U.P.B. Sci. Bull., Series B, Vol. 74, Iss. 3, 2012 ISSN 1454-2331

ION EXCHANGE ISOTHERMS FOR BINARY SYSTEMS PREDICTED BY SURFACE COMPLEXATION MODEL

Corina M. BOHDANA[1], Eugen PINCOVSCHI[2], Ana-Maria S. OANCEA[3]

Schimbul ionic este o metodă importantă pentru tratarea apelor potabile şi depoluarea apelor uzate. Scopul lucrării a fost de a simula izotermele de schimb ionic în modelul formării complecşilor pe suprafaţă pentru sisteme binare. Calculele au fost efectuate variind sistematic constantele modelului, pentru a întelege influenţa valorilor numerice ale acestora asupra izotermei de schimb ionic şi pentru a pune în evidenţă cazurile în care schimbătorul de ioni preferă un anumit ion.

Ion exchange is an important method for water treatment and wastewater depollution. The aim of the present paper was to predict the ion exchange isotherms by surface complexation model for binary systems. The calculations were done varying systematically the constants of the model in order to understand the influence of their numerical values on the ion exchange isotherm, revealing the cases when the ion exchanger is selective for a certain ion.

Keywords: ion exchange equilibrium, ion exchange isotherms, surface complexation model

List of Symbols

A_0	specific surface area of the ion exchanger (m^2/g)
C_A, C_B	concentration of the ions in the external solution at equilibrium (M)
C_A^0, C_B^0	concentration of the ions in the initial external solution (M)
$C(A)_{St,A}, C(B)_{St,B}$	concentration at equilibrium of the free ions, in their corresponding Stern layers (M)
$C(B,A)$	electric capacity of the capacitor formed by the Stern layers of ions B and A, supposing that the Stern layer of ions B is the first layer next to the ion exchanger surface and the Stern layer of ions A is the second one (F/m^2)
$C(R-A_{wA})$	concentration at equilibrium of the surface complexes formed by counterions A (M)

---

[1] PhD student Depart. Research and Development, Purolite SRL, Aleea Uzinei 11, 505700, Victoria, Romania, e-mail: corina_bohdana@yahoo.com

[2] Prof., Depart. of Enviromental Protection, University POLITEHNICA of Bucharest, Romania

[3] Prof., Depart. of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania

$C(R-B_{wB})$	concentration at equilibrium of the surface complexes formed by counterions B (M)
$C(R^{zR})$	concentration of the ion exchanger of valence z(R) (M)
F	Faraday constant (96500 C/mol)
K^A	thermodynamic constant of formation of surface complex R - A_{w_A} (dimensionless)
K^B	thermodynamic constant of formation of surface complex R-B_{w_B} (dimensionless)
$K_A^B = K^B/K^A$	ion exchange equilibrium constant defined in SC (dimensionless)
$m(B,A)$	the slope of the linear regression $\log K_A^B$ *vs.* y_B - SCM constant
N	total equivalent concentration of the external solution (eq/L)
$q_{\max}$	maximum resin loading in given condition (mol/g)
Q_A^B	generalized separation factor defined in SCM (dimensionless)
R	gas constant (8.314 J/mol K)
T	temperature (K)
X_A, X_B	equivalent ionic fraction of ions A and B in the liquid phase at equilibrium, respectively (dimensionless)
Y_B, Y_A	equivalent ionic fraction of ions A and B in the resin phase at equilibrium, respectively(dimensionless)
z_A, z_B	valence of the corresponding ions
$z(R)$	valence of the ion exchanger defined in SCM as equal to the smallest common multiple of the valences of the two counterions taken with opposite sign
w_A, w_B	stoichiometric factor of the corresponding ions; $w_i = -z(R)/z(i)$; in our case $w_A = 2$; $w_B = 1$.

1. Introduction

Ion exchange resins are extensively used in chemical, hydrometallurgical, electronic and nuclear industries for ion separation from an aqueous stream. The ion exchange is a unit operation frequently applied in water treatment and in wastewater depollution [1]. The monovalent/divalent ion exchange process is very important in water softening and heavy metals removal from wastewaters. In industrial columns the cation exchangers are initially in hydrogen or sodium ion form and the anion exchangers are in chloride or hydroxyl form, and these counterions are often exchanged with divalent ions. Design of an industrial separation by ion exchange needs the knowledge of the ion exchange isotherms.

In recent years, the surface complexation model [2] was extended to polymeric ion exchangers. The surface complexation model takes into account the presence of the electrical forces and their effect to the ion exchange process and it could be considered from this point of view to be a better model than the classical adsorption models often used for describing the ion exchange equilibria. Previous papers shown that the simulated isotherms for binary systems in surface complexation model, using the constants of the model determined by experiment, were in good agreement with the experimental ion exchange isotherms [2-5]. This observation supports the aim of the present work, which is the systematic study of the dependence of the shape of the ion exchange isotherms on the numerical values of the constants of the surface complexation model, for monovalent/divalent ion exchange equilibria in diluted external solution of 0.01 eq/L, a case very often encountered in practical applications.

2. Surface complexation model for polymeric ion exchangers

The surface complexation model (SCM) has been developed for ion adsorption from aqueous solutions on hydrous oxides minerals. Höll and co-workers extended this model to ion exchange processes on polymeric ion exchangers [2]. The ion exchanger is supposed to be a fictitious plane surface carrying ionized functional groups uniformly distributed. For cation exchangers the charge is negative and for anion exchangers is positive. Each kind of counterions forms a separate Stern layer parallel to the resin surface, with the same area and located at well defined distances, determined by the intrinsic ionic size and the solvated ionic radius of the ion. A small amount of counterions are located in the diffuse layer.

The counterions of one kind, located in their corresponding Stern layer, form "surface complexes" with the ionic charges distributed on the resin surface through all kinds of physical and chemical interactions [2]. The electric potential generated by the fixed charges is normal to the surface and drops from its value at the surface to a definite lower values in the first Stern layer, then in the second Stern layer and decreases across the diffuse layer to zero [2]. The ion exchange process is represented in SCM by the replacement of one kind of surface complexes formed by one kind of counterions with another kind of surface complexes formed by the other counterions.

The ion exchange of a monovalent ion A with a divalent ion B can be described in SCM by the replacement of a surface complex formed by simultaneous interaction between two monovalent ions A from their Stern layer and two monovalent fixed charges on the ion exchanger surface with a surface complex formed by interaction between the divalent ion B from its Stern layer and two monovalent fixed charges on the ion exchanger surface. The equations of the surface complexes formation are:

$$R^{z(R)} + w_a (A)_{St,A} \Leftrightarrow R - A_{w_A} \tag{1}$$

$$R^{z(R)} + w_B (B)_{St,B} \Leftrightarrow R - B_{w_B} \tag{2}$$

The thermodynamic stability constants of these surface complexes are:

$$K^A = \frac{C(R - A_{w_A})}{C(R^{z(R)})[C(A)_{St,A}]^{w_A}} \tag{3}$$

$$K^B = \frac{C(R - B_{w_B})}{C(R^{z(R)})[C(B)_{St,B}]^{w_B}} \tag{4}$$

for activity coefficients equal to unity (ideal case), where *C* denote the molar concentration of the surface complexes and of the free ions in their corresponding Stern layers. These equations express the affinity of the ion exchanger R for the corresponding counterions. The ion exchange process is represented by the surface complexes replacement:

$$R - A_{w_A} + w_B(B)_{St,B} \Leftrightarrow R - B_{w_B} + w_A(A)_{St,A} \tag{5}$$

where w_A, w_B are the stoichiometric coefficients defined as the ratio between the resin valence *z(R)* and the corresponding counterion valence, multiplied with –1. The resin valence has opposite sign to the counterions and is equal to the smallest common multiple of the valences of the two counterions [2]. The corresponding thermodynamic ion exchange constant for the ideal case is:

$$K_A^B = \frac{K^B}{K^A} = \frac{C(R - B_{w_B})[C(A)_{St,A}]^{w_A}}{C(R - A_{w_A})[C(B)_{St,B}]^{w_B}} \tag{6}$$

The ratio of the concentration of the surface complexes was replaced with the ratio of the resin loading with the corresponding two counter-ions (equivalent ionic fractions Y_A and Y_B), supposing that all counter-ions in the resin phase are involved in surface complexes (neglecting the contribution of free counterions from the Stern layer and from the diffuse layer to the corresponding resin loadings). The concentration of the free counterions in the Stern layer was expressed as a function of their concentration in the external solution (C_A and C_B) and the electric potential in the Stern layer, assuming a Boltzmann distribution of ions in the electric field. Supposing that the counterions B form the Stern layer which is the closest to the ion exchanger surface and the counterions A form the second Stern layer from the surface, the unknown difference between the electric potentials in the Stern layers B and A was obtained from the electric capacitance of the capacitor formed by these Stern layers (*C(B,A)*), and after transformations [2] equation (6) becomes:

$$\log Q_A^B = \log \frac{Y_B C_A^{w_A}}{Y_A C_B^{w_B}} = \log K_A^B + \frac{|z(R)|}{\ln 10} \frac{F^2 q_{\max}}{A_0 C(B,A) RT} Y_A \tag{7}$$

where Q_A^B is called *the generalized separation factor*, which can be measured at different resin loadings. The intercept of the linear regression of $\log Q_A^B$ *vs.* Y_A is the logarithm of the ion exchange constant defined in the model. The slope *m (B, A):*

$$m(B,A)=\frac{|z(R)|}{\ln 10}\frac{F^2 q_{\max}}{A_0 C(B,A)RT} \tag{8}$$

is also an important constant of SCM, and equation 7 become:

$$\log Q_A^B=\log\frac{Y_B C_A^{w_A}}{Y_A C_B{}^{w_B}}=\log K_A^B+m(B,A)Y_A \tag{9}$$

The slope is positive if the sequence of the two Stern layers is correctly assumed [2]. The generalized separation factor Q_A^B can be determined by measuring the loading of the ion exchanger with ions A and B, expressed as ionic fractions Y_A and Y_B, together with the molar concentrations of the two counterions in the liquid phase at equilibrium, C_A and C_B. The two SCM constants for a binary system, $\log K_A^B$ and $m(B,A)$, can be obtained from the linear regression 9 for given conditions (temperature and total equivalent concentration of the external solution).

3. Prediction of the ion exchange isotherms in surface complexation model

Equation 9 can be used also to predict the ion exchange isotherm if the model constants are known. Höll and co-workers developed a computer program [2-4] for calculation of the concentrations at equilibrium of two counterions in ion exchanger phase and the liquid phase. Equation 9 was transformed replacing the molar concentrations of ions with the equivalent ionic fractions, knowing that:

$$C_A=X_A\cdot N/z_A \tag{10}$$

$$C_B=X_B\cdot N/z_B \tag{11}$$

where the total equivalent concentration N of the external solution is:

$$N=C_A^0|z_A|+C_B^0|z_B| \tag{12}$$

obtaining:

$$\log Q_A^B=\frac{Y_B(X_A N/z_A)^{wA}}{Y_A(X_B N/z_B)^{wB}}=\log K_A^B+m(B,A)\cdot Y_A \tag{13}$$

In the case investigated in this paper $w_A = 2$, $w_B = 1$, and $N = 0.01$ eq/L. Equation 13 together with the following equations:

$$X_A+X_B=1 \tag{14}$$

$$Y_A+Y_B=1 \tag{15}$$

forms a system of three equations with four unknown variable X_A, X_B, Y_A, Y_B. Giving to one variable values between zero and unity, the other three variables can be calculated by solving numerically the above system of equations 13-15.

The input data in the program were: $z_A, z_B, C_A^0, C_B^0, \log K_A^B, m(B,A)$, and the output was a multicolumn file: X_A, X_B, Y_A, Y_B. The predicted ion exchange isotherms in dimensionless coordinates Y_A *vs* X_A or Y_B *vs.* X_B can be plotted.

4. Results and discussion

The results obtained for the dimensionless ion exchange isotherms predicted in SCM for monovalent/divalent ion exchange in dilute external solutions (0.01 eq/L) for values of constants of the model systematically varied are presented in Figure 1.

Such a systematical study was not reported until now in the literature and it is interesting because monovalent/divalent exchange occurs often in industrial separations by ion exchange.

A convex ion exchange isotherm describes a system at equilibrium when the ion exchanger prefers the counterion for which, in the graph were represented the concentrations at equilibrium in the solid and liquid phases, and a concave one when the exchanger prefers the other counterion. Selectivity of an ion exchanger is indicated by the deviation of the isotherm from the diagonal.

The values of the slopes $m(B,A) = tg\alpha$ as a function of the angle α, which changes from 0 to 90^o, are presented in Table 1.

The analysis of the ion exchange isotherms given in Figure 1 reveals that for a given ion exchange constant the increase of the slope *m(B,A)* increases the preference for divalent ion B, for monovalent/divalent ion exchange in dilute external solution. For $\log K_A^B$ < -2.0 the ion exchanger prefers the monovalent ion A instead of B for any slope *m(B,A)*, while for $\log K_A^B$ = -2.0 and *m(B,A)* < 0.5 the selectivity reverses at around $X_B = 0.5$, but for $\log K_A^B$=-2.0 and *m(B,A)* > 0.5 the ion exchanger prefers ion B.

Tabel 1

Slope *m(B, A)* as a function of the angle α

$m(B,A) = tg\alpha$	α °
0	0
0.005	0.29
0.01	0.6
0.1	6
0.5	27
1.0	45
2.0	64
3.0	72
5.0	78.7
7.0	81.9

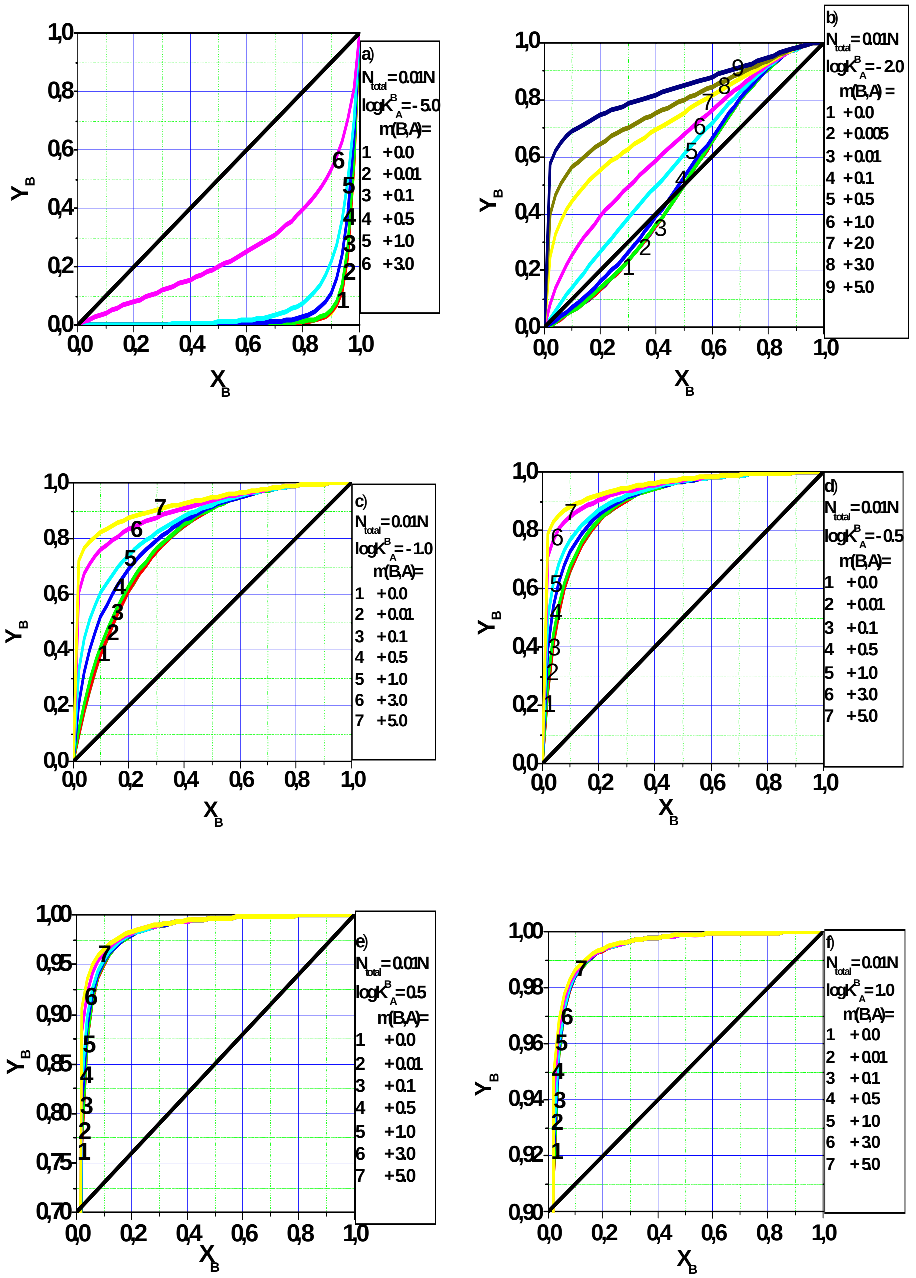

Fig.1. Comparison between the dimensionless isotherms predicted by SCM for monovalent/divalent ion exchange for a given $\log K_A^B$ at different values of *m(B, A)*.

The ion exchanger is selective for ion B if $\log K_A^B$ > -1.0 for any value of the slope, and for $\log K_A^B$ > 0.5 the influence of the slope on the ion exchange isotherm is negligible. It can be concluded that for systems with an ion exchanger which strongly prefers the divalent ion (high selectivity), the shape of the ion exchange isotherm is not sensitive to the accuracy in the experimental determination of the slope, as compared to the low selectivity case.

5. Conclusions

The ion exchange isotherms for monovalent/divalent exchange in dilute external solutions were predicted using surface complexation model, for constants of the model varied systematically. The equilibrium concentrations were computed using a computer program reported in literature which solves numerically a nonlinear system of equations. For binary ion exchange, the model has two constants: the logarithm of the ion exchange equilibrium constant ($\log K_A^B$) and the "slope" (*m(B,A)*), a constant correlated with universal constants, temperature, the maximum loading, the ion exchanger specific surface area and the electrical capacity of the capacitor formed by the two Stern layers of the two counterions. The results reveal that the ion exchanger prefers the divalent ion if $\log K_A^B$ > -2.0 for any value of the slope, and the selectivity increases if the slope increases. The contribution of the slope value on the ion exchange isotherm decreases, if the ion exchange constant increases. For $\log K_A^B$ > 0.5 the slope practically do not influence the isotherm. These results show also that an accurate experimental determination of the slope is necessary for low values of the ion exchange constants, while for high values of the ion exchange constant less accuracy in the slope determination is not critical.

REFERENCES

[1] *F. Helfferich*,Ion Exchange, Dover Publications, Inc. New York, 1995

[2] *W.H.Höll, M.Franzreb, J.Horst and S.H.Eberle,* Description of Ion Exchange Equilibria by Means of the Surface Complexation Theory, in Ion Exchange and Solvent Extraction, J.A. Marinski and Y.Marcus editors, **vol.11**, Marcel Dekker, New York, 1993, p. 151-210

[3] *A.M.S.Oancea, C.Drinkal, W.H.Höll,* Evaluation of exchange equilibria on strongly acidic ion exchangers with gel-type, macroporous and macronet structure, Reactive & Functional Polymers, **68**, 2008, pp.492-506

[4] *A.M.S. Oancea, C. Drinkal and W.H. Höll*, Langmuir and Surface Complexation Models for Ion Exchange Equilibria on Strong Acid Resins, Journal of Ion Exchange, **18**, no. 4, 2007, pp. 162-167

[5] *C.M.Bohdana, D.S.Cantea, E.Pincovchi and A.M.S. Oancea*, Proton/magnesium Ion Exchange Equilibrium on Sulfonated Hyper-Crosslinked Resin. Sorption and Surface Complexation Models, Rev. Chim., Bucharest, **62**, no.2, 2011, pp. 233-239.