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ON THE ACTION OF SURFACE-ACTIVE SUBSTANCES ON THE KINETICS OF THE DISSOLUTION OF CALCIUM CARBONATE IN MINERAL ACIDS

Information on the influence of surface-active substances on the dissolution of carbonates in acids is very limited. At the same time, the study of the action of inhibitors on the rate of dissolution of carbonates in acids is of not only scientific but also practical interest, especially in processes of acid leaching of individual elements from carbonate ores. Directly related to the question under consideration is only one work known to us, by P. A. Rehbinder (1), in which the influence of fatty and aromatic acids and phenols on the rate of dissolution of individual calcite crystals in aqueous solutions of sulfuric and hydrochloric acids was investigated. It was found that *n*-heptylic acid considerably decreases the rate of dissolution of calcite single crystals in hydrochloric acid.

In carrying out the present work, primary attention was devoted to the search for new surface-active substances that most effectively suppress the dissolution of calcium carbonate in acids. To this end, the influence was studied of more than twenty substances of the following different classes of compounds.

1. Hydrophilic high-molecular-weight substances: wood glue, agar-agar, starch, gelatin, gum arabic, and sulfite-alcohol spent liquor.
2. Anion-active substances: *n*-heptylic and oleic acids.
3. Cation-active substances: a) salts of aliphatic amines—octadecylamine, triethylamine, triisoamylamine, trioctylamine, an amine of composition $R—CH_2—CH(NH_2)—CH_3$, where R is a hydrocarbon radical with 13-16 carbon atoms, and a mixture of petroleum amines; b) salts of aromatic amines—aniline, *p*-toluidine, α-naphthylamine; c) salts of quaternary ammonium bases—trimethylethyl- and tetraethylammonium.
4. Individual representatives of other classes of compounds, for example dimethylsiloxane and others.

The selection of suppressors of the dissolution of calcium carbonate in acids was based chiefly on differences in their chemical structure, i.e., on differences in hydrophilic groups and hydrophobic radicals, as well as differences in the character of the intermediate bonds between them (2). It should be borne

Figure 1

Figure 1: Figure 1

in mind that establishing the dependence of the properties of surface-active substances on their structure is connected with the question of selecting one or another property for investigation. This task presents no special difficulties when the question concerns such physicochemical properties as surface tension or solubilizing capacity. On the contrary, it proves considerably more difficult when such technologically important properties as passivating action, flotation and emulsifying capacity, and others are to be investigated.

At the present stage of the work, we did not set ourselves the task of an in-depth physicochemical study of the nature of the processes taking place, but limited ourselves only to studying the qualitative influence of additives on the rate of dissolution of calcium carbonate in acids.

In Fig. 1, as an example, curves are given showing the dependence of the rate of dissolution of calcite crystals (1500 mm^2) on time in a 0.77 M hydrochloric acid solution for *n*-heptylic, oleic, and isooctylphosphoric acids. These kinetic curves were constructed on the basis of averaged data for each point from 4-6 experiments. Along the ordinate is plotted the dissolution rate dx/dt, in milligrams of $CaCO_3$ per minute, calculated from the volume of carbon dioxide gas evolved. In all cases experiments were carried out in parallel with and without the introduction of surface-active substances, which makes it possible to establish the influence of the latter on the dissolution rate. Since the objective of the study was to establish the relative change in the rate of the process upon introducing surface-active substances into the solution, determination of the surface area of the crystals, which changes during dissolution, was of no interest in the present case. As is seen from Fig. 1, among these surface-active substances isooctylphosphoric acid has the greatest suppressing effect on the dissolution of calcite.

Fig. 1. Influence of surface-active substances on the rate of dissolution of calcite over time in a hydrochloric acid solution.
1 —without additive; 2 —0.00024 mol/l of *n*-heptylic acid; 3 —0.00024 mol/l of oleic acid; 4 —approximately 0.0003 mol/l of isooctylphosphoric acid.

The study of the action of the other substances listed above was carried out on calcite ground to a particle size of $-0.5 + 0.175$ mm, in sulfuric acid solution. Into round flat-bottom flasks with narrow necks, of 250 ml capacity, were placed 50 ml of 0.5 M sulfuric acid solution and a solution of the surface-active substance. After identical weighed portions (2–3 g) of calcite were simultaneously placed into the solution, the contents of the flasks, as in the experiments with hydrochloric acid, were mixed on a shaking apparatus for a definite time (1.5-2.5 hours). The solution was then centrifuged, and the final acidity of the solution was determined by titration with KOH using methyl red. By comparing the mean values of $CaCO_3$ dissolution in blank experiments and in experiments with the surface-active substance, the relative percentage suppression of dissolution was calculated.

For substances that showed a definite passivating action, curves were constructed for the dependence of the relative percentage suppression of calcite dissolution (ε) on their concentration (C). As is seen from Fig. 2 (curve 3), the concentration of cetyl sulfate in the solution has a substantial influence on the suppression of calcite dissolution. In this case the maximum suppression (about 14%) is observed at a relatively low concentration of cetyl sulfate (0.08-0.15 g/l); a further increase in concentration to 0.55 g/l decreases the suppression to 6.5%. Additives of glue and agar-agar proved considerably less effective (curves 2 and 1). The sulfuric acid salts of a mixture of naphthenic amines, *n*-toluidine, and octadecylamine proved rather effective (curves 4, 5, and 6).

Salts of other amines proved to be more effective inhibitors. The maximum suppressing action among the substances tested by us was shown by the sulfuric acid salts of triisoamylamine, trioctylamine, and α-naphthylamine (Fig. 3). As a rule, the steepest rise of the curves of the dependence of the passivating action of amine salts on their concentration in solution is observed at low concentrations. In the present case, the study of the influence of additions of sulfuric acid α-naphthylamine was carried out on the calcite fraction -0.175 mm, and that of triisoamylamine and trioctylamine on the fraction $-0.40 + 0.315$ mm.

The study of the influence of additions of the sulfuric acid amine of composition $R{-}CH_2{-}CH(NH_2){-}CH_3$ and of a representative of the class of organosilicon compounds –

dimethylsiloxane—was carried out by the volumetric method, i.e., by the volume of carbon dioxide gas evolved, on a calcite fraction of 0.40-0.315 mm. In this case the concentration of the amine was 0.63 g/l, and that of dimethylsiloxane 1.30 g/l. The experimental results are presented in Table 1.

In Table 1 the sign (+) denotes an accelerating effect, expressed in relative percent. As is evident from Table 1, the effect of the amine on the dissolution of calcium carbonate is quite distinctive. The considerable suppression that occurs at the initial moment of time rapidly decreases, and after 8-10 min from the start of the reaction, on the contrary, an acceleration of calcite dissolution is observed. This fact, occurring under conditions of decreasing sulfuric acid concentration, is apparently explained by a decrease in the strength of the $CaSO_4$ layer on the surface of calcium carbonate caused by the influence of this inhibitor ([3]). As with amines, the passivating action of dimethylsiloxane additives weakens with time.

Table 1

Effect of a sulfuric-acid amine of composition $R{-}CH_2{-}CH(NH_2){-}CH_3$ and of dimethylsiloxane on the dissolution of calcite in 0.5 M sulfuric acid

Time from start of reaction, min	Relative suppression of calcite dissolution, %, sulfuric-acid salt R—CH_2—CH(NH_2)—CH_3	Relative suppression of calcite dissolution, %, dimethylsiloxane
2	+45.0	+18.0
5	+12.9	+18.0
10	−3.3	+17.5
20	−11.0	+15.3
30	−10.0	+14.0

Of the substances tested by us, gelatin, starch, gum arabic, cresol and xylenol aerofloats, sulfuric-acid salts of triethylamine, aniline, trimethylethyl- and tetraethylammonium did not exert any appreciable effect on the dissolution of calcite, regardless of their concentration (up to 3 g/l), or of the order in which they were introduced into the solution.

Fig. 2. Effect of the concentration of agar-agar (1), glue (2), cetyl sulfate (3), sulfuric-acid salts of mixed naphthene amines (4), *p*-toluidine (5), and octadecylamine (6) on the dissolution of calcite in 0.5 M H_2SO_4.

Fig. 3. Effect of the concentration of sulfuric-acid salts of α-naphthylamine (1), trioctylamine (2), and triisoamylamine (3) on the dissolution of calcite in 0.5 M H_2SO_4.

Thus, as a result of the investigation of a large assortment of substances belonging to various classes of compounds, definite concepts have been obtained concerning the inhibiting action of surface-active substances on the dissolution of calcium carbonate in sulfuric acid. Some amines are very effective suppressors of calcium carbonate dissolution. It is characteristic that, for both aliphatic and aromatic amines, a definite regularity is observed in the increase of the suppressing-

···of the action with the development of the hydrophobic part of the molecule. For example, in the series aniline—*p*-toluidine—α-naphthylamine, an increase in the depressing action is observed in accordance with the increasing complexity of the hydrophobic radical. With the same number of carbon atoms in the amines, amines of isomeric structure apparently should exert a stronger action owing to their greater hydrophobicity. As a rule, as the solubility of the amine in water decreases, its suppressing action increases. In contrast to the lower representatives of quaternary ammonium salts, which proved ineffective, salts of quaternary ammonium bases containing alkyl groups with a larger number of carbon atoms, for example C_8 and higher, cannot be considered in advance unsuitable as inhibitors of the dissolution of calcium carbonate in acids.

In conclusion, we consider it our pleasant duty to express our sincere gratitude to Academician P. A. Rebinder for his useful comments in the preparation of the present work.

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