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

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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 \( \Delta n_1 \) 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 \( \Delta H_{int} \) is much larger than that observed for barium sulfate in the absence of oil. The absolute binding of water \( (\Delta n_1) \) and solute \( (\Delta n_0) \) 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has been studied on solid powder (e.g., alumina, silica, glass powder) by several investigators (1-3, and Nag, A., unpublished data).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 \( (A_d) \) of the barium sulfate particles, determined by palmitic acid adsorption, was \( 8.0 \pm 0.5 \text{ m}^2/\text{g} \). Doubly refined peanut oil, called groundnut oil in India (density 0.92 g/cm³, b.p. above 200°C), was purchased from the market and was used as a polar oil. Nujol (density 0.85 g/cm³, 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 \( (W_1 \text{ in grains}) \) of a specially designed weighing bottle \( (5 \text{ mL capacity}) \) with its lid was taken. A definite amount \( (\approx 1.0 \text{ g}) \) of stock powdered solid was placed inside the weighing bottle and the weight of the bottle containing the inorganic oxide \( (W_s \text{ g}) \) 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 \( (\text{called the reference solution}) \) 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 \( (W_2 \text{ in grams}) \) 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:

\[
n_1 = \frac{W_2 - (W_1 + W_d)}{W_d M_w} \tag{1}
\]

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 by isopiestic equilibrium by direct titration. From the known acid concentration, the relative vapor pressure \( (p/p_o) \) or the activity of water \( (a_w) \) 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 a 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 \( (n_1) \) and solute \( (n_2) \) adsorbed per gram of barium sulfate were calculated as follows:

\[
n_1 = \frac{W_s - (W_1 + W_d + W_s)}{W_d} \frac{1}{M_w} \tag{2}
\]
\[ n_2^t = \frac{W_s/M_s}{W_d} \]  

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:

\[ n_1^t - n_2^t \cdot X_1 \cdot X_2 = (m_2 - n_1) \cdot X_2 \quad [4] \]

\[ n_2^t - n_1^t \cdot X_2 \cdot X_1 = (m_2 - n_1) \cdot X_1 \quad [5] \]

**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 \( p/p_o \). 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):

\[ \frac{p/p_o}{n_1(1 - p/p_o)} = \left( \frac{C - 1}{n_1^mC} \right) \cdot \frac{p/p_o}{n_1^mC} \quad [6] \]

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.

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**

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. (°C)</th>
<th>( n_1^o \times 10^4 ) (moles/g)</th>
<th>( \Delta G^w ) (J/g)</th>
<th>Constant (C) of BET equation</th>
<th>( n_1^m \times 10^4 ) (moles/g) from BET plot</th>
<th>Surface area (( A_w )) from BET plot (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium sulfate</td>
<td>10</td>
<td>2.8</td>
<td>5.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>25</td>
<td>2.8</td>
<td>6.0</td>
<td>17.6</td>
<td>3.2</td>
<td>19.0</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>50</td>
<td>0.88</td>
<td>3.9</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Barium sulfate + 4% polar oil</td>
<td>25</td>
<td>5.1</td>
<td>12.0</td>
<td>20.0</td>
<td>5.5</td>
<td>33.5</td>
</tr>
<tr>
<td>Barium sulfate + 8% polar oil</td>
<td>25</td>
<td>7.3</td>
<td>56.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Barium sulfate + 8% nonpolar oil</td>
<td>50</td>
<td>1.4</td>
<td>7.8</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

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