

APPARENT AND PARTIAL SPECIFIC SORPTION OF OXINE BY MONTMORILLONITE AND SILICA GEL IN BINARY MIXTURES

A. K. HELMY, E. A. FERREIRO, AND S. G. DE BUSSETTI
 Universidad Nacional del Sur, 8000 Bahía Blanca, República Argentina

Abstract—Oxine sorption by binary mixtures of montmorillonite and silica gel was studied at pH 5 as a function of oxine concentration and mixture composition. The investigation was made to resolve the problem of the determination of the oxine sorbed by each substance, inasmuch as the total amount sorbed by the mixture is the only value accessible experimentally. By the application of the thermodynamic method of partial quantities, the apparent and partial specific sorption by the clay and by the gel were calculated. These sorption values were found to increase with oxine concentration and to decrease as the proportion of the clay increased in the mixtures.

Key Words—Adsorption, Mixtures, Montmorillonite, Oxine, Silica gel, Specific sorption.

INTRODUCTION

Despite the many investigations of sorption from solution by solids in a wide range of natural and industrial systems, several problems remain. One of these is the determination of the amount sorbed by each in a mixture of sorbents. Thus, in a simple mixture of two sorbents, the amount sorbed by each is unknown, because the experimentally determined value is the difference between the initial and final concentration of sorbate in solution, which represents (in absence of solvent sorption) the total amount sorbed by both sorbents. The simplest way to resolve the problem is to assume an ideal mixture of sorbents and to distribute the total amount between the two, assuming that each sorbent acts independently. This state of affairs is not known beforehand, and the theoretical problem involved deserves consideration. In the following study we treat the problem of the determination of the amount sorbed by each component in a mixture of sorbents using the thermodynamic concept of partial quantities. The equations developed are applied to the sorption of oxine by a mixture of montmorillonite clay and silica gel.

THEORETICAL CONSIDERATIONS

If the adsorption of oxine by each material in a mixture of clay and silica follows the Langmuir equation, one may write for silica gel (Graham, 1953):

$$n_1 = a_1C/(1 + b_1C); \quad (1)$$

and for the clay:

$$n_2 = a_2C/(1 + b_2C), \quad (2)$$

where n_1 and n_2 are amounts sorbed in mmole/g, a and b are constants, and C is the oxine concentration.

At a particular concentration of oxine in a mixture of the two substances, n_1 and n_2 are constants inde-

pendent of the proportions of the sorbents in the mixture. Hence, the total amount X in millimoles sorbed by the mixture may be written as

$$X = w_1n_1 + w_2n_2, \quad (3)$$

where w_1 is the weight of silica in the mixture in grams and w_2 is that of the clay. Eq. (3) requires that a straight line be obtained by plotting X against w_2 , where w_1 , n_1 , and n_2 are constants. Such a straight line was not observed experimentally, as may be judged by the curves in Figure 1, indicating that the mixture deviated from ideality and independent sorption by each substance was not conserved in the mixture.

Properties which are not conserved on mixing, such as volume, entropy, free energy (and now sorption), are usually evaluated by thermodynamic methods employing partial quantities. In other words, corresponding to any extensive property are several partial quantities, the sum of which should give the value of the extensive quantity. Applying this concept to the sorption of oxine by a binary mixture of silica gel and clay,

$$X = w_1\bar{x}_1 + w_2\bar{x}_2, \quad (4)$$

where X is the total amount sorbed in mmoles and \bar{x}_1 and \bar{x}_2 are the partial specific sorption by silica gel and clay, respectively, in mmole/g. The partial quantities are defined by:

$$\bar{x}_1 = (\partial X/\partial w_1)_{T,P,w_2}, \quad (5)$$

and

$$\bar{x}_2 = (\partial X/\partial w_2)_{T,P,w_1}. \quad (6)$$

The evaluation of the partial quantities is usually made by means of so-called "apparent quantities," because the latter are the values obtained experimentally. Thus, if the total amount of oxine sorbed by a mixture of silica and clay is determined, while keeping constant

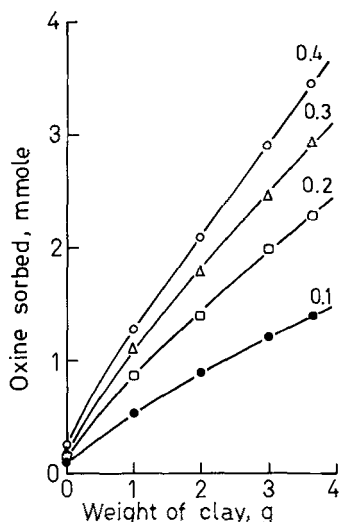


Figure 1. Total sorption vs. weight of clay in mixtures containing constant amount of silica gel (3.52 g). Values on curves are oxine concentrations in mmole/liter.

both the oxine concentration and the amount of gel and varying the amount of clay in the mixture, the apparent specific sorption by montmorillonite, ϕx_2 , can be defined as follows:

$$\phi x_2 = (X - w_1 x_1) / w_2 \quad (7)$$

The numerator of Eq. (7) represents the difference between total sorption by a mixture and the sorption by the pure gel which it contains. The experimental data obtained for ϕx_2 can then be fitted by least square methods to the second order equation:

$$\phi x_2 = \phi x_2^0 + a_2 w_2^{1/2} + b_2 w_2 \quad (8)$$

where ϕx_2^0 represents the specific sorption at infinite dilution of clay particles in the presence of a constant amount of gel and constant equilibrium oxine concentration, and a_2 and b_2 are constants. From Eq. (8) the partial specific sorption can be calculated directly as follows (Lewis and Randall, 1961):

From Eqs. (7) and (8),

$$X = w_1 x_1 + \phi x_2^0 w_2 + a_2 w_2^{3/2} + b_2 w_2^2 \quad (9)$$

Differentiating with respect to w_2 ($w_1 x_1$ constant) gives:

$$(\partial X / \partial w_2) = \bar{x}_2 = \phi x_2^0 + \frac{3}{2} a_2 w_2^{1/2} + 2 b_2 w_2 \quad (10)$$

Knowing \bar{x}_2 leads to the evaluation of \bar{x}_1 through Eq. (4).

MATERIALS AND METHODS

Two substances were utilized for the preparation of the mixtures used as sorbents of oxine: (1) Montmorillonite from Cerro Bandera, Argentina, having a cation-exchange capacity of 0.92 meq/g and a glycerol surface area of 808 m²/g (Peinemann *et al.*, 1972);

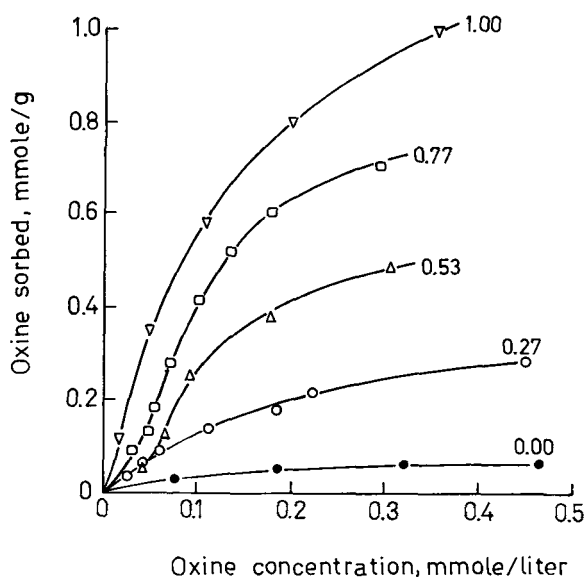


Figure 2. Oxine sorption vs. oxine concentration. Values on curves represent weight fraction of clay in the mixtures.

particles <2 μm were saturated with Ca by repeated washings with 0.5 M chloride salt followed by washing out of excess salt with the help of a centrifuge; (2) Silica gel obtained from Davison Chemical (No. 951 MS) having an average pore diameter of 67 Å and specific surface of 600 m²/g.

Analytical grade 8-hydroxyquinoline (oxine, C₉H₆NOH) was obtained from Riedel De Haën (Hanover, Germany). It had a molecular weight of 145.16 g, a melting point of 76°C, and a water solubility of about 4 mmole/liter. The pK values of oxine are: pK₁ = 5.0 and pK₂ = 9.85.

Mixtures were prepared by weighing certain amounts of clay and silica gel into 40-ml Pyrex bottles fitted with plastic covers. The powders were well mixed, and 25 ml of oxine solutions of known concentration was added. The pH was adjusted to 5 with 0.1 M HCl, and the suspensions were shaken for 10 min and then left for 48 hr with occasional shakings. The pH was then measured and oxine was determined spectrophotometrically in the filtered supernatant liquids. The measurements were carried out at a wavelength of 340 nm in solutions adjusted to pH 12.5 with NaOH. With the help of a standard curve, the oxine concentrations were obtained. The amounts of oxine sorbed were calculated as the differences between final and initial concentrations. It should be noted that at pH 5, the oxine species present in solution are the positive C₉H₆NOH₂⁺ ion and the neutral C₉H₆NOH molecule in a 1:1 proportion.

Two types of mixtures were used in the experiments:

- (1) Mixtures in which the weight of gel, w_1 , was maintained at 3.52 g/liter and in which the weight of

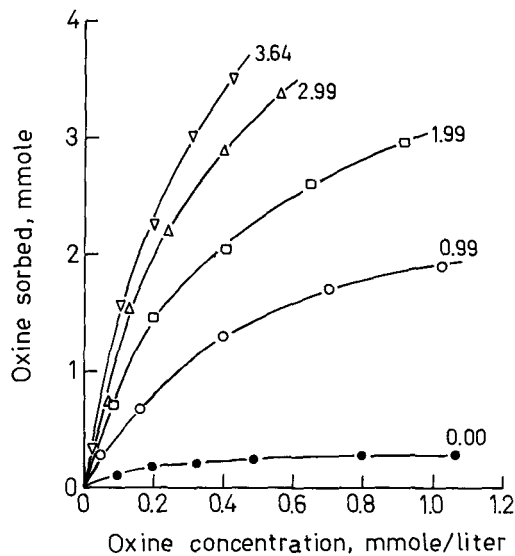


Figure 3. Total sorption of oxine vs. oxine concentration of mixtures having constant 3.52 g of gel and different weights of clay. Values on curves represent clay weight in the mixtures.

clay, w_2 , was variable at 0, 0.99, 1.99, 2.99, or 3.64 g/liter;

- (2) Mixtures in which both the gel and the clay were varied to give the following weight fractions ($w_2/(w_1 + w_2)$): 0, 0.27, 0.53, 0.77, and 1. The amounts of clay corresponding to these fractions were: 0, 0.99, 1.99, 2.98, and 3.64 g, respectively.

The amounts sorbed by the different mixtures were plotted as a function of equilibrium oxine concentrations. From the graphs, the amounts sorbed at the equilibrium concentrations 0.1, 0.2, 0.3, and 0.4 mmole/liter were then interpolated. These data were then used to calculate the apparent specific sorption using Eq. (7), and the partial values were then obtained as explained above. The following equations represent the apparent and partial specific sorption of oxine by the clay:

$$\begin{aligned} \phi_{x_2}(0.1) &= 0.523 - 0.157w_2^{1/2} + 0.029w_2, \\ \bar{x}_2(0.1) &= 0.523 - 0.234w_2^{1/2} + 0.058w_2, \\ \phi_{x_2}(0.2) &= 0.901 - 0.288w_2^{1/2} + 0.066w_2, \\ \bar{x}_2(0.2) &= 0.901 - 0.432w_2^{1/2} + 0.132w_2, \\ \phi_{x_2}(0.3) &= 1.374 - 0.637w_2^{1/2} + 0.162w_2, \\ \bar{x}_2(0.3) &= 1.374 - 0.956w_2^{1/2} + 0.324w_2, \\ \phi_{x_2}(0.4) &= 1.575 - 0.704w_2^{1/2} + 0.177w_2, \text{ and} \\ \bar{x}_2(0.4) &= 1.575 - 1.056w_2^{1/2} + 0.354w_2. \end{aligned}$$

Values between parentheses represent the oxine concentrations in mmole/liter.

RESULTS AND DISCUSSION

The sorption of oxine by mixtures of clay and silica gel from solutions of concentration as high as 1.2

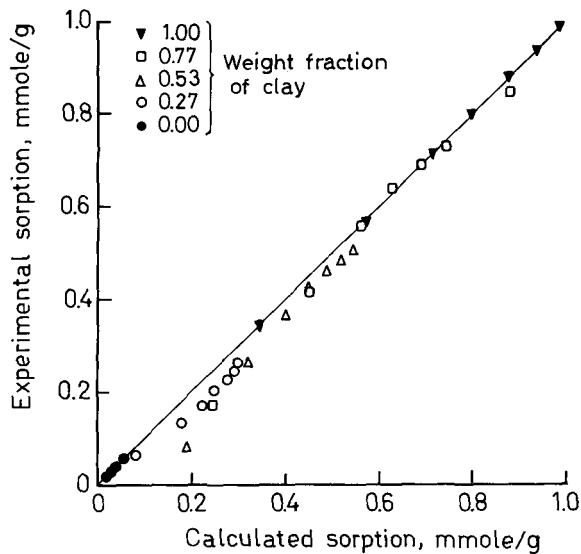


Figure 4. Experimental values of oxine sorbed by montmorillonite and silica gel in mixtures vs. values calculated by assuming that each sorbent acted independently, as in ideal mixtures.

mmole/liter at pH 5 is given in Figure 2 for mixtures covering the range of weight fractions from 0 to 1 and in Figure 3 for mixtures containing a constant amount of gel of 3.52 g and different amounts of clay. As may be seen, the curves are of the high affinity L type, according to the Giles *et al.* (1974) classification. At a concentration of <0.1 mmole/liter, however, several

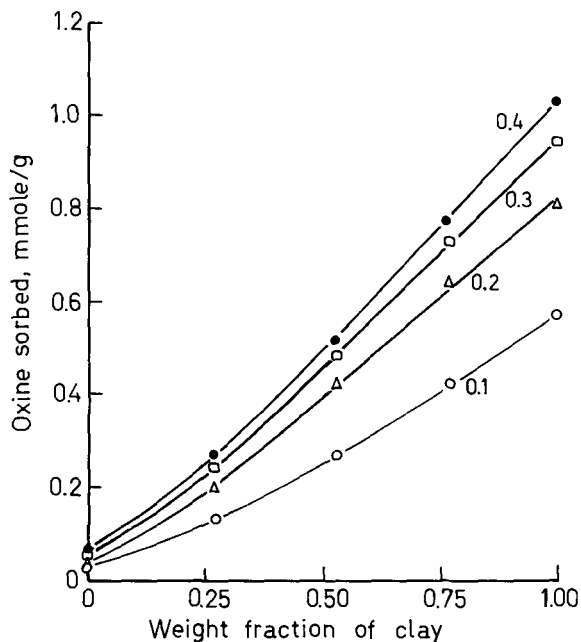


Figure 5. Oxine sorption by mixtures of clay and silica gel vs. weight fraction of clay in the mixture.

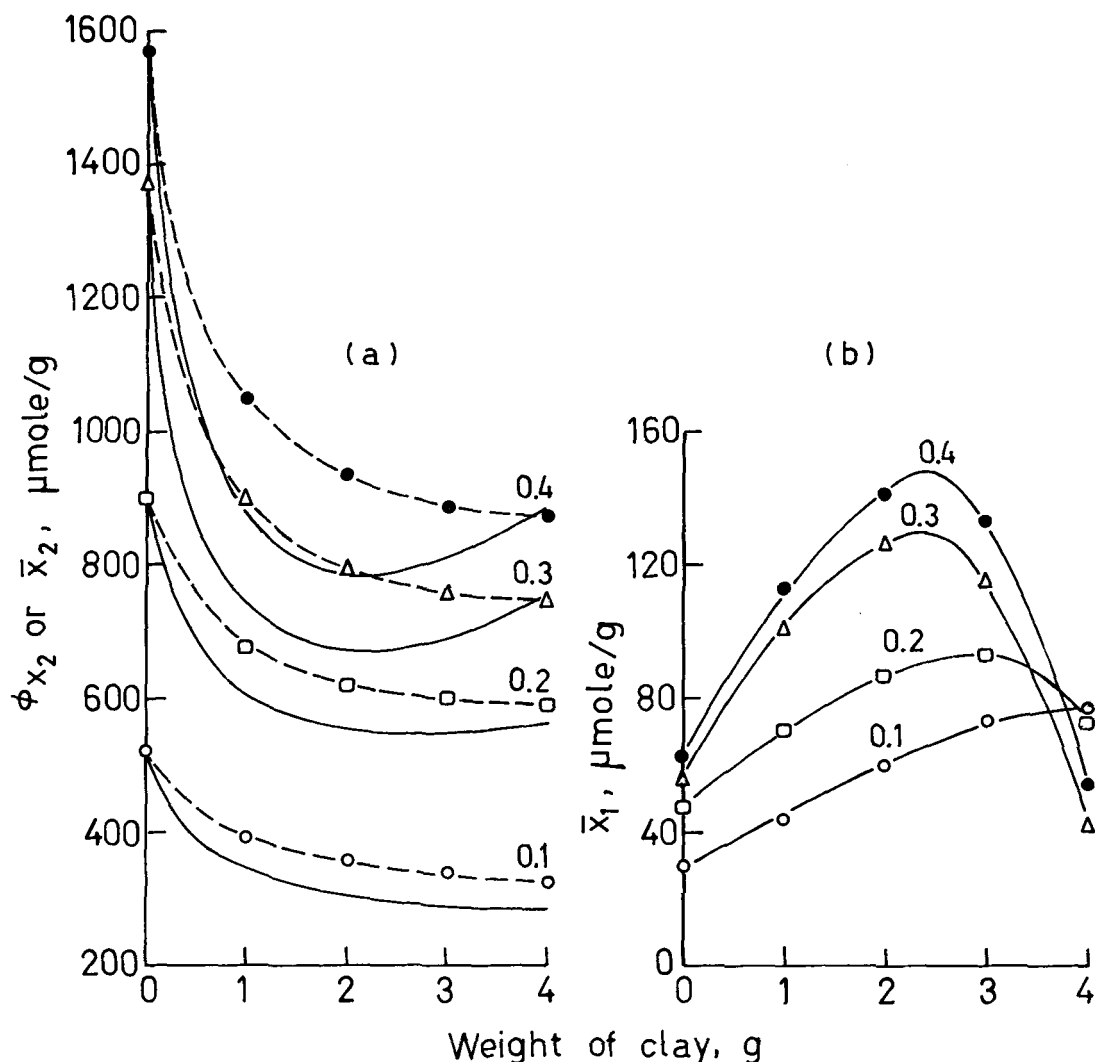


Figure 6. (a) Apparent (dashed lines) and partial (solid lines) specific sorption of montmorillonite vs. weight of clay in mixtures containing constant amount of silica gel (3.52 g). (b) Same as (a), but for partial specific sorption of silica gel.

of the curves exhibit some curvature to produce an S-shaped isotherm, which is an indication of competition between the solvent water with oxine for presence in the surface zone.

In Figure 4, the experimentally determined total amounts of oxine sorbed by mixtures of montmorillonite and silica gel are plotted against the amounts calculated, assuming that each substance sorbed in-

Table 1. Apparent ϕx_2 (mmole/g) and partial \bar{x}_2 (mmole/g) specific sorption of clay and silica gel \bar{x}_1 (mmole/g) at different concentrations of oxine and weight of clay (w_2).

Wt. of clay (g)	Oxine concentration											
	0.1 mmole/liter			0.2 mmole/liter			0.3 mmole/liter			0.4 mmole/liter		
	ϕx_2	\bar{x}_2	\bar{x}_1	ϕx_2	\bar{x}_2	\bar{x}_1	ϕx_2	\bar{x}_2	\bar{x}_1	ϕx_2	\bar{x}_2	\bar{x}_1
0	0.52	0.52	0.03	0.90	0.90	0.05	1.37	1.37	0.06	1.58	1.58	0.06
1	0.40	0.35	0.04	0.68	0.60	0.07	0.90	0.74	0.10	1.05	0.87	0.11
2	0.36	0.31	0.06	0.62	0.56	0.09	0.80	0.67	0.13	0.94	0.79	0.14
3	0.34	0.29	0.07	0.60	0.55	0.09	0.76	0.69	0.12	0.89	0.81	0.13
4	0.32	0.28	0.06	0.59	0.57	0.07	0.75	0.76	0.04	0.88	0.88	0.05

Weight of silica gel is constant at 3.52 g.

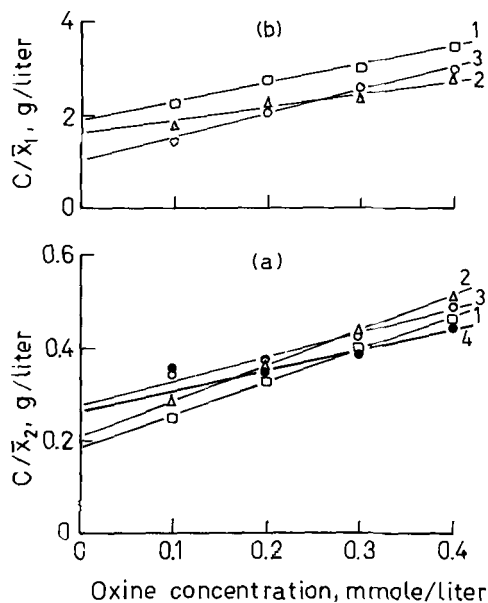


Figure 7. Values of oxine concentration/partial specific sorption vs. oxine concentration for (a) montmorillonite and (b) silica gel.

dependently according to its weight in the mixture, i.e., if 1 g of clay sorbed 1 mmole of oxine, 0.5 g in the mixture sorbed 0.5 mmole and so forth. If upon mixing, the behavior was ideal, all data should lie on the straight line traced in the figure. Only the points corresponding to the pure sorbents, however, lie on the line, and the deviations from the line are more pronounced as the proportion of gel increased in the mixtures.

Not only Figure 4 shows that clay and silica gel do not form ideal mixtures of sorbent, but also the data shown in Figure 5 lead to the same conclusion. If the mixtures had been ideal, straight lines should have been obtained. Furthermore, judging by the curvature of the traces, the deviations from ideal mixtures were more pronounced the lower the oxine concentration and the higher the proportion of the sorbent with the lesser oxine sorption affinity, i.e., silica gel.

As discussed above, the application of the concept of partial quantities resolves the problem of the determination of the amounts sorbed in nonideal mixtures. The data obtained by this concept are given in Table

1 and in Figures 6a and 6b, in which the apparent and partial specific sorption by the clay and the partial specific sorption by silica gel are plotted against the weight of the clay in the sorbent mixture. As may be seen from the illustration, both the apparent and partial quantities decreased as the proportion of the clay increased in the mixtures, which is a manifestation of particle competition such that the highest value of \bar{x}_2 was obtained at infinite dilution of clay particles. Similar behavior has been reported for partial volumes of clay (Helmy *et al.*, 1968; Ferreiro and Helmy, 1971, 1972).

The variation of partial specific sorption of oxine by silica gel as the amount of clay increased in the mixtures is more complicated; it first increased, passed through a maximum, and then decreased. This behavior was probably due to several factors. In addition to the competition described above, the role played by the solvent water must be considered, as was mentioned above. Undoubtedly, more studies are needed if the problem of sorption by mixtures is to be explained satisfactorily.

Finally, in Figures 7a and 7b, the partial specific sorptions are plotted according to the Langmuir equation. As may be seen, the data appear to satisfy the requirement of such an equation.

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