Hydration of Inorganic Solid Powder in the Presence and Absence of Polar and Nonpolar Oil

Ahindra Nag
Bio-Organic Laboratory, Chemistry Department, Indian Institute of Technology, Kharagpur - 721 302, India

The hydration of powdered barium sulfate in the presence and absence of oils has been thoroughly investigated by the isopiestic vapor pressure technique. The water vapor adsorption isotherms studied at three different temperatures are in good agreement with the type II BET isotherm. Values of n_1 and Δn_1° at a given value of p/p_o in the presence of polar and nonpolar oils are always higher than the corresponding values in the absence of oil. The adsorption of water vapor depends on the nature and amount of oil present. Temperature has a significant effect on the adsorption process in the presence of oil. The magnitude of the integral enthalpy change (ΔH°_{int}) is much larger than that observed for barium sulfate in the absence of oil. The absolute binding of water (Δn_1) and solute (Δn_2) in the presence of sodium chloride are much higher than those for barium sulfate in the absence of oil.

KEY WORDS: Barium sulfate, hydration, isopiestic vapor pressure technique, nonpolar oil, polar oil.

Adsorption of water, gases, proteins and organic compounds has been studied on solid powder (*e.g.*, alumina, silica, glass powder) by several investigators (1-3, and Nag, A., unpublished data). But no information is available about the hydration of inorganic solid, such as barium sulfate particles, in the presence and absence of oil. Barium sulfate powder has been selected for this study because attempts have been made from time to time to prepare oil-containing barium sulfate suspensions for radiological purposes (4). An attempt has been made to study those phenomena that may have some importance in understanding the physicochemical characteristics associated with the preparation of stable barium sulfate suspensions with oil.

MATERIALS AND METHODS

Barium sulfate used was from E. Merck (Darmstadt, Germany). The moisture content, determined by heating at 600°C for 8 h, was 0.3% by weight of barium sulfate. The surface area (A_f) of the barium sulfate particles, determined by palmitic acid adsorption, was 8.0 ± 0.5 m^2/g. Doubly refined peanut oil, called groundnut oil in India (density 0.92 g/cm^3, b.p. above 200°C), was purchased from the market and was used as a polar oil. Nujol (density 0.85 g/cm^3, b.p. 350°C), an A.R. grade nonpolar oil, was purchased from the BDH Company (Poole, England) and was used as received.

The isopiestic vapor pressure technique has been used for measuring the uptake of oil by barium sulfate powder. At first the weight (W_1 in grams) of a specially designed weighing bottle (5 mL capacity) with its lid was taken. A definite amount (approximately 1.0 g) of stock powdered solid was placed inside the weighing bottle and the weight of the bottle containing the inorganic oxide (W_2 g) was determined. After proper correction for the initial moisture content of the barium sulfate, the weight of the dry inorganic powder (W_d) was calculated. The bottle without its lid was then allowed to float on 250 mL of a sulfuric acid solution (called the reference solution) in a specially designed vacuum desiccator. The desiccator was then evacuated appropriately and maintained at 25 ± 2°C in a chamber. The reference solution was magnetically stirred from the outside. Exchange of water vapor between the barium sulfate powder and the sulfuric acid solution does take place. Isopiestic equilibrium was found to be attained within a period of five days, after which the weight (W_3) in grams of the weighing bottle with its lid was taken. From these weight data, moles of water (n_1) adsorbed per gram of dry inorganic powder were calculated from the relation:

$$n_1 = \frac{W_3 - (W_1 + W_d)}{W_d\, M_w} \qquad [1]$$

where M_w stands for the molecular weight of water. The standard error for such measurements lies within 0.3%.

The concentration of sulfuric acid was analyzed at isopiestic equilibrium by direct titration. From the known acid concentration, the relative vapor pressure (p/p_o) or the activity of water (a_1) was directly calculated (5). The relative vapor pressure was varied between unity and zero by varying the sulfuric acid concentration in the reference vessel.

Barium sulfate powder mixed with oils was prepared as follows. A weighted amount of a particular oil was put into a weighing bottle. A required amount of barium sulfate was placed in a mortar/pestle, to which the previously weighed amount of oil was added slowly and mixed thoroughly with a spatula. The oil remaining on the inside surface of the weighing bottle was taken out by pouring a little quantity of the powder from the mortar and mixing it with the spatula. The process was repeated several times until the adhered oil was transferred as far as possible. The error involved due to this type of transfer process was negligible. A definite amount of this mixture was placed inside sample bottles, and isopiestic experiments were carried out as described earlier. At isopiestic equilibrium of an oil/solid mixture, the amount (n_1) of water adsorbed was calculated by using Eq. [1], and was expressed per gram of solid barium sulfate powder.

The study of hydration of barium sulfate powder also was carried out in the presence of electrolyte. A known weight of concentrated salt solution of known molality was placed inside the sample bottle containing barium sulfate powder, thus forming the sample mixture. The sample bottle was then placed inside the desiccator containing the reference electrolyte solution. At isopiestic equilibrium the weight of the sample bottle was taken and the number of moles of water (n_1^t) and solute (n_2^t) adsorbed per gram of barium sulfate were calculated as follows:

$$n_1^t = \frac{W_3 - (W_1 + W_d + W_s)}{W_d} \frac{1}{M_w} \qquad [2]$$

$$n_2^t = \frac{W_s/M_s}{W_d} \qquad [3]$$

where M_w and M_s are the molecular weights of water and the salt, respectively. From the molality (m_2) of the solute of the reference solution, the mole fractions X_1 and X_2 of water and solute were determined, so that the relative amounts of solvent and solute bound in moles per gram of barium sulfate were calculated from the following relations:

$$n_1^t - n_2^t \frac{X_1}{X_2} = \Delta n_1 - n_2 \frac{X_1}{X_2} \qquad [4]$$

$$n_2^t - n_1^t \frac{X_2}{X_1} = \Delta n_2 - n_1 \frac{X_2}{X_1} \qquad [5]$$

RESULTS AND DISCUSSION

In Figure 1, moles (n_1) of water vapor adsorbed per gram of barium sulfate have been plotted against water activity ranging from zero to unity at three different temperatures. The shape of the isotherms is in good agreement with that expected for a type II BET isotherm. In the range of relative humidity 0.1–0.5, n_1 is insensitive to the change of p/p_0. Qualitatively, this insensitivity is due to formation of the primary layer of water at the surface of the solid. This layer in direct contact with the surface is believed to be a monolayer (6). Adsorption, however, increases significantly beyond 0.5 relative humidity, due to the formation of multilayers of adsorbed molecules. From the linear extrapolation of n_1 in the range of 0.9 to 1.0 relative humidity, the maximum value of n_1 (to be referred to as n_1^o) has been evaluated. Values of n_1^o are presented in Table 1.

In Figure 2, values of $p/p_o/\{n_1(1 - p/p_o)\}$ calculated from the experimental data have been plotted against p/p_o. According to the BET equation, such a plot is to be linear (8):

$$\frac{p/p_o}{n_1(1 - p/p_o)} = \left(\frac{C - 1}{n_1^m C}\right) p/p_o \frac{1}{n_1^m C} \qquad [6]$$

Here, C is the BET constant related to the heat of adsorption. Also, n_1^m stands for the moles of water required to completely cover the surface of 1 g of the powdered substance with a monolayer of water. Figure 2 shows that adsorption of water vapor follows the BET equation in linear form only in the range of vapor pressure from zero to 0.3. Values of the BET constant C and n_1^m are presented in Table 1.

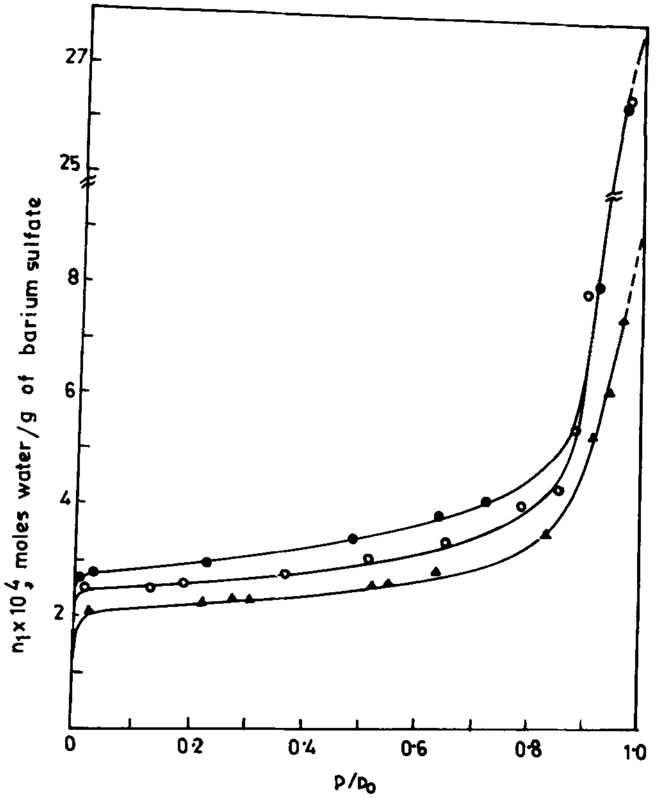

FIG. 1. n_1 *vs.* p/p_0 plot for barium sulfate at a temperature of 10°C (●), 25°C (○) and 50°C (▲).

Above 0.3 r.h., however, there is gross deviation from linearity in the BET plot. There are various reasons for the deviation of the adsorption data from the BET equation. These are discussed by Adamson (7).

From the slope and the intercept of the linear plot, the surface area (A_w) per gram of the barium sulfate powder has been calculated as 19.0 m² (Table 1). Surface area

TABLE 1

Values of n_1^o, ΔG^o_w, C, n_1^m and A_w for Barium Sulfate in the Presence and Absence of Oil at Different Temperatures

System	Temp. (°C)	$n_1^o \times 10^3$ (moles/g)	ΔG^o_w (J/g)	Constant (C) of BET equation	$n_1^m \times 10^4$ (moles/g) from BET plot	Surface area (A_w) from BET plot (m²/g)
Barium sulfate	10	2.8	5.5	—	—	—
Barium sulfate	25	2.8	6.0	17.6	3.2	19.0
Barium sulfate	50	0.88	3.9	—	—	—
Barium sulfate + 4% polar oil	25	5.1	12.0	20.0	5.5	33.5
Barium sulfate + 8% polar oil	25	7.3	56.1	—	—	—
Barium sulfate +8% polar oil	50	1.4	7.8	—	—	—
Barium sulfate + 8% nonpolar oil	25	10.6	70.2	—	—	—

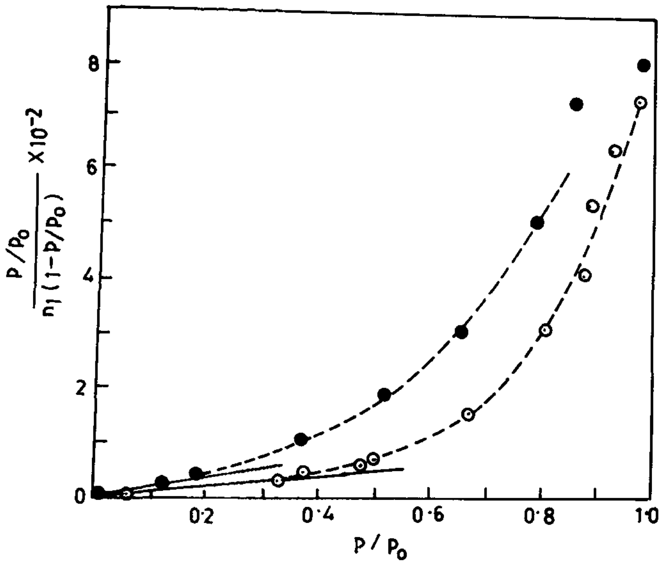

FIG. 2. Plots of $(p/p_o)/[n_1(1 - p/p_o)]$ against p/p_o at 25°C barium sulfate (●), and barium sulfate mixed with 4% polar oil (◎).

estimated in this manner is not very accurate because the BET equation remains valid only in a small range of pressure. The specific surface area (A_f) of barium sulfate determined from the adsorption of palmitic acid in benzene is lower than A_w. The ratio A_w/A_f is slightly higher than two. It has been noted (1) that this ratio for alumina and silica gels becomes 10 or more. Unlike alumina and silica, barium sulfate does not form well-defined hydrogels. Also, the Merck variety of barium sulfate used in this experiment in all probability has been prepared by powdering large crystals so that most of the particles remain in the form of single crystals and not as agglomerates of colloidal particles. The higher value of A_w in the case of barium sulfate can be explained by the fact that microcracks and micro-capillaries exist near the surface of these particles where hidden ionic groups of the crystal may be hydrated. Fatty acid molecules, however, are unable to enter these cracks and crevices. Hence, the value of A_f is less.

The free energy change $\Delta G^o{}_w$ for hydration of barium sulfate powder while bringing the relative vapor pressure from zero to unity can easily be calculated from:

$$\Delta G^o{}_w = -RT \int_{p/p_o=0}^{1} \frac{n_1}{(p/p_o)} \, d\,(p/p_o) \qquad [7]$$

Since $\Delta G^o{}_w$ is negative in all cases (Table 2), one can conclude that hydration of solid powder of barium sulfate is spontaneous in nature. However, the value of $\Delta G^o{}_w$ for barium sulfate is less than for alumina and silica. Dividing $\Delta G^o{}_w$ by A_w or A_f, the free energy change $\Delta G^o{}_{ws}$ per square meter of the surface can be calculated. $\Delta G^o{}_{ws}$ for barium sulfate, alumina and silica particles are compared in Table 2. Values of n_o^s (equal to $\Delta n_1{}^o/A_f$) for the three inorganic oxides are also compared in Table 2. In Table 3, values of the extent of adsorption, n_s (equal to n_1/A_f) per square meter of the surface for different particles also have been compared at several values of p/p_o. At 0.3 relative humidity, values of n_s for barium sulfate and silica are considerably lower in magnitude than for alumina. At 0.95 humidity, however, n_s for silica has the highest value. ΔG_{ws} and n_s thus depend significantly on the nature and structure of the solid surface.

Figure 1 shows that n_1 at a given value of p/p_o, as well as $\Delta n_1{}^o$, decreases with an increase of temperature from 25–50°C. This clearly indicates that the adsorption of water vapor is physical in nature and that the value of the heat of adsorption is relatively low. The integral enthalpy $\Delta H^o{}_{int}$ for the adsorption of water vapor by the solid powder in the range of relative humidity from zero to unity can be calculated from:

$$\Delta H^o{}_{int} = -R \int_0^{n_1{}^o} \left[\frac{T_1 T_2}{T_2 - T_1} \ln \frac{(p_2/p_o)}{(p_1/p_o)} \right] dn_1 \qquad [8]$$

Here p_2/p_o and p_1/p_o are the relative vapor pressures at temperatures T_1 and T_2, respectively, which will produce the same extent of water vapor adsorption (*i.e.*, same value of n_1) by 1 g of solid powder. Eq. [8] is based on the validity of the Clasius-Clapeyron equation, so that $\Delta H^o{}_{int}$ is the average change in the enthalpy with respect to the average temperature 1/2 $(T_1 + T_2)$. The bracketed term for different values of n_1 between zero and $\Delta n_1{}^o$ can be calculated for T_1 and T_2 from the experimental data, so that the right side of Eq. [8] can be graphically integrated. The values of $\Delta H^o{}_{int}$ and the average value of $\Delta G^o{}_{av}$ (in the temperature range of T_1 and T_2 close to each other) are given in Table 2. One finds that $\Delta G^o{}_{av}$ is close to $\Delta H^o{}_{int}$, and it appears that water vapor adsorption by powdered barium sulfate is mostly enthalpy-controlled. The contribution of entropy is relatively low in the process of hydration of the solid powder.

Hydration of barium sulfate powder also has been measured at various values of p/p_o after mixing the powder with a definite amount of nonvolatile oil. Both

TABLE 2

$n_o{}^s$ (= $n_1{}^o/A_f$) and Thermodynamic Parameters for Barium Sulfate, Alumina and Silica

	$n_o{}^s \times 10^4$ (moles/m^2)	$\Delta G^o{}_{ws}$ $\frac{(\Delta G^o{}_w)}{A_f}$ (J/m^2)	Average temperature (°K)	$\Delta G^o{}_w$ (J/g)	$\Delta H^o{}_{int}$ (J/g)
Barium sulfate	3.4	0.7	290.5	5.8	4.2
Barium sulfate	—	—	310.5	4.9	8.4
Barium sulfate + 8% polar oil	—	—	310.5	32.0	496.0
Alumina	6.7	3.4	—	—	—
Silica	7.3	1.9	—	—	—

TABLE 3

Comparison of the Values of n_s (= n_l/A_f) at Various Water Activities for Barium Sulfate, Alumina and Silica

	$n_s \times 10^5$ (moles/m^2)		
p/p_0	Barium sulfate	Alumina	Silica
0.30	3.4	20.0	6.1
0.50	3.7	21.5	10.6
0.70	4.4	25.5	18.0
0.80	5.0	26.2	26.6
0.85	5.5	26.8	37.2
0.90	7.5	28.2	49.1
0.95	31.2	39.6	60.9

polar and nonpolar oils were used for this purpose. The double-refined groundnut oil is a high-boiling liquid (b.p. above 200°C), and its vapor pressure is negligible at ordinary temperatures. The nonpolar hydrocarbon oil used was nujol, whose boiling point is also high. Hydration of the oil studied by the isopiestic method is negligible in the relative pressure range from zero to unity at prevailing temperatures. Both oils are water repellent. The vapor phase in the isopiestic experiment is assumed to be composed solely of water molecules, and the number of oil molecules in the vapor phase is taken to be negligible. The isotherms for the adsorption of water vapor by barium sulfate in the presence of different types and amounts of oil have been presented in Figure 3. It is of considerable interest that at a given value of p/p_0, values of n_1 and Δn_1° (obtained from the extrapolation of the curve) in the presence of polar and nonpolar oil are always higher than the corresponding values in the absence of oil. Increasing the amount of polar groundnut oil from 4–8%, both n_1 and Δn_1° increase to a significant extent (Fig. 3 and Table 1). Surprisingly, in the presence of 8% oil, n_1 at a given p/p_0 and the extrapolated value of Δn_1° for nonpolar oil at 25°C are higher than those in the presence of the same percentage of polar oil.

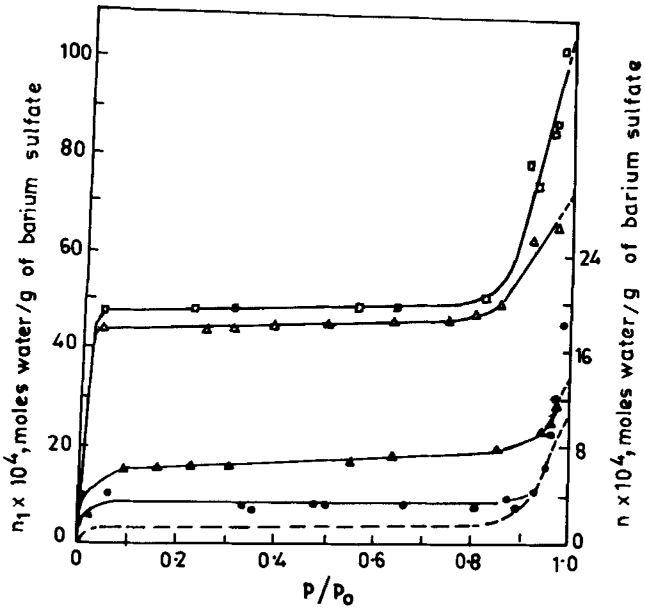

FIG. 3. n_1 *vs.* p/p_0 plots at 25°C and 50°C for various systems. Barium sulfate at 25°C (——), barium sulfate +4% polar oil at 25°C (●), barium sulfate +8% polar oil at 25°C (△), barium sulfate +8% nonpolar oil at 25°C (□), and barium sulfate +8% polar oil at 50°C (▲) (right-lower scale).

It is interesting that, although oil itself has no tendency toward adsorption of water vapor, the solid powder in the presence of an oil acquires the capacity to absorb an enhanced amount of water vapor at a given temperature. In the presence of an oil, data from n_1 at different values of p/p_0 fit the BET equation in a wider range of relative vapor pressures (Fig. 3). The specific surface area of the solid with respect to the water-binding sites is increased considerably in the presence of oil (Table 1). This means that a larger number of water molecules remain in contact on the oil-coated surface as compared to those present at the bare surface in the form of a monolayer.

The magnitude of the free energy change ($-\Delta G^\circ_w$) due to the hydration of the solid surface also increases with an increase in the percentage of the groundnut oil (Table 1). In the presence of 8% polar oil, n_1 at a given value of p/p_0 and n_1° at 50°C are significantly lower than those observed at 25°C. This again qualitatively indicates that the adsorption of water vapor at the oil-coated solid surface is physical in nature. ΔH°_{int} (*vide* Eq. [8]) for temperatures between 25 and 50°C also has been calculated from the graphical integration. This value, presented in Table 2, is about 60 times larger than that observed for barium sulfate powder in the absence of oil. All these results indicate that water upon significant interaction with ionic sites of the barium sulfate surface leads to the evolution of heat and, further, that this adsorbed water is highly ordered, so that its entropy compared to the water vapor itself is significantly lower.

Hydration of barium sulfate powder, with and without mixing with 8% groundnut oil, also has been carried out in the presence of sodium chloride. The excess water binding per gram of the solid powder has been calculated with Eq. [4]. The calculation is based on the implicit assumption that pure oil is unable to bind any significant amount of water or solute. Values of Γ_1^n (moles of solute adsorbed per gram of the solid powder) in this case also vary linearly with X_1 (Fig. 4). From the slope and intercept of this plot, values of Δn_1 and Δn_2 are calculated from:

$$\Gamma_1^n = \Delta n_1 - (\Delta n_1 + \Delta n_2) X_1 \qquad [9]$$

These values are presented in Table 4. Comparison of these values with the corresponding values of Δn_1 and Δn_2 for sodium chloride in the absence of oil shows that Δn_1 and Δn_2 have increased about four times and three times, respectively, when 8% oil is added to the sample. Thus, addition of oil considerably increases the hydration capacity of barium sulfate powder in the presence of salt. The result is consistent with that obtained for the hydration of barium sulfate with and without oil in the absence of salt. The plausible reasons for the increase of the extent of hydration in the presence of oil have been discussed already.

ACKNOWLEDGMENTS

I am grateful to D.K. Chattoraj, Department of Food Technology and Biochemical Engineering, Jadavpur University, for his helpful suggestions.

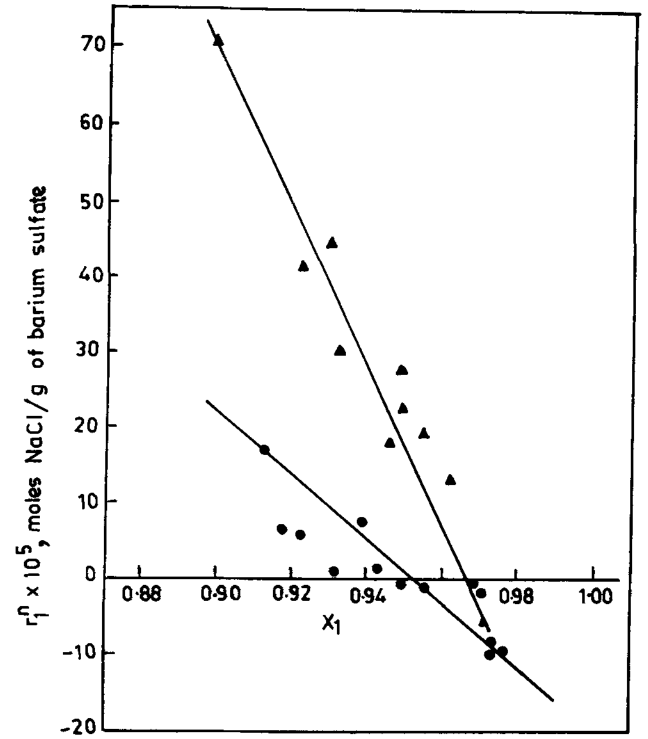

FIG. 4. Plot of Γ_1^n (moles/g) against X_1 for barium sulfate in presence of NaCl at 25°C, in absence of oil (●) and barium sulfate mixed with 8% polar oil (▲).

TABLE 4

Values of Δn_2 and Δn_2 for Barium Sulfate or Barium Sulfate and Oil Mixture in the Presence of Sodium Chloride

System	Solute	$\Delta n_1 \times 10^3$ (moles/g)	$\Delta n_2 \times 10^4$ (moles/g)
Barium sulfate	NaCl	3.0 ± 0.7	1.6 ± 0.4
Barium sulfate + 8% polar oil	NaCl	13.6 ± 2.3	5.2 ± 1.7

REFERENCES

1. Nag, A., B.K. Sadhukhan and D.K. Chattoraj, *Colloids and Surfaces 23*:83 (1987).
2. Nag, A., B.K. Sadhukhan and D.K. Chattoraj, *J. Surface Sci. Technol. 4*:91 (1988).
3. Bull, H.B., and K. Breese, *Archs. Biochem. Biophys. 137*:299 (1970).
4. Knoefil, P.K., *Radiology 66*:87 (1956).
5. Robinson, R.A., and R.H. Stokes, *Electrolytic Solutions*, Butterworths, London, 1959, p. 464.
6. Adamson, A.W., *Physical Chemistry of Surfaces*, 3rd edn., Wiley Interscience Publications, London, 1976, p. 561.
7. Adamson, A.W., *Ibid.*, pp. 566–570.

[Received October 18, 1991; accepted April 20, 1992]