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Abstract

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The Influence of the Concentration of an Electrolyte Solution (Copper Sulfate) on Exchange Sorption by Crystals of Fatty Acids

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It was found (^{1}) that crystals of fatty acids are capable of sorbing cations from aqueous salt solutions, being converted into the corresponding metallic soaps. The rate of the exchange reaction depends strongly on temperature, which is associated, in particular, with polymorphic transformations of the acid crystals and with the hydration affecting them. It was established that especially intensive penetration of metal cations into the lattice occurs near the melting temperature of the acid.

In the present work, the liberation of hydrogen ions by crystals of lauric, myristic, palmitic, and stearic acids in aqueous $CuSO_4$ solutions of various concentrations was studied; it was evaluated from the change in pH with the aid of a glass electrode and an LP-3 tube potentiometer. The $CuSO_4$ solutions with the acid crystals introduced into them were kept in closed weighing bottles at room temperature ($t \simeq 20^\circ$). To accelerate the process, the acid crystals (Kahlbaum) were ground by trituration in a mortar. The concentration of the $CuSO_4$ solutions varied within the range 0.0004–0.5 N; in this case the natural pH values arising as a result of hydrolysis lay within the range 6.0–3.8.

Figure 1 shows curves of the dependence Γ—the amount of liberated H^+ ions, calculated in equivalents for the total weighed amount of acid taken—on the initial pH values of the solutions (Table 1) for C_{16}-, C_{14}-, and C_{12}-acids at different times, up to 200 days. The curves for all acids pass through a maximum lying at pH = 4.75, corresponding to $C = 0.05\,N$ and to a 10-fold amount of salt relative to the weighed amount of acid taken. For the three indicated acids, the position of the maximum is practically independent of the chain length of the acid homolog and is determined by the nature of the electrolyte ($AgNO_3, Th(NO_3)_4, Ce(NO_3)_3$).

With shortening of the chain of the acid homolog, the height of the curve, i.e., the intensity of liberation of H^+ ions, increases. This is explained by the fact that transition to lower homologs is equivalent to raising the temperature for a higher homolog, which agrees with previous data (^{1}).

Figure 1. Dependence of Γ' on pH for crystals of palmitic (a), myristic (b), and lauric (c) acids in $CuSO_4$ solutions

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Of special interest are the reasons for the appearance of a maximum on the curve of the dependence of H^+-ion liberation on the concentration C of the solution. With increasing C_{CuSO_4}, the reaction proceeding according to the scheme

$$2RCOOH + CuSO_4 = (RCOO)_2Cu + H_2SO_4,$$

should shift to the right, although excessive accumulation of H^+ ions as a result of hydrolytic decomposition of $CuSO_4$ in concentrated solutions and as a result of exchange sorption could inhibit the exchange.

Therefore the first assumption reduces to the idea that in more concentrated solutions the reaction is slowed down because of the reverse reaction of decomposition of the copper soap being formed. This, however, is refuted by the fact that the absolute pH values attained as a result of exchange sorption in solutions of medium concentrations prove to be lower than in solutions of the highest concentrations (Table 1)*. Therefore the anomaly of exchange-sorption liberation of H^+ ions must be explained otherwise.

Fig. 1. Dependence of Γ' on pH for crystals of palmitic (*a*), myristic (*b*), and lauric (*c*) acids in $CuSO_4$ solutions

Table 1

pH values in the initial $CuSO_4$ solutions and in the same solutions after introduction into them of weighed portions of fatty-acid crystals

C	Lauric acid, initial	Lauric acid, 2 days	Lauric acid, 15 days	Lauric acid, 90 days	Lauric acid, 185 days	Palmitic acid, initial	Palmitic acid, 2 days	Palmitic acid, 5 days	Palmitic acid, 51 days	Palmitic acid, 202 days
0.5	3.90	3.03	3.02	3.00	2.86	3.94	3.93	3.85	3.53	3.3
0.2	4.22	3.04	3.02	2.95	2.75	4.27	4.10	3.80	3.41	3.3
0.1	4.47	3.02	2.95	2.87	2.78	4.53	4.06	3.68	3.43	3.32
0.05	4.68	3.20	2.93	2.90	2.70	4.75	4.10	3.78	3.45	3.36
0.02	5.00	3.32	2.95	2.87	2.70	5.01	3.98	3.70	3.45	3.30
0.01	5.13	3.43	3.01	2.96	2.83	5.20	4.02	3.98	3.55	3.38
0.005	5.32	3.50	3.15	3.05	2.97	5.39	4.12	4.08	3.70	3.52
0.002	5.59	3.68	3.29	3.40	3.20	5.65	4.22	4.19	4.02	3.76
0.001	5.72	3.92	3.47	3.53	3.42	5.82	4.31	4.28	4.19	3.89
0.0004	5.88	4.04	3.70	3.72	3.65	6.00	4.69	4.52	4.47	4.09

C	Lauric acid, initial	Lauric acid, 2 days	Lauric acid, 15 days	Lauric acid, 90 days	Lauric acid, 185 days	Palmitic acid, initial	Palmitic acid, 2 days	Palmitic acid, 5 days	Palmitic acid, 51 days	Palmitic acid, 202 days
0.0002						6.00	4.65	4.59	4.62	3.89

Lauric acid, weighed portion $m = 0.025$ g

Palmitic acid, weighed portion $m = 0.032$ g

In studying exchange sorption in $AgNO_3$ solutions on palmitic acid by the conductometric method, we found that the electrical conductivity of the $AgNO_3$ solution at first decreases, passes through minimum and then increases, exceeding the initial value (Fig. 2). This indicates that at first the total concentration of electrolyte decreases, evidently as a result of molecular sorption of $AgNO_3$, and only after, as a result of exchange, the amount of H^+ ions becomes sufficiently large does the electrical conductivity reach higher values. Hence it follows that, when considering processes of exchange sorption on crystals of fatty acids, molecular sorption must be taken into account. This also followed from our previous data with $Th(NO_3)_4$.

Fig. 2

Molecular sorption should increase with increasing electrolyte concentration; therefore the decrease in the rate of liberation of H^+ ions with increasing $CuSO_4$ concentration may be connected with the influence of molecular sorption. It should be noted that the retardation of the reaction at higher values of $C_{\mathrm{CuSO_4}}$ cannot be attributed to a decrease in the activity of the solution. Apparently, the chief role is played by the kinetics of the process, depending on the occurrence of certain potential barriers.

Delays in the process of liberation of H^+ ions are less pronounced for the shortest homologues of the acids; consequently, an increase in the activity of the acid and in the mobility of its molecules in the crystal, i.e., in the "looseness" of the lattice, corresponding to an increase in the temperature of the higher homologues of the acids, diminishes the action of the retarding barriers. This assumption is confirmed by additional experiments carried out with increased charges of the acid (stearic) in solutions of higher concentrations than that corresponding to the maximum of the curve $\Delta[H^+] = f(C)$.

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* The LP-3 potentiometer, according to its certificate, provides an accuracy of pH ± 0.1. Here values are given to hundredths of a pH unit. They cannot be considered accurate in all cases; however, in many series of experiments, with stable operation of the potentiometer, they apparently correctly reflect the course of the change of pH with concentration.

Table 2

Values of pH for stearic acid crystals in $CuSO_4$ solutions

Charge of stearic acid, g	$C =$ 0.2N, initial	$C =$ 0.2N, after 262 h.*	$C =$ 0.01N, initial	$C =$ 0.01N, after 168 h.*	$C =$ 0.002N, initial	$C =$ 0.002N, after 116 h.*
0.0355	4.16	4.01	5.20	3.94	5.53	4.01
0.1775	4.18	3.54	5.20	3.69	5.51	3.85
0.8875	4.18	3.17	5.17	3.55	5.48	3.81

* The time indicated here refers to attainment of a certain practical limit of pH change.

In the experiments corresponding to the curves in Fig. 1, small charges of acids were taken, corresponding to 0.000125 g-equiv. With an increase in the acid charge, the rate of liberation of H^+ ions—and, together with it, the course of the curve $\Delta[H^+] = f(C)$—changes markedly, and the anomalous curve with a maximum becomes a normal curve of continuous increase of $\Delta[H^+]$ with C. At the same time the pH decreases to much lower values than the smallest values attained with small charges (Table 2). This is seen from Fig. 3 for stearic acid (in this case the maximum $\Delta[H^+]$ at a small charge lies at a lower concentration than for the acids C_{12}, C_{14}, and C_{16}).

An increase in the acid charge means that, per unit surface of the sorbent, there is a smaller amount of adsorbed substance retarding the process, i.e., the specific influence of the passivator decreases. Owing to the large surface of the sorbent, in a short time the reaction has time to proceed only in the surface layers, without penetrating deep into the crystal. Therefore the "blocking" action of the adsorbed anions is almost not manifested.

The penetration of the electrolyte into the acid lattice apparently begins in the more damaged parts of the crystal, at its corners and edges, where the packing

acid molecules is less perfect and the polar groups are more accessible to electrolyte molecules. Apparently, hydration of the polar groups of the acid molecules and adsorption of the electrolyte on them weaken the interaction between oppositely oriented acid molecules in the crystal. This is especially promoted by an increase in temperature or a shortening of the homolog' s chain. The exchange process consists of a number of stages: hydration of the polar groups of the acid molecules, weakening or rupture of the bonds between oppositely

Fig. 3. Dependence of $\Delta[H^+]$ on C (a) and on m (b) for crystals of stearic acid in $CuSO_4$ solutions.

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oriented acid molecules and dissociation of the carboxyl group with liberation of an H^+ ion, replacement of the latter by a metal cation and formation of a molecule of metallic soap, the appearance of a nucleus of a soap crystallite and its growth. In this connection, the ratio of the lattice parameters of the acid and the soap, as well as the radius of the cation, probably has great significance.

Molecular sorption may proceed on undissociated molecules and is most intensive at low temperatures. In polymorphic transformations of crystals, the acid molecules in them can probably, for a short time, become "monomers" from "dimers." At the moment of rupture or weakening of the hydrogen or dipole bond between two acid molecules, they acquire a greater capacity for dissociation and exchange. Therefore a polymorphic transformation accelerates exchange reactions (in addition to the simple increase in the internal surface of the crystal due to its restructuring).

The transition of sorption from exchange to molecular with increasing electrolyte concentration was observed on gelatin [2], but in that case it was not indicated that molecular sorption can inhibit exchange sorption.

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REFERENCES

[1] A. A. Trapeznikov, DAN, **47**, 277, 349 (1945); A. A. Trapeznikov, M. E. Lipets, ZhFKh, **21**, 109 (1947); M. E. Lipets, A. A. Trapeznikov, ZhFKh, **23**, 981 (1949). [2] A. G. Pasynsky, Z. Zolotareva, ZhFKh, **16**, 27 (1942).

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