CHEMISTRY

ADSORPTION THEORY OF EQUILIBRIA OF COMPLEXES IN SOLUTION

EXPRESSION FOR $\bar{n}$ SIMILAR TO THAT OF SIPS' ADSORPTION ISOTHERM

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(Received 17 November 1965)

According to the contemporary theory of step equilibria of complexes in solution, we have

$$Y = \frac{C_M}{(M)} = \sum_{i=0}^{N} \beta_i (L)^i, \qquad (1)$$

$$\bar{n} = \frac{C_L - (L)}{C_M} = \frac{d \ln Y}{d \ln (L)} =$$

$$= \sum_{i=1}^{N} i\beta_i (L)^i \Big/ \sum_{i=0}^{N} \beta_i (L)^i. \qquad (2)$$

In a previous report[1], one of the authors considered that there is similarity between the adsorption and the complex formation in solution, the solute and the adsorbent being similar to the ligand and the metal ion respectively. Thus in the Freundlich adsorption isotherm, e.g.,

$$x/m = k(C)^b, \qquad (3)$$

C corresponds to (L), x is the amount of adsorbed solute, which is proportional to the total concentration of complexed ligands, i.e., $C_L - (L)$, and m is proportional to C_M, so that

$$\bar{n} = \frac{C_L - (L)}{C_M} \propto \frac{x}{m},$$

or

$$\bar{n} = k'(L)^b,$$

$$\ln Y = \int_0^{(L)} \bar{n} d \ln (L) = \frac{k'}{b}(L)^b. \qquad (4)$$

The above relationships were verified by plotting $\log \bar{n}$ vs. $\log(L)$ or $\log \log Y$ vs. $\log(L)$ and satisfactory straight lines were obtained for a number of complex systems as follows:

Tl^+ and SCN^- complex system:

$$\log Y = 0.758(L)^{0.900}, \quad \bar{n} = 1.57(L)^{0.900},$$

Pb^{++} and SCN^- complex system:

$$\log Y = 1.66(L)^{0.832}, \quad \bar{n} = 3.17(L)^{0.832}.$$

Later, we and Pai Ming-chang found[2] some other complex systems to have fitted the Langmuir equation better than Freundlich's, e.g.,

Cd^{++}–pyridine system:

$$\bar{n} = \frac{22.3(L)}{1 + 6.63(L)},$$

$$Y = [1 + 6.14(L)]^{3.365};$$

UO_2^{++}–CH_2ClCOO^- system:

$$\bar{n} = \frac{25.0(L)}{1 + 8.42(L)};$$

Zr^{4+}–F^- system:

$$\bar{n} = \frac{6.21 \times 10^5 (L)}{1 + 1.067 \times 10^5 (L)};$$

Pb^{++}–NO_3^- system:

$$Y = [1 + 0.608(L)]^4.$$

In the present report, we have further generalized the expressions to those similar to Sips' adsorption isotherm[3] so that they can be fitted to the experimental curves of the most complex systems:

$$\bar{n} = \frac{Na(L)^b}{1 + a(L)^b},$$

$$\log Y = \frac{N}{b} \log [1 + a(L)^b]. \qquad (5)$$

These expressions include the Langmuir isotherm (when $b = 1$) and the Freundlich isotherm (when $a(L)^b \ll 1$) as two special cases.

In order to determine the constants N, a, b in (5) from the experimental data, we put[4]

$$a(L)^b = x^b,$$

$$\frac{b \log Y}{N} = X, \qquad \frac{\bar{n}}{N} = \theta,$$

so that (5) reduces to

$$\theta = \frac{x^b}{1 + x^b}, \qquad X = \log(1 + x^b). \qquad (6)$$

If the experimental curve is $Y = f(L)$, then we find the relations between X and x, taking b as a parameter (Table 1).

Table 1

X as a Function of x

x	$b = 1.2$		$b = 1.0$		$b = 0.8$		$b = 0.6$	
	$1 + x^b$	X	$1 + x^b$	X	$1 + x^b$	X	$1 + x^b$	X
10^{-2}	1.00398	0.001730	1.01000	0.004321	1.02512	0.010774	1.06310	0.026573
10^{-1}	1.06310	0.026573	1.10000	0.041393	1.15849	0.063892	1.25119	0.097323
1	2.00000	0.301030	2.00000	0.301030	2.00000	0.301030	2.00000	0.301030
10	16.489	1.22657	11.0000	1.04139	7.3096	0.863894	4.9811	0.69733
10^2	252.19	2.40173	101.000	2.00432	40.811	1.61078	16.849	1.22657
10^3	3982.1	3.60011	1001.00	3.00043	252.19	2.40173	64.096	1.80683

Plot $X = f(x)$ for different values of b on a transparent paper (standard curves in Fig. 1) and fit it with the experimental $\log Y = f(L)$ curve. If the standard curve with parameter b fits the experimental one best, and the origin of the standard curve is at L_1 and $\log Y_1$, then

$$b = b_1, \qquad a = (L_1)^{-b_1}, \qquad N = b_1 \log Y_1.$$

If the available experimental data are $\bar{n} = f(L)$, then we plot the standard curves $\theta = f(x)$, and the constants N, a, b may be determined by a similar process.

Figure 2 is the experimental $\log Y$ vs. (L) curve for the $Bi^{+++}-Cl^-$ system[5], which fits the standard curve for $b = 0.7$ best, with the origin at $L_1 = 0.15$, $\log Y_1 = 10.5$, so that

$$b = 0.7, \qquad a = (0.15)^{-0.7} = 3.77,$$

$$N = 0.7 \times 10.5 = 7.35,$$

$$\log Y = 10.5 \log [1 + 3.77(L)^{0.7}].$$

Figure 3 is the experimental $\bar{n}$ vs. (L) curve for the $UO_2^{++}-Ac^-$ system[6], which fits the standard θ vs. x curve for $b = 1.3$ best, with the origin at $L_1 = 7.8 \times 10^{-2}$ and $\bar{n}_1 = 3.0$, so that

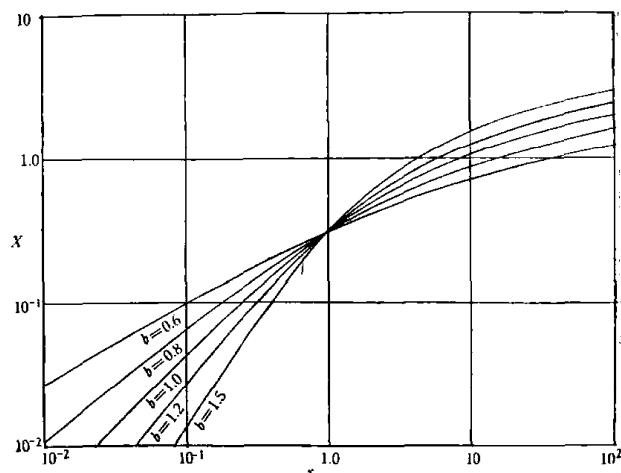$$b = 1.3, \qquad a = (7.8 \times 10^{-2})^{-1.3} = 550,$$
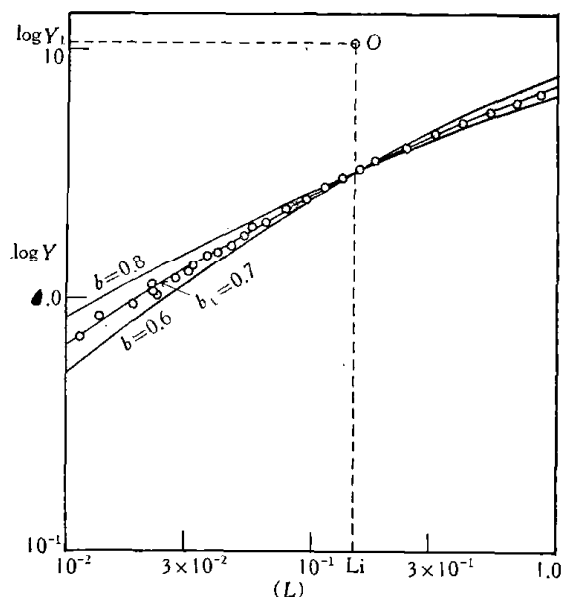
$$N = 3.0,$$

Fig. 1. Standard curves.

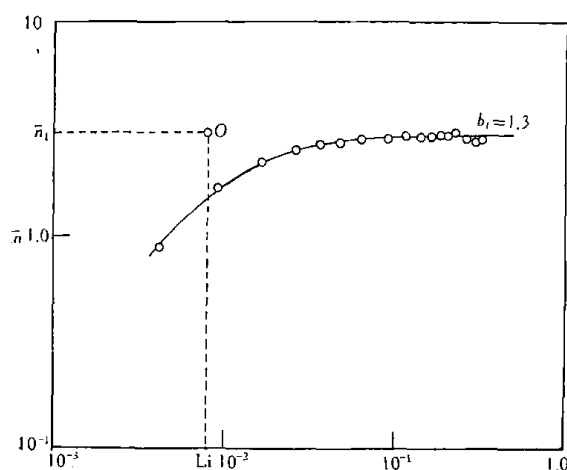Fig. 2. $\log Y$ as a function of (L) for the
Bi^{+++}-Cl$^-$ system.

Fig. 3. $\bar{n}$ as a function of (L) for the
UO$_2^{++}$-Ac$^-$ system.

$$\bar{n} = \frac{3.0 \times 550 \ (L)^{1.3}}{1 + 550(L)^{1.3}}.$$

In order to study the scope of applicability of the proposed method we have analysed more than one hundred complex systems of different types, and found that there are two types of complex equilibria. The first type consists of those of chelate systems which are very stable, and the separation between the successive stability constants is very sharp and distinct. To these systems the theory of successive step formation applies very well. Complexes of the second type are those of monodentate ligands, especially of inorganic ligands, which are not very stable and the successive formation of the complexes is vague and indistinct. For these systems the adsorption theory applies better.

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