971. [b] G. H. Nancollas and R. Paterson, *J. Inorg. Nucl. Chem.*, 1967, **29**, 565. [c] G. H. Nancollas and B. V. K. S. R. A. Tilak, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3643. [d] Equation (4a) used to compute y'. [e] A. Lj. Ruvarac, Ph.D. Thesis, Belgrade University, 1970.

$$\log \kappa_m = \tfrac{1}{2}[\log \kappa(0) + \log \kappa(1) + \bar{B}] \qquad (10)$$

easily shown that log K can be estimated from equation (11).

$$\log K = \int_0^1 \log \kappa(\bar{x})\,d\bar{x} = \tfrac{1}{3}[\log \kappa(0) + \log \kappa(1) + \log \kappa_m] \qquad (11)$$

Results

The four methods outlined above have been compared for a number of systems in the literature. The results are collected in the Table. It is evident that methods (*a*), (*c*), and (*d*) mostly give results which agree well with each other, except for system 6 due to the fact that only the range $\bar{x}_{Li} < 0.5$ was studied. Here method (*d*) is expected to give the best value, no uncertain extrapolations being needed.

Method (*b*) is in good accord in several cases with the others but fails for systems 3, 6, and 8. This is due to the fact that the coordinates of the inflexion point are not the same as those corresponding to log K. Since the polynomial in method (*c*) is used in (*b*) it is possible to derive an expression between the constants *b*, *c*, and *d* necessary (but probably not sufficient) for equation (5) to give a good estimate of log K.

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