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Adsorption of Lauryl Sulfate from Electrolyte Solutions on Cobalt Hydroxide

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Abstract

The adsorption of lauryl sulfate on cobalt(II) hydroxide from solutions of inorganic salts has been found to change as follows: without salt > chloride > bromide ⩾ nitrate > sulfate ⩾ phosphate. Adsorption in the presence of acids increases in the following series: without acid > hydrochloric > sulfuric > phosphoric, and is higher than in the presence of salts. The surface concentration of lauryl sulfate adsorbed from a suspension without electrolyte is about 0.9 μmol/m^2. The surface coverage of hydroxide by lauryl sulfate is about 1/5 of a monolayer, but it decreases in the presence of electrolyte. The law of mass action was applied to characterize the effect of solution composition on the adsorption of lauryl sulfate on cobalt(II) hydroxide.

INTRODUCTION

The adsorption of surface-active substances from aqueous solutions onto sparingly soluble inorganic precipitates is of great importance for several reasons. First, advantage can be taken of the phenomenon in wastewater treatment (*1*); second, the hydrophobization of the minerals' and precipitates' surface which takes place due to adsorption of surface-active substances (collectors) makes foam separations possible for the recovery of metals, etc. (*2–9*).

The froth flotation process for recovery of valuable minerals from ores represents the oldest and largest scale practical adsorptive bubble separation technique. Adsorption at mineral–water interfaces is controlled in many cases by the electric double layer (EDL). Huang and

Stumm (*10*) described studies on specific adsorption of cations on alumina. Chen et al. (*11*) reported the results of adsorption of phosphate on alumina and kaolinite. Breeuwsma and Lyklema (*12*) discussed the adsorption of inorganic ions on hematite. Davis et al. (*13*) and Sprycha (*14*) published the results of surface ionization and complexation at the oxide–electrolyte solution interface. Drzymala et al. (*15*) determined surface dissociation constants for solid oxide–water solution systems. Most papers deal with the adsorption of inorganic ions on oxides. Because the surfactant ions also function as counterions in the EDL, their surface concentration will depend on competition with any other counterions in the solution. Many investigations of EDL effects on minerals in electrolyte solutions have been carried out which deal with surfactant surface concentrations (*2–5*, *9*). Kummert and Stumm (*16*) presented the results of surface complexation of organic acids on alumina. Somasundaran and Fuerstenau (*17*) as well as Somasundaran et al. (*18*) presented results of lauryl sulfonate and alkylammonium cations adsorption at alumina–solution and at quartz–solution interfaces in the context of EDL structure and competition of chloride anions. The above-mentioned papers also review the work of other researchers in this field. These studies indicate the direction to be followed in elucidating the processes of precipitate flotation of hydroxides and adsorbing colloid flotation.

Precipitate flotation of hydroxides was introduced much later than mineral flotation (*6–9*). It is obvious that, in the technological process of hydroxide precipitation, inorganic ions remain in the aqueous suspension of metal hydroxide(s). Therefore, the object of many authors' studies is the effect of these ions on the efficiency of precipitate flotation of these hydroxides. The presence of inorganic salts in suspensions of hydroxides has been found to affect negatively the efficiency of hydroxide foam separation with anionic collectors [Rubin et al. (*19*, *20*), Wilson et al. (*21–25*), Sanak (*26*), Bhattacharyya et al. (*27*), Jurkiewicz and Waksmundzki (*28*, *29*), and Jurkiewicz (*30–32*)]. To explain this statement, Kiefer et al. (*33*), Bhattacharyya et al. (*27*), and Jurkiewicz (*31*, *32*) studied the adsorption of collectors and electrokinetic potential of hydroxide precipitate in solutions of electrolytes. Currin et al. (*34*) showed by statistical mechanical methods that anionic surfactant can be displaced from the solid surface by the addition of salts. These studies may provide a better understanding of the changes in hydroxide flotation characteristics under the influence of inorganic salts. The purpose of the present studies is to obtain results allowing further interpretation of the process of precipitate flotation of hydroxides and the adsorption of anionic surfactants onto a hydroxide surface; it was hoped to relate these to ion properties and the structure of electrolytes. Also, we here make application of the "principles of chemical equilibrium" for characterization of the effect of solution composition on the adsorption of an anion surfactant.

EXPERIMENTAL

Cobalt hydroxide precipitate produced by POCh Gliwice was used as the adsorbent. The particles had a mean diameter of 10 μm and S_{BET} specific surface area of 0.483 m^2/g, determined chromatographically from the thermal desorption of nitrogen (*35*, *36*).

Sodium lauryl sulfate (BDH Laboratory Division, England) was used as the adsorbate. Initially a stock solution of lauryl sulfate was prepared at a concentration of 10^{-2} M/dm^3 in (1:1) ethanol–water. Next, a solution of concentration 10^{-4} M/dm^3 of lauryl sulfate was obtained by diluting the stock solution with water or salt solution. These solutions were used in the experiments described in the present paper.

Inorganic reagents—sodium salts (chloride, bromide, nitrate, sulfate, carbonate, and phosphate) and acids (hydrochloric, sulfuric, and phosphoric)—were analytically pure grade (POCh Gliwice).

The adsorption of lauryl sulfate was run by the dynamic method, using a Plexiglas column (30 cm high and 0.9 cm diameter) of the type K9/30 (Chemicals Uppsala, Sweden). Three grams of cobalt hydroxide was placed in a beaker and covered with 25 cm^3 of redistilled water for 24 h. The pH of the suspension was about 8. Then the suspension was poured into a column. The hydroxide precipitate formed a bed about 3 cm high and 0.9 cm diameter. Then fresh electrolyte and surfactant solutions (lauryl sulfate at 10^{-4} M/dm^3 concentration) were poured onto the precipitate. The elution rate was determined by the height of the hydroxide precipitate bed. The eluate was collected by fractions of volume 2 cm^3 each, in which lauryl sulfate was determined by the methylene blue method (*37*, *38*) on a spectrophotometer Spekol (C. Zeiss). The negative effect of electrolyte anions on surfactant determinations was eliminated by applying the backwash procedure (*38*). From the difference between the initial concentration of lauryl sulfate and that after adsorption (in the eluate), the amount of the surfactant adsorbed was calculated. Next, the surface coverage of the hydroxide (θ) by adsorbed molecules of lauryl sulfate related to a monomolecular cover was calculated. We assume that the area occupied by a lauryl sulfate ion is 33 $Å^2$ (*39*, *40*).

Surface site density (of −CoOH groups) was calculated from crystal plane models of surface structure (*41*, *42*). It is known that cobalt hydroxide crystallizes in the trigonal system in class C6, with the dimensions of the unit cell being $a = 3.195$ Å and $b = 4.66$ Å (*43*). No data have been found in the scientific literature concerning the involvement of the particular crystallographic faces in the structure of the surface of hydroxide molecules. However, it is known that the greatest cleavage and density of the metal atoms is in the 001 face. It was therefore assumed that this face plays the greatest part in the formation of the surface of hydroxide precipitation (*44*). The area of this face of the unit cell is $S_{001} = 8.84$ Å^2. As one $-Co^+$ ion statistically falls in one cellface, with which one OH^- group can be connected, the surface density of the OH^- groups is $N_s = 1.13 \times 10^{19}$ OH^- groups/m^2 (0.2×10^{-4} M/m^2). On the basis of these data, coverage of surface sites (θ_1) with adsorbed lauryl sulfate was calculated in relation to the total number of surface hydroxyl groups.

RESULTS

Figures 1(A) and 2 show the surface concentration of lauryl sulfate and the surface coverage (θ and θ_1) as functions of the volume of solution of 1:1 type sodium salt (with univalent anions Cl^-, Br^-, NO_3^-) and lauryl sulfate passed through the hydroxide. The initial pH of the solution was about 5.6, and that of the eluate was about 8. From an analysis of the adsorption curves, it appears that adsorption initially increases linearly with the volume of solution passed through the hydroxide, after which this growth gradually decreases, and at sufficiently high volume of eluate (over 20 cm^3), adsorption assumes a constant value. This means that for a small volume of the eluate the adsorption density and the coverage of the hydroxide surface is proportional to the volume of the eluate, and hence to the amount of lauryl sulfate introduced onto the hydroxide bed.

From the figures it appears that saturation of hydroxide surface is achieved after the filtration of about 20 cm^3 of the solution, and then about 0.9 μmol/m^2 of lauryl sulfate is adsorbed, while in the presence of 5×10^{-2} M/dm^3 salt of Cl^-, Br^-, and NO_3^- (when five hundredfold excess of salt concentration relative to the lauryl sulfate concentration is in solution) the adsorption is decreased to 0.64, 0.50, and 0.42 μmol/m^2, respectively. When the salt concentration is 10^{-1} M/dm^3 (excess of salt concentration relative to the lauryl sulfate concentration in solution is a thousandfold), lauryl sulfate adsorption decreases to 0.50 μmol/m^2 for Cl^- and to about 0.20 μmol/m^2 for Br^- and NO_3^-.

Figure 1(B) shows that lauryl sulfate adsorption and coverage of the

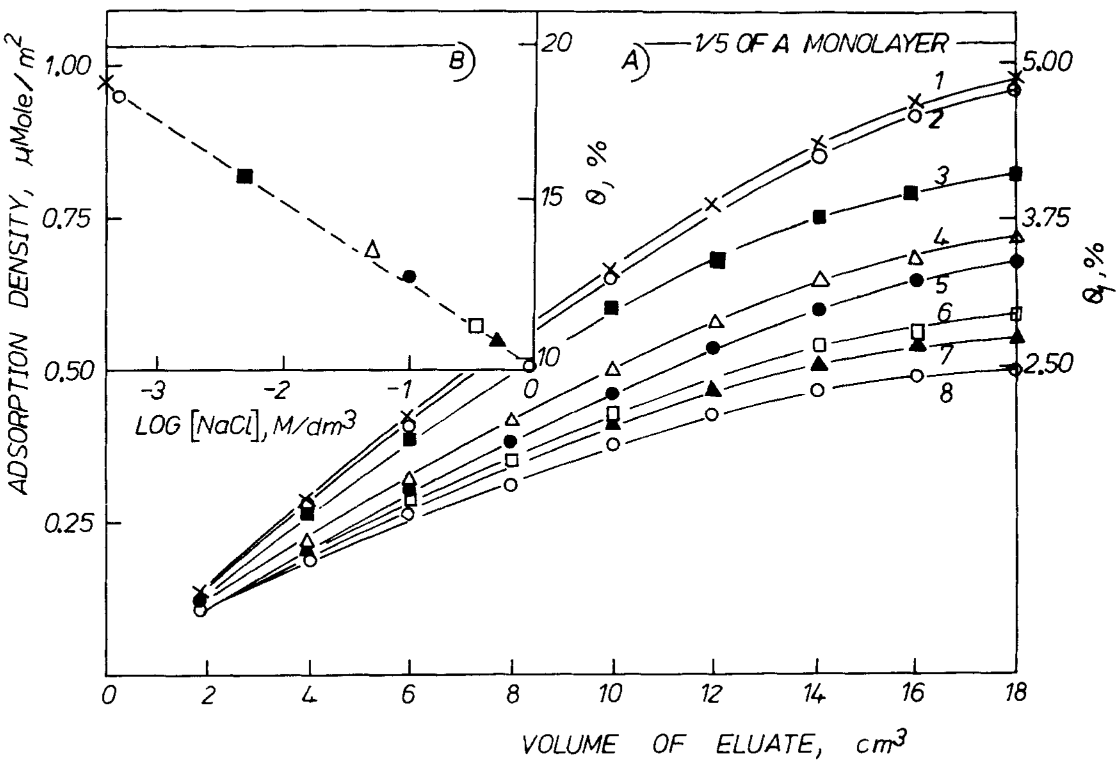

FIG. 1. Lauryl sulfate adsorption from chloride solutions and surface coverage (θ and θ_1): (A) in relation to eluate volume, (B) in relation to chloride concentration at the eluate volume equal to 20 cm^3. (1) Without salt, (2) 5×10^{-4} M/dm^3 NaCl, (3) 5×10^{-3} M/dm^3 NaCl, (4) 5×10^{-2} M/dm^3 NaCl, (5) 10^{-1} M/dm^3 NaCl, (6) 3×10^{-1} M/dm^3 NaCl, (7) 5×10^{-1} M/dm^3 NaCl, (8) 9×10^{-1} M/dm^3 NaCl.

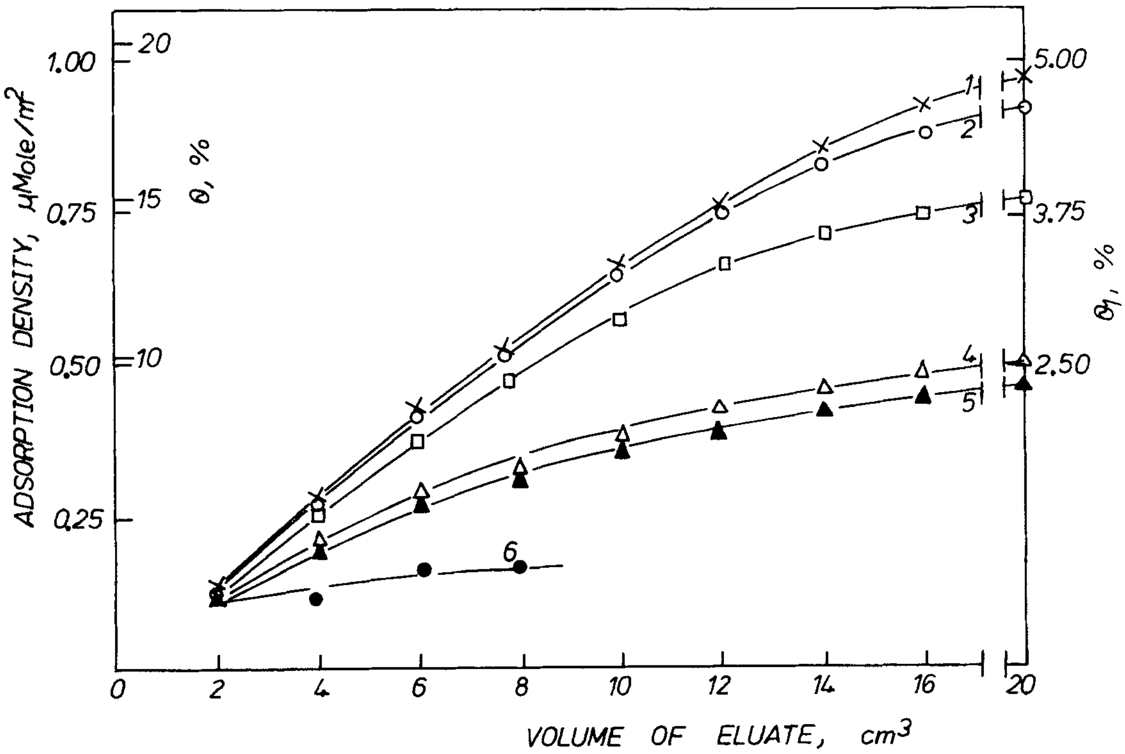

FIG. 2. Lauryl sulfate adsorption from bromide solutions (2, 4, 6) and nitrate solutions (2, 3, 5, 6) in relation to eluate volume. (1) Without salt, (2) 5×10^{-4} M/dm^3 NaBr or $NaNO_3$, (3) 5×10^{-3} M/dm^3 $NaNO_3$, (4) 5×10^{-2} M/dm^3 NaBr, (5) 5×10^{-2} M/dm^3 $NaNO_3$, (6) 10^{-1} M/dm^3 NaBr or $NaNO_3$.

hydroxide surface linearly decrease as Cl^- concentration increases up to about 0.9 M/dm^3. Then θ decreases from about 19% (about 1/5 of a monolayer) to about 9.5%, and θ_l decreases from 5% to 2.5%. A very similar conclusion can be drawn from Fig. 2.

It appears that the extent of lauryl sulfate adsorption and the surface coverage in the presence of 1:1 type salts change in the following series: without salt > Cl^- > Br^- $\gg$ NO_3^- and decrease with an increase in the concentration of these anions.

Figures 3–5 illustrate lauryl sulfate adsorption from solutions containing Na salts of types 1_2:2 and 1_3:3 which dissociate to yield polyvalent anions. The eluate pH of the sulfate and phosphate solutions was about 8 [where the predominant form of phosphate is the divalent anion HPO_4^{2-} (*11*, *45*)], while the eluate pH of carbonate solutions was in range 10–11.2 [where the predominant form of carbonate at ~pH 10 is HCO_3^-, whereas at ~pH 11 it is CO_3^{2-} (*45*)]. From the course of the adsorption curves it appears that the change in lauryl sulfate adsorption in relation to the volume of eluate is analogous to what was seen in Figs. 1 and 2, but the change in lauryl sulfate adsorption in relation to the concentration of salts with polyvalent anions has a more complex course than that seen for salts with a univalent anion. As can be seen from Figs. 3–5, lauryl sulfate adsorption at first decreases with increasing concentration of sulfate, carbonate, or phosphate up to about 5×10^{-2} M/dm^3, but with a further increase in the concentration of the electrolyte, the adsorption increases.

From an analysis of the adsorption curves in Figs. 3(B)–5(B), it appears that after collecting 20 cm^3 of the eluate, the adsorption from a solution without salt is about 0.9 $\mu mol/m^2$ ($\theta \approx 19\%$) whereas from 5×10^{-2} M/dm^3 of salt solution it is 0.42 $\mu mol/m^2$ ($\theta \approx 9\%$) for sulfate, 0.40 $\mu mol/m^2$ ($\theta \approx 8\%$) for carbonate, and also about 0.40 $\mu mol/m^2$ for phosphate. After increasing the salt concentration up to 10^{-1} M/dm^3, the amount of lauryl sulfate adsorption onto hydroxide increases and is 0.54 $\mu mol/m^2$ ($\theta \approx 11\%$) for sulfate, 0.52 $\mu mol/m^2$ ($\theta \approx 10\%$) for carbonate, and 0.52 $\mu mol/m^2$ for phosphate. From the results presented it appears that lauryl sulfate adsorption decreases in the following series: without electrolyte > sulfate > carbonate $\gg$ phosphate.

Next, the effect of acids on lauryl sulfate adsorption onto a hydroxide surface was studied. To do this, solutions containing 10^{-4} M/dm^3 of surfactant and 5×10^{-2} M/dm^3 of acid were introduced onto the hydroxide bed. The initial pH of these solutions was about 1.2, whereas the eluate pH was about 7.5. The results of the experiments are illustrated in Fig. 6. From the curves in this figure it appears that lauryl sulfate adsorption after filtering 20 cm^3 of the solution changes as follows: 0.9

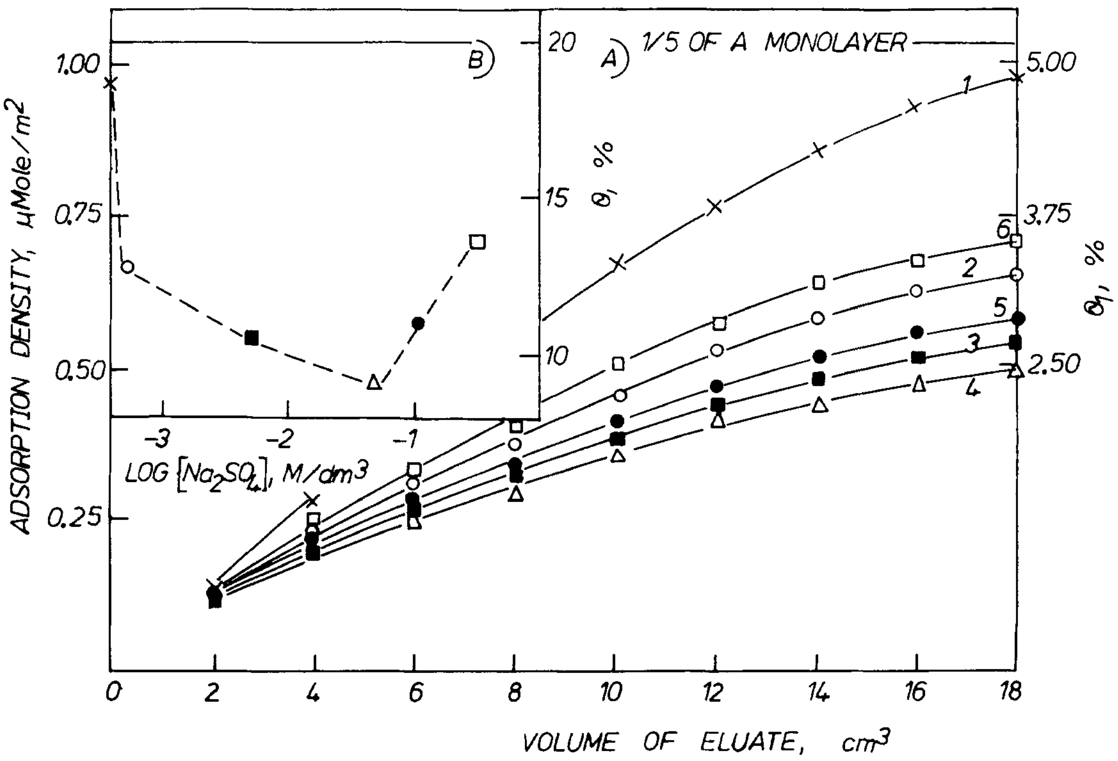

FIG. 3. Lauryl sulfate adsorption from sulfate solutions: (A) in relation to eluate volume, (B) in relation to sulfate concentration at the eluate volume equal to 20 cm^3. (1) Without salt, (2) 5×10^{-4} M/dm^3 Na_2SO_4, (3) 5×10^{-3} M/dm^3 Na_2SO_4, (4) 5×10^{-2} M/dm^3 Na_2SO_4, (5) 10^{-1} M/dm^3 Na_2SO_4, (6) 3×10^{-1} M/dm^3 Na_2SO_4.

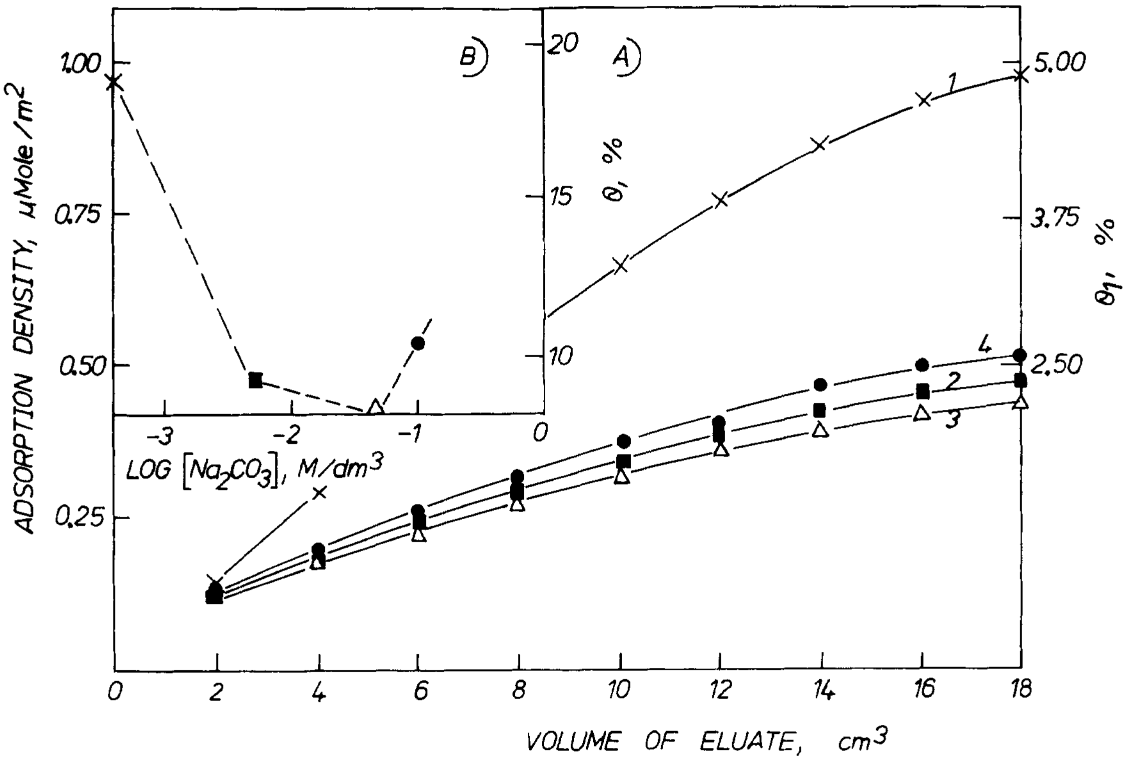

FIG. 4. Lauryl sulfate adsorption from carbonate solutions: (A) in relation to eluate volume, (B) in relation to carbonate concentration at the eluate volume equal to 20 cm^3. (1) Without salt, (2) 5×10^{-3} M/dm^3 Na_2CO_3, (3) 5×10^{-2} M/dm^3 Na_2CO_3, (4) 10^{-1} M/dm^3 Na_2CO_3.

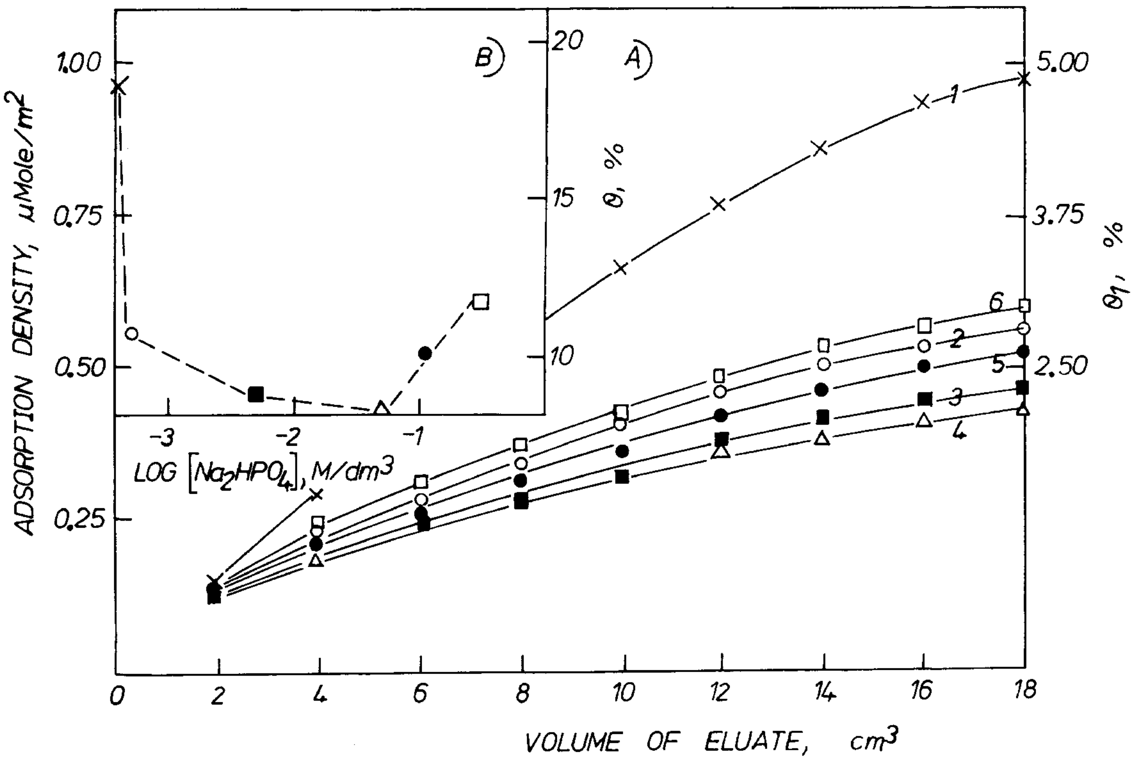

FIG. 5. Lauryl sulfate adsorption from phosphate solutions: (A) in relation to eluate volume, (B) in relation to phosphate concentration at the eluate volume equal to 20 cm^3. (1) Without salt, (2) 5×10^{-4} *M*/dm^3 Na_2HPO_4, (3) 5×10^{-3} *M*/dm^3 Na_2HPO_4, (4) 5×10^{-2} *M*/dm^3 Na_2HPO_4, (5) 10^{-1} *M*/dm^3 Na_2HPO_4, (6) 3×10^{-1} *M*/dm^3 Na_2HPO_4.

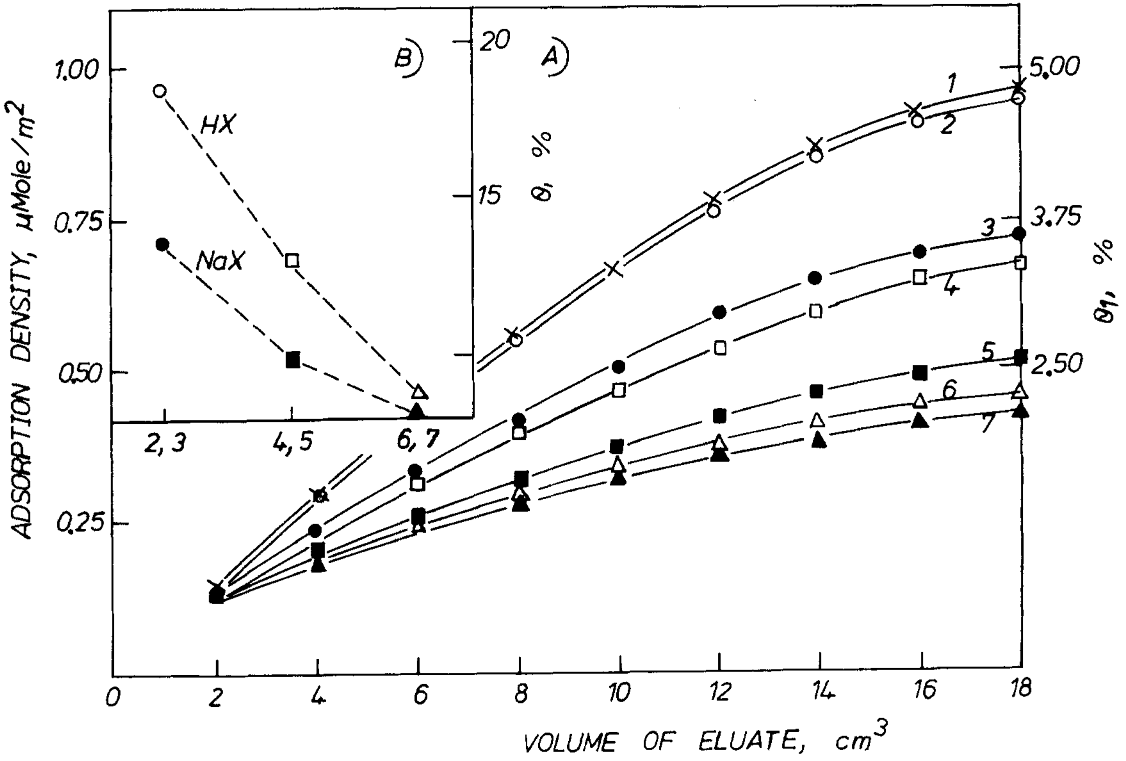

FIG. 6. Lauryl sulfate adsorption from solutions of various acids (2, 4, and 6) and their salts (3, 5, and 7): (A) in relation to eluate volume, (B) for various anions (HX, acids; NaX, salts) at eluate volume equal to 20 cm^3. (1) Without acid or salt, (2) HCl, (3) NaCl, (4) H_2SO_4, (5) Na_2SO_4, (6) H_3PO_4, (7) Na_2HPO_4.

μmol/m^2 without acid, 0.88 μmol/m^2 for HCl, 0.64 μmol/m^2 for H_2SO_4, and 0.42 μmol/m^2 for H_3PO_4. This series is similar to that illustrating the effect of salts of these acids on lauryl sulfate adsorption. However, the adsorption in the presence of acids (Curves HX and 2, 4, 6) is higher than that in the presence of salts (Curves NaX and 3, 5, 7). From a comparison of the differences in lauryl sulfate adsorption from solutions of the acids and their salts, it appears that these differences become smaller and smaller with decreasing acid strength: $pK_{HCl} = -3$; $pK_{H_2SO_4} = 0.4, 1.92$; $pK_{H_3PO_4} = 2.1, 7.2, 12.0$ (*46*).

Furthermore, lauryl sulfate adsorption from solutions without salt at initial pH values of 10.8 and 5.6 was determined. The pH of the eluate was about 10.1 and 8, respectively. From the experiments it appears that lauryl sulfate adsorption from solutions is higher at lower pH. After filtering 20 cm^3 of solutions at pH 5.6 through the hydroxide, 0.9 μmol/m^2 ($\theta \approx 19\%$) lauryl sulfate was adsorbed and 0.62 μmol/m^2 ($\theta \approx 13\%$) from a solution at pH 10.8.

Figure 7 illustrates the kinetics of the solution filtration through the hydroxide at a salt concentration of 10^{-1} *M*/dm^3. It can be seen that the filtration rate depends on the nature of the salt. This is characterized by the following value of the filtration times of 20 cm^3 of the solutions: 58 min for chloride, 64 min for sulfate, 71 min for phosphate. From the above there results the following sequence of the filtration flow rate of the tested salt solutions: chloride < sulfate < phosphate.

DISCUSSION

The Effect of the Concentration and Nature of Electrolyte

For an interpretation of the adsorption process of lauryl sulfate at hydroxide precipitate–solution interfaces, the most often used model (the site-binding model) of the electrical double layer is mentioned (*2–5*, *9–18*, *47*). Hydrogen and hydroxyl ions are potential determining ions for metal hydroxides, and the surface charge of the hydroxide might be considered to result from adsorption–dissociation of H^+ from the surface hydroxyl groups. Due to this, the cobalt hydroxide surface in water is covered with positive $-CoOH_2^+$, negative $-CoO^-$, and neutral $-CoOH$ surface sites. The charge of the hydroxide surface largely depends on the pH of the suspension. At the pH of the isoelectric point (IEP), the numbers of positive and negative surface sites per unit area are equal. It was found earlier (*32*) that the IEP of cobalt hydroxide occurs at a pH close to 9.8,

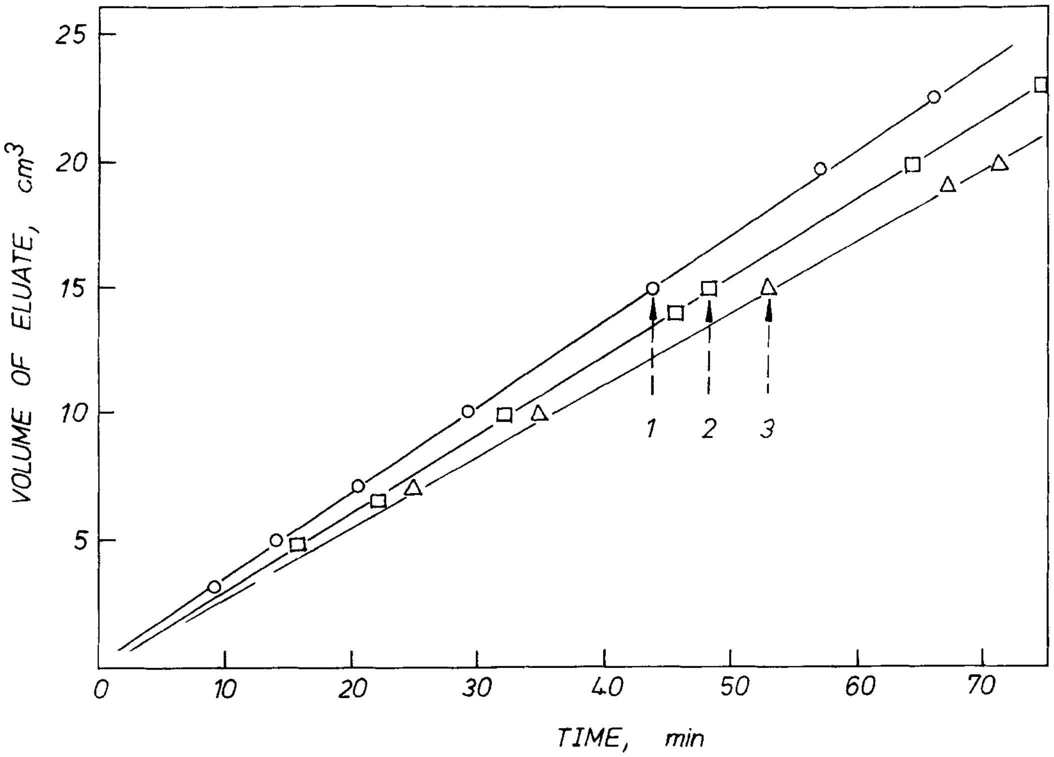

FIG. 7. Kinetics of filtration of solutions of various salts at 5×10^{-2} *M*/dm^3 concentration of (1) NaCl, (2) Na_2SO_4, (3) Na_2HPO_4.

whereas at a pH of about 8 the electrokinetic potential of cobalt hydroxide is +15 mV. In the present experiments the pH of the hydroxide suspension in water and also the pH of the eluate (adsorption pH) was about 8, lower than the IEP pH. Then on the cobalt hydroxide surface we have $[-\mathrm{CoOH_2^+}] > [-\mathrm{CoO^-}]$.

Lauryl sulfate as the adsorbate and the inorganic salts used for the experiments are strong electrolytes, present in dissociated form in aqueous solution.

From the above data and those reported in the literature (*2–5*, *9–18*, *47*), it appears that adsorption onto hydroxide may result from the interaction of ionizable surface sites with lauryl sulfate ($\mathrm{RSO_4^-}$) or inorganic anions (X^{n-}). Yates et al. (*47*) call these surface species "ion pairs." Davis et al. (*13*) prefer the term "surface complex." From the above considerations it may be concluded that anions present in the solution with active adsorption centers (surface positive sites) form adsorption complexes (surface complexes) of type $-\mathrm{CoOH_2^+,RSO_4^-}$ and $m(-\mathrm{CoOH_2^+}),\mathrm{X}^{n-}$, where $1 \leqslant m \leqslant n$. Hence the total number of surface sites, N_s, is distributed among all surface species. This may be depicted by the following scheme:

$$N_s = [-\mathrm{CoOH_2^+}] + m[m(-\mathrm{CoOH_2^+}),\mathrm{X}^{n-}] + [-\mathrm{CoOH_2^+,RSO_4^-}] + [-\mathrm{CoOH}] + [-\mathrm{CoO^-}] + [-\mathrm{CoO^-,Na^+}] \quad (1)$$

Our experiments show that in a suspension without electrolyte, lauryl sulfate occupies (θ_1) about 5% of the total amount of all surface sites (constitutes about 20% of a monolayer) and θ_1 decreases with increasing electrolyte concentration, and also according to the specific properties of the anions (see Figs. 1–6).

We assume that the $\mathrm{RSO_4^-}$ anion interacts with one positive surface site. However, the area occupied by one $\mathrm{RSO_4^-}$ anion is about four times larger than that required for the hydroxyl group [33 Å^2 for $\mathrm{RSO_4^-}$ (*39*, *40*) and 8.84 Å^2 for $\mathrm{OH^-}$, see Experimental]. Due to this, a lauryl sulfate anion adsorbed on one surface site may block or screen such neighboring sites.

In our experiments, an inorganic anion excess in comparison with the concentration of lauryl sulfate anions favored the formation of surface complexes with inorganic anions $m(-\mathrm{CoOH_2^+}),\mathrm{X}^{n-}$, where $1 \leqslant m \leqslant n$. As suggested by Pushkarev and Trofimov (1), Somasundaran et al. (*17*, *18*), Robertson et al. (*24*), Kiefer et al. (*33*), Currin et al. (*34*), and others (*2–5*, *9*), the effect of inorganic anions on lauryl sulfate adsorption may be connected with the competitive forces interacting between these ions and the positive surface site. Figures 2–5 indicate that the competition results in a decrease of lauryl sulfate adsorption from solutions of inorganic salts as the salt concentration increases and in the following series: without salt > chloride > bromide ⩾ nitrate > sulfate > carbonate ⩾ phosphate.

This can be supported by the results of Fuerstenau and Healy (*2*), Davis et al. (*13*), Breeuwsma and Lyklema (*12*), and Lewandowski and Tustanowski (*48*) that the series of increasing inorganic anion adsorption onto an oxide and hydroxide may be denoted as follows: chloride < nitrate < sulfate < carbonate < phosphate. Thus the sequence of increasing lauryl sulfate adsorption in the presence of inorganic anions is the reverse of that of increasing adsorption of these anions, as expected.

From our earlier studies (*31*, *32*) it appears that the addition of lauryl sulfate and inorganic electrolyte to zinc hydroxide or cobalt hydroxide suspension causes a electrokinetic potential decrease and a shift of the precipitate IEP toward lower pH values, the higher the electrolyte concentration and anion valency are. It should be noted that it is a specific adsorption which results in shifts of pH IEP. These results are similar to the changes of electrokinetic potential of precipitates of hydroxide, carbonate, and phosphate noted by Nazarova et al. (*49*). From these studies and those reported in the literature (*2–4*, *11*, *12*, *16*), we conclude that specific adsorption makes the properties of the hydroxide precipitate–salt solution interface similar to those of interfaces between the solution and precipitates formed by the metal with other anion(s) in the electrolyte solution. Accordingly, the electrokinetic potential of the metal hydroxide in the presence of X^{n-} anions assumes values similar to the electrokinetic potential of the metal salt with the same anions. Similar effects have been found by Szczypa (*50*, *51*) for ores.

In the presence of acids, the adsorption of lauryl sulfate increases in comparison with adsorption from salt solutions (see Fig. 6, Curves HX and NaX) in the following series: without acid > HCl > H_2SO_4 > H_3PO_4. Accordingly, the effect of acid on lauryl sulfate adsorption should be connected with the change of the electrostatic state of the hydroxide surface via H^+ reactions with the neutral and negative surface sites (*2–5*, *9–18*). This causes the surface charge and electrokinetic potential of the precipitate to increase. Therefore, in an acidic medium the state of the hydroxide surface results from the condition that $[-CoOH_2+] > [-CoO^-]$. At the same molar concentration of tested acids, this results from the increase of their acidity (*46*). Similarly, for this reason lauryl sulfate adsorption is higher, the stronger the acid.

The adsorption of lauryl sulfate from alkaline solutions is lower, the higher the OH^- concentration. As regards the effect of OH^- anions on the properties of the hydroxide surface, it has been found that they cause a decrease in the electrokinetic potential of the precipitate due to OH^- reactions with the neutral and positive surface sites. Therefore, in an alkaline medium over pH IEP (9.8), a state of the metal hydroxide surface results such that $[-CoOH_{2}+] < [-CoO^-]$. In this situation, lauryl sulfate adsorption decreases.

Coming back to the problem of lauryl sulfate adsorption from salt solution, it should be added that only in the presence of chloride anions does adsorption decrease as salt concentration increases up to 0.9 M/dm^3. However, with increasing concentration of sulfate, carbonate, or phosphate anions in the initial lauryl sulfate-electrolyte solution, the amount of lauryl sulfate remaining in eluate at first increases (i.e., lauryl sulfate adsorption at first decreases) and then the amount of lauryl sulfate remaining in the eluate decreases (i.e., lauryl sulfate adsorption increases). The adsorption minimum occurs near the concentration of 5×10^{-2} M/dm^3. As is known, the presence of electrolyte decreases the critical micelle concentration of the surfactant in solution. Due to that fact, micelles were formed in solutions of some salts, although the lauryl sulfate concentration was 10^{-4} M/dm^3, and the critical micelle concentration in water of lauryl sulfate is about 6×10^{-3} M/dm^3 (*6*). Besides, a polyvalent anion (sulfate, carbonate, and phosphate) plays the role of a bridge joining the positive surface sites of the hydroxide particles. As a result, sparingly soluble surface complexes (cobalt with an inorganic anion) are formed (between particles of the hydroxide bed). Therefore, the filtration time (Fig. 7) increases in the following direction: chloride < sulfate < phosphate [it appears that the influence of anions on the rate of solution filtration grows in the direction of decreasing cobalt anion solubility (*45, 52, 53*)], and filtration of the lauryl sulfate aggregates on the precipitate bed may be possible, and the remaining lauryl sulfate decreases in eluate. Hence, an increase in lauryl sulfate adsorption from solution over 5×10^{-2} M/dm^3 salt is apparent, and virtual filtration on the precipitate bed occurs. Salting out the activity of electrolyte is here in agreement with Hofmeister's series (*54*).

Application of the Law of Mass Action for Adsorption

A positive surface site on cobalt hydroxide may form an adsorption complex both with lauryl sulfate anions RSO_4^- and anions of the inorganic electrolyte X^{n-}. For the formation of both adsorption complexes the same free surface sites constitute an active adsorption center; therefore, the interaction of the solution anions with hydroxide can be described by

$$m(-\mathrm{CoOH}) + m\mathrm{H}^+ \begin{cases} \xrightarrow[(1)]{+\,m\mathrm{RSO}_4^-} m(-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-) & (2) \\ \xrightarrow[(2)]{+\,\mathrm{X}^{n-}} m(-\mathrm{CoOH}_2^+),\mathrm{X}^{n-} & (3) \end{cases}$$

where (1) and (2) are the adsorption interactions which may be competition reactions or anion exchange. Various aspects of these reactions were discussed in the first part of this paper. Due to the interaction of anions from the solution with positive surface sites, adsorption complexes of type of ion pairs $-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-$ and $m(-\mathrm{CoOH}_2^+),\mathrm{X}^{n-}$ (where $1 \leqslant m \leqslant n$) or weakly dissociated compounds, and even surface compounds of low solubility are formed (especially during adsorption of polyvalent anions). The interaction may be characterized according to the law of mass action by the apparent stability quotients ($K_{\mathrm{RSO}_4^-}$) for lauryl sulfate anions and ($K_{\mathrm{X}^{n-}}$) for inorganic anions (Eqs. 4–6):

$$K_{\mathrm{RSO}_4^-} = \frac{[-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-]}{[-\mathrm{CoOH}][\mathrm{H}^+][\mathrm{RSO}_4^-]} \tag{4}$$

$$K_{\mathrm{X}^{n-}} = \frac{[m(-\mathrm{CoOH}_2^+),\mathrm{X}^{n-}]}{[-\mathrm{CoOH}]^m[\mathrm{H}^+]^m[\mathrm{X}^{n-}]} \tag{5}$$

and

$$K_{\mathrm{X}^{n-}}^{1/m} = \frac{[-\mathrm{CoOH}_2^+,1/m\mathrm{X}^{n-}]}{[-\mathrm{CoOH}][\mathrm{H}^+][\mathrm{X}^{n-}]^{1/m}} \tag{6}$$

These considerations refer to Region I of the adsorption isotherm of surfactants, distinguished by Somasundaran and Fuerstenau (*17*), Fuerstenau and Healy (*2*), and Kiefer et al. (*33*), when the surfactant ions are adsorbed individually (hemimicelles of surfactant are not formed), without interactions between sites. Adsorption of RSO_4^- occurs when $-\mathrm{CoOH}_2^+$ is free (i.e., it is not blocked or screened) or if it is allowed by the equilibrium constant of X^{n-} to exchange RSO_4^- for X^{n-}.

Hence, the Eq. (1) from the first part of this paper may be written:

$$N_s = [-\mathrm{CoOH}_2^+] + [-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-] + [-\mathrm{CoOH}_2^+,1/m\mathrm{X}^{n-}] + [-\mathrm{CoOH}] + [-\mathrm{CoO}^-] + [-\mathrm{CoO}^-,\mathrm{Na}^+] \tag{7}$$

Next, we introduce into Eq. (7) the expressions for [$-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-$] and [$-\mathrm{CoOH}_2^+,1/m\mathrm{X}^{n^-}$] from Eqs. (4) and (5) and for [$-\mathrm{CoOH}_2^+$], [$-\mathrm{CoO}^-$], and [$-\mathrm{CoO}^-,\mathrm{Na}^+$] from the formation interactions of surface positive and negative sites (K_+ and K_-) and surface complexes (K_{Na^+}) with inorganic cation [e.g., Davis et al. (*13*), Chen et al. (*11*), Sprycha (*14*)].

Then we obtain

$$N_s = [-\mathrm{CoOH}]\left(1 + \frac{[\mathrm{H}^+]}{K_+} + K_{\mathrm{RSO}_4^-}[\mathrm{H}^+][\mathrm{RSO}_4^-] + K_{\mathrm{X}^{n^-}}^{1/m}[\mathrm{H}^+][\mathrm{X}^{n^-}]^{1/m} + \frac{K_-}{[\mathrm{H}^+]} + \frac{K_{\mathrm{Na}}[\mathrm{Na}^+]}{[\mathrm{H}^+]}\right) \tag{8}$$

The lauryl sulfate adsorption can be expressed by the distribution coefficient, α, of RSO_4^-. The distribution coefficient is the ratio of concentrations of lauryl sulfate immobilized by adsorption and free (migrating) molecules of lauryl sulfate. By taking into account the definition of $K_{\mathrm{RSO}_4^-}$ (Eq. 4), we have

$$\alpha = \frac{[-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-]}{[\mathrm{RSO}_4^-]} = K_{\mathrm{RSO}_4^-}[-\mathrm{CoOH}][\mathrm{H}^+] \tag{9}$$

We use Eq. (8) to eliminate [$-$CoOH] from Eq. (9), then

$$\alpha = \frac{K_{\mathrm{RSO}_4^-}[\mathrm{H}^+]N_s}{1 + \frac{[\mathrm{H}^+]}{K_+} + K_{\mathrm{RSO}_4^-}[\mathrm{H}^+][\mathrm{RSO}_4^-] + K_{\mathrm{X}^{n^-}}^{1/m}[\mathrm{H}^+][\mathrm{X}^{n^-}]^{1/m} + \frac{K_-}{[\mathrm{H}^+]} + \frac{K_{\mathrm{Na}^+}[\mathrm{Na}^+]}{[\mathrm{H}^+]}} \tag{10}$$

From Eq. (10) it follows that the distribution coefficient of RSO_4^- may decrease with an increasing concentration of electrolyte and inorganic anions valence, and with the increasing interaction of surface positive sites with electrolyte anions which is characterized by $K_{\mathrm{X}^{n^-}}^{1/m}$.

To justify this assumption, data are presented in Fig. 8 as α vs log [NaX] (in M/dm^3).

α in relation to log [NaCl] and the volume of the eluate are shown in Fig. 8(A). This is presented by three curves which from top to bottom subsequently correspond to 10, 14, and 20 cm^3 of the eluate. From the

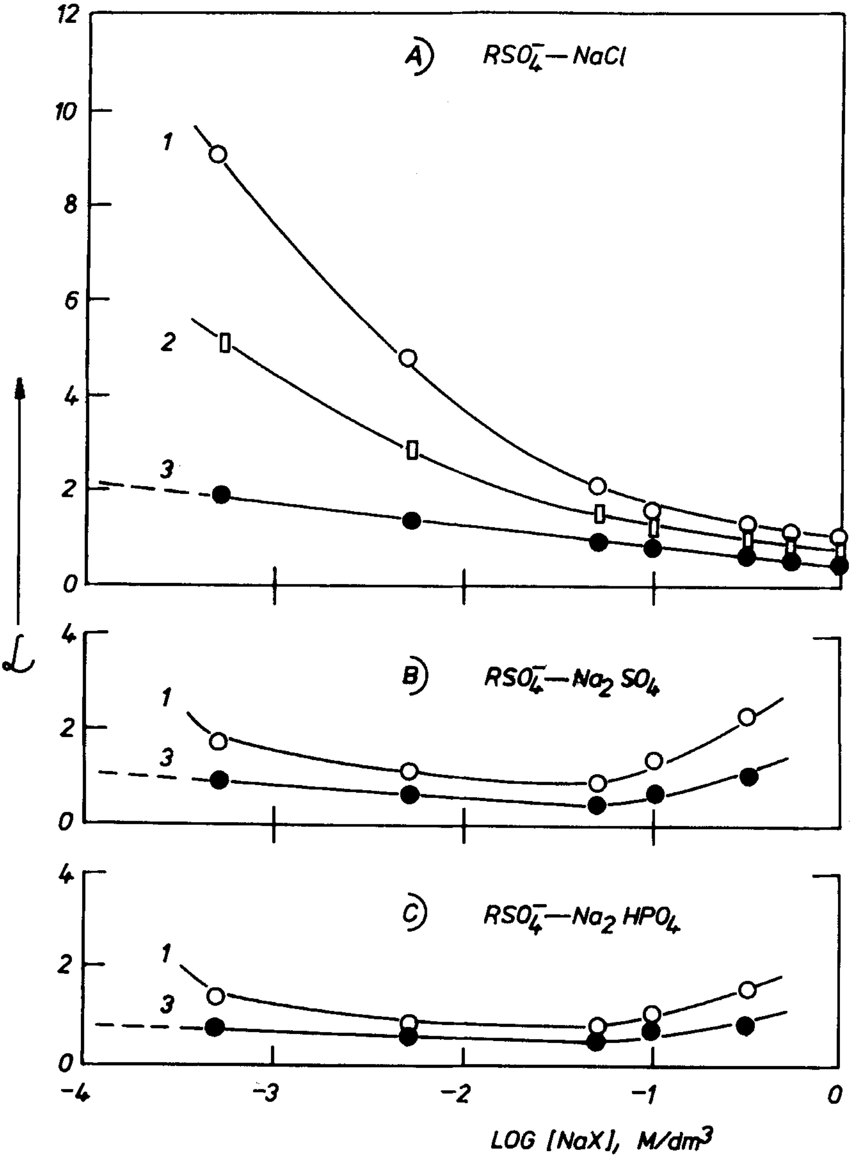

FIG. 8. The change of α in relation to log concentration of sodium salt (chloride, sulfate, and phosphate) at various eluate volumes: (1) 10 cm^3, (2) 14 cm^3, and (3) 20 cm^3.

figure it can be seen that with a volume increase the curves become more and more linear. After passing about 20 cm^3 of solution through the cobalt hydroxide bed, a near-linear decrease of α as a function of log [NaCl] was obtained. This is connected with the fact that, with an increase in the eluate volume, adsorption saturation of the hydroxide surface is approached more and more closely. After about 20 cm^3 of solution is passed through the column, an adsorption equilibrium is established (e.g., Fig. 1A). It may be assumed that all adsorption complexes are then characterized by $K_{RSO_4^-}$ and $K_{X^{n-}}$ of solution anions interaction with the hydroxide surface. It is obvious that the adsorption saturation volume has been limited by lauryl sulfate concentration in solution (10^{-4} M/dm^3), by the mass of the cobalt hydroxide bed (3 g), and the adsorption pH (about 8). A change of these conditions should lead to a changed eluate volume, for which a linear dependence of α vs log [NaX] is obtained.

Figure 8(B) illustrates the change of α as a function of log [Na_2SO_4] after passing 10 and 20 cm^3 (Curves 1 and 3) of solution through the hydroxide bed. As the figure shows, both curves have their minima near a sulfate concentration of 5×10^{-2} M/dm^3. This was explained in the first part of this paper. From an analysis of the curves in Fig. 8(B) it also follows that with increased eluate volume the curve segments on the left of the minimum assume a straight line more and more. After 20 cm^3 of eluate is collected, almost a linear decrease of α as a function of log [Na_2SO_4] can be observed. The elucidation of the above is analogous with that for chlorides based on an approach to the adsorption saturation (equilibrium) condition with increasing eluate volume, and hence to the amount of lauryl sulfate introduced onto the hydroxide bed. The possibility of fixation of two surface positive sites of hydroxide by the SO_4^{2-} anion is responsible for the fact that the slope of the straight line α vs log [Na_2SO_4] is about half as large as that of the straight line α vs log [NaCl]. The slope, about 1/2 that shown in Fig. 8(A), points to competitive adsorption of SO_4^{2-} anions in relation to RSO_4^- anions at a 1:2 ratio. This fact confirms two-site adsorption of a sulfate anion and that one sulfate anion blocks two surface positive sites. This fact accounts for similar adsorption of Cl^-, i.e., one chloride anion blocks one surface positive site.

Analogous conclusions are drawn from the results presented in Fig. 8(C) which characterizes lauryl sulfate adsorption from phosphate solutions. The course of α vs log [Na_2HPO_4] is similar to that for sulfate solutions, i.e., minima are present in both functions at about 5×10^{-2} M/dm^3 of salts, and the slope of the straight line α–log [Na_2HPO_4] is about half as large as that of the straight line α–log [NaCl]. This facts points to competitive adsorption of phosphate anions in relation to lauryl sulfate anions at about a 1:2 ratio [at the pH at which adsorption occurred, the predominant form of phosphate is the divalent anion (*11*, *45*)].

From the discussion of the adsorption results it appears that earlier assumptions and theoretical conclusions concerning competitive adsorption of anions of lauryl sulfate and inorganic salts have been experimentally confirmed. Experiments on the verification of the simple theoretical relationship are now in progress in our laboratory.

CONCLUSIONS

The formation of the adsorption complexes of inorganic anions $m(-\mathrm{CoOH}_2^+),\mathrm{X}^{n-}$ (where $1 \leqslant m \leqslant n$) makes lauryl sulfate adsorption impossible or difficult and, therefore, it has a negative effect on the effectiveness of the precipitate flotation of cobalt hydroxide and on the degree of removal of anionic surfactant from solution. However, if the adsorption complex of lauryl sulfate $-\mathrm{CoOH}_2^+,\mathrm{RSO}_4^-$ is formed, the hydroxide sediment may undergo hydrophobization and precipitate flotation may occur.

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