Academician Vikt. I. SPITSYN, V. V. GROMOV

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Academician Vikt. I. SPITSYN, V. V. GROMOV

EFFECT OF ELECTROLYTES ON THE ABSORPTION OF DYES BY RADIOACTIVE PRECIPITATES OF Ba*SO_4

The sorption properties of radioactive precipitates in solutions depend on many factors, as well as on the surface charge that arises as a result of the continuous emission by it of β- or α-particles ([1]-[3]). The magnitude and sign of this charge are determined by the amount and nature of the radioactive isotope introduced into the sorbent and, in addition, evidently, by the composition of the solid phase-solution system.

A significant role of the surface charge of a radioactive salt in the sorption process was demonstrated using, as an example, the absorption by active barium sulfate of dyes from aqueous solutions ([2]-[4]). However, changes in the sorption properties of $BaSO_4$ were observed under conditions in which the liquid phase, apart from dyes and Ba^{2+}, ${SO_4}^{2-}$ ions, contained no extraneous impurities. It was of interest to carry out experiments with dye solutions containing certain amounts of neutral, well-dissociated salts, for example NaCl, $NaNO_3$, $Mg(NO_3)_2$.

Radioactive precipitates of Ba*SO_4 were prepared by the method described previously ([5]). Their surface was measured with a Deryagin instrument and by the BET method. The values of the surface area and the specific radioactivity of $BaSO_4$ are given in Table 1.

More accurate surface-area values should be considered to be the results obtained by the BET method (nitrogen adsorption).

Dye solutions of methylene blue and acid orange used in the experiments were prepared with distilled water, which had been boiled for 5 hr with the corresponding $BaSO_4$ samples and then left to stand with the precipitates for about a month. This made it possible to work under conditions in which the concentration of Ba^{2+} and ${SO_4}^{2-}$ ions did not change during the experiments as a result of possible dissolution of $BaSO_4$. After this, definite amounts of NaCl, $NaNO_3$, or $Mg(NO_3)_2$ salts, chemically pure grade, were added to the dye solutions. The initial dye concentration was chosen so that the experimental results lay in the saturation region of $BaSO_4$ (the horizontal portion of the sorption isotherms). Thus, for methylene blue it reached 50 mg/l, and for acid orange 200 mg/l. The

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

pH of the solutions was 5.2–5.4 and did not change during the experiments. The amount of salts added was 10^{-3}–10 g/l.

Table 1

Characteristics of Ba^*SO_4 precipitates used in the experiments

No.	Specific radioactivity, S^{35} mCu/g	Specific surface area, m^2/g (Deryagin instrument)	Specific surface area, m^2/g (BET method)	Crystal radius, cm
1	0	4.9	4.3	$1.4 \cdot 10^{-4}$
2	10.5	5.6	5.7	$1.2 \cdot 10^{-4}$
3	100.0	9.4	8.0	$0.8 \cdot 10^{-4}$

The experimental procedure was as follows. Definite amounts of $BaSO_4$ precipitate, 0.4 g in the case of acid orange and 3 g in the case of methylene blue, were shaken for 30 min in conical flasks at a temperature of $25 \pm 0.5^\circ$ with 25 ml of solution. It had been shown beforehand that sorption equilibrium is completely established within 10–15 min. Samples were then taken, the solid phase was separated from the liquid by centrifugation, and the dye content in the solution was determined spectrophotometrically at the

instrument SF-2M. All data were obtained from three parallel experiments. The relative error, calculated from the deviation from the mean value, did not exceed 4%. The results of the investigation are shown in Figs. 1, 2.

In the absence of foreign ions, the uptake of acid orange, which has a colored anion, is the greater the higher the specific radioactivity of Ba^*SO_4, i.e., the greater the positive charge of the surface. As the concentration of Na^+, Cl^-, and NO_3^- in solution increases, the sorption of the dye by radioactive and inactive precipitates becomes identical.

Fig. 1. Sorption of acid orange on barium sulfate as a function of the concentration of added electrolyte, NaCl, $NaNO_3$.
1 –inactive precipitate; radioactive precipitates Ba^*SO_4, 2 –10.5 mCi/g; 3 –100.0 mCi/g.

Fig. 2. Sorption of methylene blue as a function of the concentration of added electrolyte. 1, 2 –solutions of NaCl, $NaNO_3$; 3, 4 –solution of $Mg(NO_3)_2$.
a –inactive precipitate; *b* –$BaSO_4$, 10.5 mCi/g.

Here, beginning at electrolyte concentrations of ~ 1 mg-equiv/l, the magnitude of adsorption by radioactive precipitates decreases, approaching the sorption value for the inactive sample. Finally, at salt concentrations of ~ 0.1 g/l, the process is masked by the onset of salting out of the dye, which corresponds to the rise of the sorption curve. The experimental data for $NaNO_3$ solutions coincide exactly with those for NaCl and therefore are not shown separately in the figure. Addition of even small amounts of $Mg(NO_3)_2$ leads to instantaneous precipitation of the dye.

Since methylene blue contains a colored cation, its sorption by radioactive Ba^*SO_4 decreases as the sign of the surface charge of the precipitate shifts in the positive direction. In other respects the changes are similar to those observed for acid orange. There is likewise no difference in the effect of NaCl and $NaNO_3$ on dye sorption. The presence of $Mg(NO_3)_2$ in solution sharply decreases the uptake of methylene blue. However, if the electrolyte concentration is expressed in g-equiv/l, the regularities in the change of dye sorption are identical, irrespective of the magnitude of the charge of the electrolyte ions.

Thus, when foreign ions are present in solutions at a sufficient concentration, radioactive and nonradioactive sorbents behave identically: the surface charge no longer plays a role.

Let us estimate the change in the surface charge of Ba^*SO_4 crystals in solution that arises from the escape of β-particles of S^{35} beyond the crystal. If the emitter is distributed uniformly in a sample of radius r, then, taking self-absorption into account, the number of β-particles (I_1) leaving the surface is expressed—

is given by the following formula (^{6}):

$$I_1 = \frac{kN_0\varepsilon(\mu, r)}{4\pi r^2}, \quad \left[\frac{\beta\text{-particles}}{\text{cm}^2 \cdot \text{sec.}}\right], \tag{1}$$

where N_0 is the number of decays per 1 sec in a sphere of radius r, k is a constant equal to $\frac{3}{4\pi\mu}$, and $\varepsilon(\mu, r)$ is a function of r and μ (the mass absorption coefficient), allowing for self-absorption of β-particles in the sample, equal to

$$\left[\frac{(2\mu r + 1)e^{-2\mu r} - 1}{2\mu^2 r^2} + 1\right].$$

When β-particles leave the surface of a spherical precipitate particle, the volume of the surrounding solution becomes negatively charged relative to the radioactive crystal. In this case, neglecting the possibility of charge leakage through the walls of the vessel in which the whole system is contained, and disregarding the factor of ionization of the solution, the process of "discharging" the precipitate can be related to the reverse current (I_2) of charges from the solution to the precipitate:

$$I_2 = \sigma E = \sigma \frac{Q}{R^2}, \tag{2}$$

where σ is the specific electrical conductivity of the solution, Q is the charge of a sphere of radius r, R is a distance equal to the mean radius of the precipitate crystals, i.e. $\bar{r}$, and E is the intensity of the electrostatic field created by the charge Q.

Equating equations (1) and (2), we obtain

$$Q = K' \frac{N_0 \varepsilon(\mu, r)}{\sigma}. \tag{3}$$

It follows from expression (3) that, other conditions being equal, the greater the electrical conductivity (σ) of the surrounding solution, the smaller the surface charge of the radioactive precipitate. For a $\mathrm{Ba^*SO_4}$ preparation with a specific activity of 100 mCi/g, the calculated charge values according to formula (3) are given in Table 2.

Table 2

Magnitude of the surface charge of $\mathrm{Ba^*SO_4}$ **in NaCl solution,** $r \cong 10^{-4}$ **cm,** $\mu = 216$ **cm^2/g** (^{7})

NaCl concentration, g/l	σ, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	Charge of a sphere of radius $\sim r$, coul/cm^2
0	$2 \cdot 10^{-6}$	$3 \cdot 10^{-14}$
0.001	$6 \cdot 10^{-6}$	$1 \cdot 10^{-15}$
0.01	$6 \cdot 10^{-5}$	$1 \cdot 10^{-16}$
0.1	$2 \cdot 10^{-4}$	$3 \cdot 10^{-16}$
1	$2 \cdot 10^{-3}$	$3 \cdot 10^{-17}$

Thus, in NaCl solutions of 1 g/l ($\sim 0.02\,N$), the surface charge of $\mathrm{Ba^*SO_4}$ is practically absent. As is evident from Figs. 1 and 2, precisely at this salt concentration the sorption properties of the active and inactive barium sulfate samples become identical. Any electrolytes will exert the same influence on the surface charge of radioactive precipitates arising from the decay of the radioactive isotope contained in the solid. Taking radiation ionization in the crystals and the liquid phase into account, the charge should probably become smaller already at lower electrolyte concentrations.

The decrease in dye uptake by radioactive $\mathrm{Ba^*SO_4}$ precipitates in the presence of electrolytes may depend on the change in the ionic strength of the solution, competition of ions during adsorption, reduction of the surface charge of the crystal due to the increase in the electrical conductivity of the solution (σ), and salting-out of the dyes. The first two factors may be neglected in the electrolyte concentration range $10^{-4} \div 10^{-7}$ g-equiv/l. Thus, the convergence of the adsorption properties of active and inactive $BaSO_4$ samples in the middle portions of the curves in Figs. 1 and 2 is determined by the decrease in the charge of the radioactive precipitates. With increasing concentration of electrolyte ions in the solution, all the other factors play a role.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
4 I 1964

REFERENCES

1. P. Curie, M. Curie, C. R., **130**, 647 (1900).
2. Vikt. I. Spitsyn, V. V. Gromov, DAN, **123**, 722 (1958).
3. Vikt. I. Spitsyn, V. V. Gromov, Radiokhimiya, **1**, No. 2, 181 (1959).
4. Vikt. I. Spitsyn, V. V. Gromov, Radiokhimiya, **4**, No. 5, 532 (1962).
5. L. D. Belyakova, V. V. Gromov et al., DAN, **138**, 1139 (1961).
6. A. M. Efimov, *Metallurgy and Metal Science*, collected volume, Publishing House of the Academy of Sciences of the USSR, 1958, p. 382.
7. F. Larson, A. R. Maass et al., Anal. Chem., **21**, 1206 (1949).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.