

Theory of adsorption equilibria analysis based on general equilibrium constant expression

Abdul Sattar Ali KHAN

*Chemistry Division, Pakistan Institute of Nuclear Science and Technology,
P.O. Nilore, Islamabad-PAKISTAN
e-mail: abdulesattar_alikhan@email.com*

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Adsorption equilibria were analyzed on the basis of general equilibrium constant expression for the development of fundamental adsorption equations (Freundlich, Langmuir, and BET) in connection with the establishment of a general approach towards physical interpretations of adsorption parameters. Theoretically it was proved that Freundlich plot analysis cannot be used to find useful parameters such as the monolayer adsorption capacity of an adsorbent. The present theory also indicated that the adsorption process with known value of monolayer adsorption capacity can be studied for finding various equilibrium constants on the basis of the Fronaeus equation, which is commonly used in the complexation process. The applications of the Langmuir equation in finding the ligand number of a complex as well as the magnitude of equilibrium constant required for the analysis of the BET equation in the multilayer liquid phase adsorption process was also discussed. It was concluded that the general approach towards exploration and physical interpretation of adsorption parameters can be developed by analyzing the adsorption equilibria on the basis of general equilibrium constant expression in accordance with the law of mass action.

Key Words: Insight, adsorption, complexation, adsorption layer, ligand number, thickness of adsorbed layer, Langmuir, equilibrium constant, law of mass action

Introduction

Adsorption is related to the removal of a substance called an adsorbate from the gaseous (or liquid) phase by a solid material called an adsorbent.¹ The adsorption process is recognized as an important process in the field of separation technology.^{2–6}

The adsorption process is primarily studied by fitting the data to Freundlich, Langmuir, and Brunauer-Emmett-Teller (BET) equations. The Freundlich isotherm⁷ is based on an empirical equation while the

Langmuir equation^{8,9} is applicable only for a monolayer adsorption process. The BET equation¹⁰ is a theoretical expression developed on the basis of statistical analysis of adsorption sites occupied during multilayer gas adsorption. It is commonly used in the gas phase adsorption process for finding the monolayer adsorption capacity of an adsorbent.¹¹

Over the years, a wide variety of other adsorption models have been formulated by using more than one approach, which resulted in diversities in the physical interpretation of adsorption parameters.¹²⁻¹⁴ Due to the diversity in adsorption models, sometime it becomes a challenge to clarify a given isotherm model in various adsorption systems due to a lack of information about the exact nature of model parameters.¹⁴ It was, therefore, desired to develop a general approach for the analysis of adsorption equilibria. Thus, the aim of the present work was to explore the nature of fundamental adsorption isotherms (Freundlich, Langmuir, and BET isotherm) on the basis of general equilibrium constant expression in accordance with the law of mass action.

Theory

Analysis of adsorption equilibria

The adsorption equilibria were analyzed on the basis of step-wise and overall equilibrium constants expressions. For this purpose, the adsorption of an adsorbate “A” from liquid (or gaseous) phase onto solid adsorbent “M” was generally expressed as:



where “s” is the stoichiometric number of moles of adsorbate adsorbed on one mole of adsorption sites present on adsorbent. The formation of species “MA_s” can be expressed by the following step-wise equilibrium expressions:



Thus MA_s type species may be formed in the sth step according to the following expression:



If each adsorption site is occupied by only one adsorbate and each adsorbed adsorbate provides a site for adsorption of adsorbate in the next layer, then on the basis of Eqs. (2) to (5) it can be anticipated that the magnitude of “s” represents the number of adsorption layers. Thus the step-wise equilibrium constant for the formation of the first and second layer can be expressed as:

$$K_1 = \frac{[MA]}{[M][A]} \quad (6)$$

$$K_2 = \frac{[MA_2]}{[MA][A]} \quad (7)$$

By multiplying Eq. (6) by Eq. (7) one gets:

$$K_1 K_2 = \frac{[MA_2]}{[M][A]^2} = \beta_2 \quad (8)$$

The “ β_2 ” is the overall equilibrium constant for the following equilibrium expression:



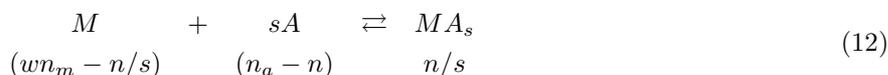
Similarly, the step-wise and overall equilibrium constant for the formation of the s^{th} layer can be expressed as:

$$K_s = \frac{[MA_s]}{[MA_{(s-1)}][A]} \quad (10)$$

$$\beta_s = \frac{[MA_s]}{[M][A]^s} = K_1 K_2 \dots K_s \quad (11)$$

The “ β_s ” is the overall equilibrium constants of the equilibrium given in Eq. (1) and the “ K_s ” is the step-wise equilibrium constant of the equilibrium given in Eq. (5).

The adsorption process proceeds in a step-wise manner leading to the formation of different layers. However, it is more advantageous to analyze the adsorption equilibria on the basis of overall equilibrium constant expressions “ β_s ” for ease in simplification of the complicated mathematical expression of the fraction of number of moles of adsorbate adsorbed at a given equilibrium pressure (or concentration). In this connection, consider a case where “ n_a ” number of moles of the adsorbate are added to a given volume “ V ” of solution, out of which “ n ” moles are adsorbed by “ w ” grams of the adsorbent having “ n_m ” number of moles of adsorption sites per gram; then the overall equilibrium expression along with number of moles of various species participating in the formation of the s^{th} layer can be represented as:



In order to get the unit of equilibrium constant in terms of mole L^{-1} , the number of moles of adsorbate left in the solution “ $(n_a - n)$ ” at equilibrium condition can be expressed in terms of equilibrium concentration “[A]” by considering the volume of solution. Thus the overall equilibrium constant expression can be written as:

$$\beta_s = \frac{n/s}{(wn_m - n/s)[A]^s} \quad (13)$$

where the overall equilibrium constant “ β_s ” has unit of $(\text{mole } L^{-1})^{-s}$. In the case of adsorption of a gas, the equilibrium concentration “[A]” is replaced by equilibrium pressure “P” to give:

$$\beta_s = \frac{n/s}{(wn_m - n/s)P^s} \quad (14)$$

Since equilibrium pressure is commonly expressed in unit of “Torr”, the unit of overall equilibrium constant “ β_s ” in Eq. (14) is “ Torr^{-s} ”. The formation of multilayers is more common in the gas phase adsorption process; therefore, Eq. (14) was utilized in subsequent analysis of adsorption equilibria.

Freundlich adsorption model

If the adsorption process occurs in such a way that any next layer is formed after completion of all previous adsorption layers at a given equilibrium pressure, then in such a case the rearrangement of Eq. (14) gives:

$$\frac{n}{wn_m} = \left(1 - \frac{n}{swn_m}\right) s\beta_s P^s \tag{15}$$

$$\frac{n}{w} = \left(1 - \frac{n}{swn_m}\right) s\beta_s n_m P^s \tag{16}$$

Eq. (16) is equivalent to an empirical Freundlich equation.⁷ It indicates that the coefficient of the empirical Freundlich equation is dependent on more than one parameter. At the lower range of coverage, i.e. where “n” approaches zero, the coefficient of Eq. (16) becomes:

$$\alpha = s\beta_s n_m \tag{17}$$

Thus the coefficient of the Freundlich equation can be regarded as constant in the region of low coverage provided “s” remains constant over the given range of equilibrium pressure. Since both “s” and “β_s” are variables and depend on the stoichiometry of the adsorption equilibria, the Freundlich equation Eq. (16) is not applicable in finding useful adsorption parameters like the monolayer adsorption capacity of an adsorbent.

BET adsorption model

If the adsorption process leads to the formation of different layers at a given equilibrium pressure, then in such a case Eq. (15) can be expressed as a sum of terms with different value of “s” to give:

$$\frac{n}{wn_m} = \left(1 - \frac{n}{wn_m}\right) \beta_1 P + \left(1 - \frac{n}{2wn_m}\right) 2\beta_2 P^2 \dots + \left(1 - \frac{n}{swn_m}\right) s\beta_s P^s \tag{18}$$

The rearrangement and separation of variables gives:

$$\frac{n}{wn_m} = \frac{\beta_1 P + 2\beta_2 P^2 + 3\beta_3 P^3 \dots + s\beta_s P^s}{1 + \beta_1 P + \beta_2 P^2 + \beta_3 P^3 \dots + \beta_s P^s} \tag{19}$$

$$\frac{n}{wn_m} = \frac{\sum_1^s s\beta_s P^s}{1 + \sum_1^s \beta_s P^s} \tag{20}$$

Further rearrangement of Eq. (20) gives rise to an Froneaus integral equation^{15,16} of the form:

$$\ln F = \int_0^P \left(\frac{n}{wn_m}\right) \frac{dP}{P} \tag{21}$$

where

$$F = 1 + \sum_1^s \beta_s P^s \tag{22}$$

The integral in Eq. (21) can be evaluated numerically on the basis of the trapezoidal rule. The Froneaus equation is extensively used in complexation studies for evaluation of various equilibrium constants.^{15,16} Thus the adsorption process can be treated like a complexation process provided that the monolayer adsorption capacity “ n_m ” of the adsorbent is known. In fact, the evaluation of the monolayer adsorption capacity of an adsorbent prior to the determination of various equilibrium constants can be considered the main difference between adsorption and complexation studies.

Eq. (20) can be applied to calculate the estimated number of moles of adsorbate adsorbed at a given equilibrium pressure (or concentration) using the known values of various overall equilibrium constant and monolayer adsorption capacity of the adsorbent. Since the monolayer adsorption capacity “ n_m ” is an unknown parameter in adsorption studies, Eq. (20) was simplified to get an expression applicable for finding the monolayer adsorption capacity of the adsorbent by expressing the overall equilibrium constants in terms of the product of corresponding step-wise equilibrium constants in accordance with Eq. (11) along with the assumption that the step-wise equilibrium constants of any adsorption layer except the first one are equivalent in magnitude. On the basis of this assumption, the ratio of equilibrium constant for the formation of the first layer to that of any next layer can be expressed as:¹⁰

$$\frac{K_1}{K} = C \quad (23)$$

where “ K ” is the equilibrium constant for the formation of any layer other than the first one and “ C ” is the ratio of “ K_1 ” to “ K ”. On introducing Eq. (23) into Eq. (20) one may get:

$$\frac{n}{wn_m} = \frac{CKP \sum_1^s s (KP)^{s-1}}{1 + C \sum_1^s (KP)^s} \quad (24)$$

For $KP < 1$, which is possible at lower equilibrium pressure (or concentration in the case of adsorption from solution), the sum of the terms in the denominator of Eq. (24) can be simplified on the basis of the power series in “ KP ” to give:

$$\sum_1^s (KP)^s = \frac{KP}{1 - KP} \quad (25)$$

The sum of terms in the numerator of Eq. (24) is the derivative of the sum of the terms in the denominator; thus on taking the derivative of Eq. (25) one gets:

$$\sum_1^s s (KP)^{s-1} = \frac{1}{(1 - KP)^2} \quad (26)$$

Substitution of values of the summation terms from Eq. (25) and (26) into Eq. (24) and rearrangement give:

$$\frac{n}{wn_m} = \frac{CKP}{(1 - KP)(1 - KP + CKP)} \quad (27)$$

If the value of equilibrium constant “ K ” is known then Eq. (27) can be rearranged to give the following equation

similar to the BET equation:¹⁰

$$\frac{1}{\frac{n}{w} \left(\frac{1}{KP} - 1 \right)} = \frac{1}{Cn_m} + \frac{(C-1)}{Cn_m} KP \quad (28)$$

At saturated vapor pressure “ P^o ” equilibrium exists only between the liquefied gas layer and saturated vapors; therefore, one can assign a reference value of “ $1/P^o$ ” to equilibrium constant “ K ”.¹⁰ Thus the magnitude of “ KP ” in the case of gaseous adsorption process can be given as:

$$KP = \frac{P}{P^o} \quad (29)$$

Since $P^o \gg P$ in the region of lower equilibrium pressure, it fulfills the condition of $KP < 1$ in Eq. (25). Thus the BET equation is valid only in the lower equilibrium pressure region. The slope and intercept of the BET plot on the basis of Eq. (28) are commonly used in the evaluation of monolayer adsorption capacity for surface area measurement.^{11,17} In the case of adsorption from liquid phase, the equilibrium pressure “ P ” in Eq. (28) can be replaced by equilibrium concentration “[A]”. However, in this case, the magnitude of equilibrium constant “ K ” must be known experimentally for onward evaluation of monolayer capacity on the basis of the BET plot.

Langmuir adsorption model

Since the adsorption process occurs in a step-wise manner leading to the formation of different layers and the formation of the first adsorption layer is more favorable at lower equilibrium pressure (or concentration in the case of adsorption from solution), Eq. (14) for $s = 1$ can be rearranged to give the following linear form of Langmuir adsorption equation:^{8,9}

$$\frac{1}{(n/w)} = \frac{1}{n_m} + \frac{1}{n_m K_1 P} \quad (30)$$

where “ K_1 ” is the first step-wise equilibrium constant and is equal to “ β_1 ”. The magnitude of intercept and slope of the Langmuir plot can be utilized to find “ n_m ” and “ K_1 ”. At higher equilibrium condition, the Langmuir plot may deviate from linearity due to the formation of more than one adsorption layer at a given equilibrium pressure.

The formation of the last layer is more favorable in the region of higher equilibrium pressure (or concentration). Thus the estimated value of “ K ” required for evaluation of the monolayer adsorption capacity of adsorbent on the basis of the BET plot in the liquid phase adsorption process can be obtained from the linear portion of the Langmuir plot in the region of higher equilibrium concentration. In such condition, according to Eq. (5), analysis of the intercept of the linear portion of the Langmuir plot may give “ s ” time higher value of monolayer adsorption capacity “ n_m ” due to the formation of “ s ” number of adsorption layers in the last step. Thus the analysis of the Langmuir plot in the region of higher equilibrium concentration can also be utilized in finding the maximum number of adsorption layers and ligand number in adsorption and complexation studies, respectively.

Experimental

Adsorption study of nitrogen gas on surface area reference material

In order to confirm the validity of the Langmuir plot in the region of low equilibrium pressure for finding the monolayer adsorption capacity, the nitrogen adsorption on surface area reference material (SARM), Cat No.2005 having reference BET surface area of $107 \text{ m}^2 \text{ g}^{-1}$ provided by Quantachrome Instruments USA was studied by using Autosorb-1C, (Quantachrome, USA) at liquid nitrogen temperature.

Complexation study of uranyl ions with acetate ions

The application of the Langmuir plot in finding the ligand number of a complex was investigated on the basis of complexation of uranyl ions with acetate ions at 0.1 M ionic strength maintained by using NaNO_3 . The pH was measured with a Metrohm model 781 pH/ ion meter with combination glass electrode and temperature sensor. All chemicals were of analytical grade purity and the temperature was maintained at 25°C . The equimolar (0.25 M) mixture of acetic acid and sodium acetate was added in small increments to 30 mL of electrolyte containing 1.5×10^{-4} mol of uranyl ions. The equilibrium concentration of acetate ions after complexation was evaluated at given pH on the basis of the following expression obtained by rearrangement of the relation between pK_a and pH:¹⁸

$$[A] = \text{antilog} \left[(\text{pH} - \text{pK}_a) - \log \left(\frac{f_{AV}}{1000(n_{HA} - n_{H^+} + n_{H^+}^0)} \right) \right] \quad (31)$$

where pK_a is the negative logarithm of the dissociation constant of acetic acid and its value was taken as 4.76 for acetic acid.¹⁹ "V" is the total volume of solution (in mL), " n_{HA} " is the number of moles of acetic acid added, " $n_{H^+}^0$ " is the number of moles of hydrogen ions present in the electrolytic solution containing only uranyl ions, and " n_{H^+} " is the total number of moles of hydrogen ions present in solution after each addition of the mixture of acetic acid and acetate ions. The value of " n_{H^+} " in a given volume of solution was evaluated on the basis of the following relations:

$$n_{H^+} = \left(\frac{a_{H^+}}{f_{H^+}} \right) \frac{V}{1000} \quad (32)$$

$$a_i = C_i f_i \quad (33)$$

where " a_i " is the activity, " f_i " is the activity coefficient and " C_i " is the concentration of given ion. The activity of hydrogen ions was obtained from pH, which is the negative logarithm of hydrogen ions activity. Similarly, the magnitude of " $n_{H^+}^0$ " was evaluated in 30 mL of electrolyte containing only uranyl ions. The magnitude of activity coefficient of ions was calculated on the basis of the following Davies equation:²⁰

$$-\log f_i = \alpha Z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \quad (34)$$

where " Z_i " is the charge of an ion, "I" is the ionic strength, and " α " is a constant depending on the temperature and dielectric constant of the solution. The values of " α " and "I" were evaluated by using the following

relationships:

$$\alpha = \frac{2.621 \times 10^3}{T^{3/2}} \text{ (for aqueous solution)} \quad (35)$$

$$I = \frac{1}{2} \sum Z_i^2 C_i \quad (36)$$

where “T” is the temperature in Kelvin.

Results and discussion

Evaluation of monolayer adsorption capacity of SARM

The monolayer adsorption capacity of SARM was evaluated on the basis of nitrogen adsorption study. In order to analyze the BET and Langmuir plots, the number of moles of nitrogen gas adsorbed per gram of SARM at different relative pressures was calculated from the volume of nitrogen gas adsorbed using the relation:

$$\frac{n}{w} = \frac{dV_{ad}}{M} \quad (37)$$

where “d” is the density of gas, “ V_{ad} ” the volume of gas adsorbed per gram of SARM, and “M” the molecular weight of nitrogen gas (28.0134 g mol⁻¹). Figure 1 gives the BET plot on the basis of Eq. (28). The occurrence of a slight curvature in the BET plot at the higher relative pressure region is attributed to the theoretical condition for obtaining Eq. (25) and the slight difference in the magnitude of step-wise equilibrium constants for the formation of different adsorbed layers. The analysis of the slope and intercept of the linear portion of the BET plot in the lower relative pressure region (0.05 to 0.3) gave the monolayer adsorption capacity of 1.068×10^{-3} mol g⁻¹. The surface area “ S_a ” of SARM was calculated by using the relation:

$$S_a = n_m N A_{cs} \quad (38)$$

where “N” is the Avogadro’s number (6.022×10^{23} molecules/mole) and “ A_{cs} ” is the cross-sectional area of nitrogen molecule (16.2×10^{-20} m²). The surface area of the SARM was calculated to be 104 m² g⁻¹, which was close to the reference value of 107 m² g⁻¹.

The curvature in the Langmuir plot (Figure 2) was more apparent due to the existence of more than one adsorption layer at a given equilibrium pressure. The monolayer adsorption capacity was also evaluated from the intercept of the Langmuir plot in the region of low equilibrium pressure. The observed value of monolayer adsorption capacity (1.347×10^{-3} mol g⁻¹) was in the same range as obtained from the BET plot. It indicated the validity of the fact that the formation of the first adsorption layer is more favorable in the region of low equilibrium pressure. Here it was desired to discuss the application of monolayer adsorption capacity in the analysis of thickness of adsorbed layer (t), which can be calculated on the basis of the following relation:

$$t = D\bar{n} \quad (39)$$

where “D” is the diameter of adsorbate molecule, which is 3.54×10^{-10} m for nitrogen molecule, and “ \bar{n} ” is the fraction of number of adsorption layers, which can be obtained on the basis of the following relation:

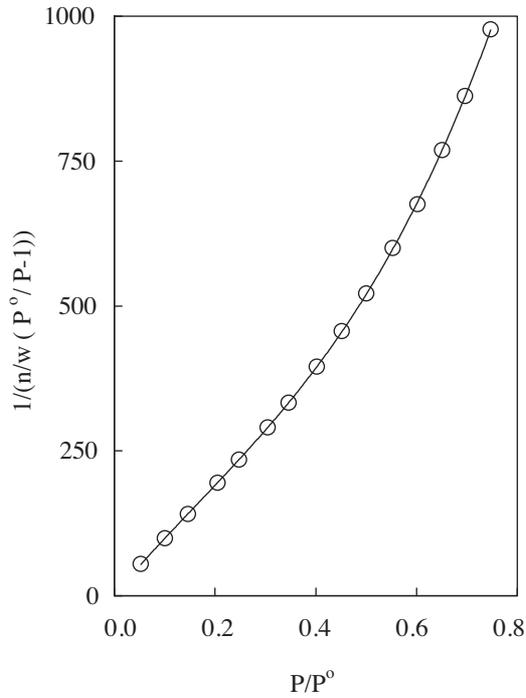


Figure 1. BET plot of nitrogen adsorption on surface area reference material (SARM).

$$\bar{n} = \frac{n}{wn_m} \tag{40}$$

The thickness of the adsorbed nitrogen layer in Angstroms can also be evaluated on the basis of the following de Boer equation:²¹

$$t = \left[\frac{13.99}{\log \left(P^0/P \right) + 0.034} \right]^{1/2} \tag{41}$$

The de Boer equation is considered valid up to a relative pressure of 0.75.²¹ The resemblance of data of thickness of the adsorbed layer evaluated on the basis of Eq. (39) and (41) up to a relative pressure of 0.75 as shown in Figure 3 indicated the validity of Eq. (39) in adsorption layers analysis.

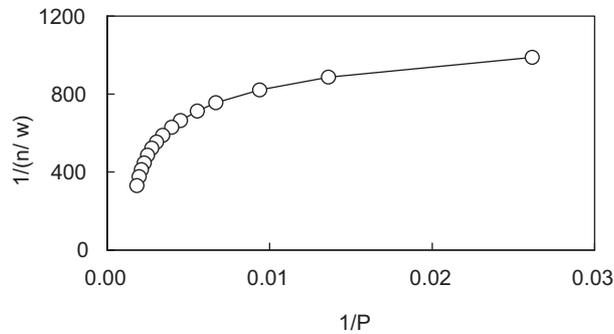


Figure 2. Langmuir plot of nitrogen adsorption on SARM.

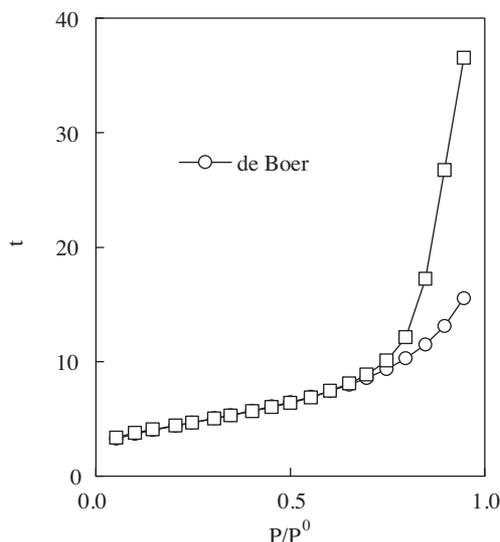


Figure 3. Plot of thickness of adsorbed layer “t” (in Angstrom) as a function of relative pressure “P/P°” (thickness data obtained on the basis of Eq. (39) and (41)).

Evaluation of ligand number of uranyl acetate complexes

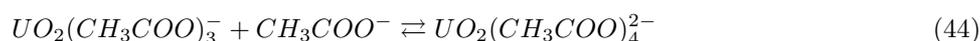
The maximum ligand number “s” of uranyl acetate complexes was determined on the basis of the Langmuir equation using the fact that the step-wise complexation process leads to the formation of the last complex in the region of higher equilibrium concentration of ligand ions where the Langmuir equation may be expressed as:

$$\frac{1}{n} = \frac{1}{sn^{\circ}} + \frac{1}{sn^{\circ}K[A]} \quad (42)$$

where

$$n^{\circ} = wn_m \quad (43)$$

The numbers of moles of acetate ions complexed “n” were determined by taking the difference of number of moles of acetate ions added and the number of moles found at equilibrium state after complexation. The “n°” is a known parameter in complexation studies and, in the present case, it was equal to 1.5×10^{-4} mol corresponding to the number of moles of uranyl ions added to the solution. The magnitude of “sn°” was obtained from the intercept of the linear portion of the Langmuir plot (Figure 4) in the region of higher equilibrium concentration of acetate ions. The calculated values of “sn°” was close to 6.0×10^{-4} mol, which is 4 times higher than the actual value of “n°”. It is attributed to the existence of the following fourth step in the course of formation of uranyl acetate complexes:



The average value of step-wise equilibrium constant “K” for the formation of higher order uranyl acetate complexes was calculated from the slope of the Langmuir plot and found to be $92 \text{ (mol L}^{-1}\text{)}^{-1}$. On using this value of “K” in Eq. (28), the BET plot (Figure 5) in the region of lower equilibrium concentration of acetate

ions gave “ n^o ” of 1.54×10^{-4} mol, which is almost equal to the actual number of moles of uranyl ions present in solution. It indicated the resemblance between complexation and adsorption processes. This result also indicated that one may utilize the equilibrium constant data obtained from the linear portion of the Langmuir plot in the region of higher equilibrium concentration in finding the monolayer adsorption capacity from the BET plot of the adsorption process occurring from the liquid phase.

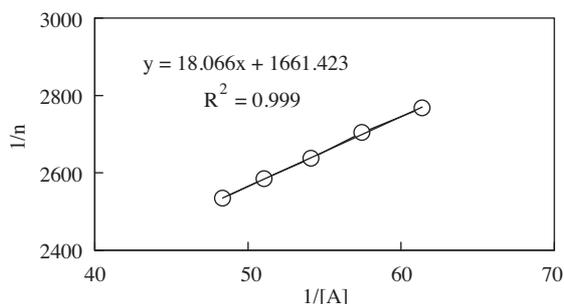


Figure 4. Langmuir plot in the region of high equilibrium concentration of acetate for evaluation of ligand number (“ n ” is the number of moles of acetate ions complexed and “[A ” is the equilibrium concentration in mol L⁻¹ of acetate ions).

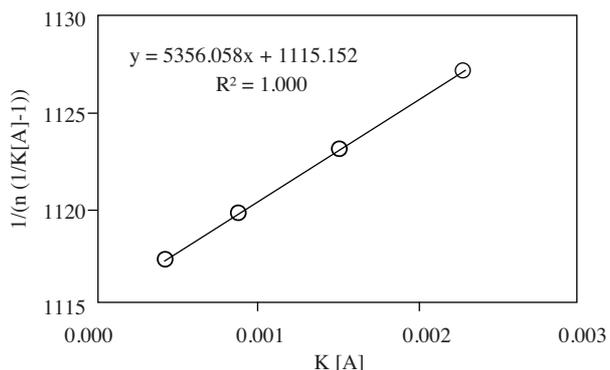


Figure 5. BET plot in the region of low equilibrium concentration of acetate ions “[A ” for evaluation of number of moles of uranyl ions present in solution on the basis of complexation data.

The exact values of various step-wise equilibrium constants of uranyl acetate complexes were evaluated from overall equilibrium constants obtained from the data in Figure 6 on the basis of the plot of the polynomial function “ F ” vs. “[A ”]. The positive values of coefficients of “ F ” up to 4 degrees of polynomial were observed, which confirmed the existence of maximum 4 acetate ions in uranyl acetate complexes. The magnitudes of various step-wise equilibrium constants were obtained on the basis of Eq. (11), which gives the relationship between step-wise and overall equilibrium constants. The values of K_1 , K_2 , K_3 , and K_4 were 534, 134, 61, and 23 (mol L⁻¹)⁻¹ respectively. The average value of equilibrium constants of the last 3 complexes was close to the value of “ K ” obtained from the analysis of linear portion of the Langmuir plot in the region of higher equilibrium concentration of acetate ions.

Advantages of the present theory

The present theory proved the fact that the adsorption process can be studied just like the complexation process provided that the monolayer adsorption capacity of the given adsorbent is known. Since the fundamental adsorption equations (Freundlich, Langmuir, and BET) were developed on the basis of general equilibrium constant expression in accordance with the law of mass action, one can easily understand, interpret, and explore the physical nature of various adsorption parameters. It was the advantage of physical interpretations made on the basis of the present theory that the Langmuir equation was modified to a suitable form applicable for finding the ligand number of a complex and the magnitude of “ K ” required for analysis of BET equation in liquid phase adsorption study.

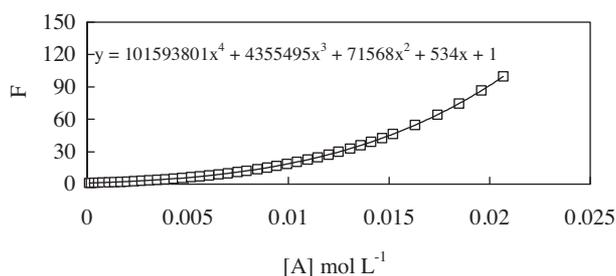


Figure 6. The plot of polynomial function “F” vs. equilibrium concentration of acetate ions “[A]” used for evaluation of overall and step-wise equilibrium constants.

Conclusions

A general approach towards physical interpretation of adsorption parameters may be established on the basis of general equilibrium constant expression in accordance with the law of mass action. It was shown theoretically that the Freundlich equation is not applicable in finding useful adsorption parameters. The linear portion of the Langmuir plot in the region of low and high equilibrium pressure (or concentration) may, however, be analyzed to obtain useful parameters in adsorption and complexation studies.

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