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Separating Nonionic Surfactants and Zinc(II) in Water Recovery

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ABSTRACT

The sorption of zinc(II) in the presence of nonionic surfactants (alkylmonoethers ALM-10, oxyethylated alcohols OS-20) in the hydrogen-containing form of Purolite C 106 carboxylic acrylcationic exchanger has been investigated to consider the possibility of the simultaneous control of both Zn(II) and surfactants in sewage effluents. Sorption isotherms were measured, both distribution and diffusion coefficients were calculated, and the progress of zinc(II) sorption in various forms was estimated. The sorption of zinc(II) cations, the molecules of surfactant, and the products of their interaction take place simultaneously. The mutual action of zinc(II) and the surfactant leads to an increase in the rate of their intraparticle diffusion and the degree of saturation of the cation exchanger. However, it also leads to a decrease in the equilibrium sorption of both zinc(II) and surfactant. The sorption of free molecules of surfactant is predominant. Zinc(II) take-up proceeds as follows: 1) free cations on the basis of complex (ionic + coordinate) bonding; 2) free cations on the basis exclusively of coordinate bonding; 3) cations bonding to the surfactant molecules.

INTRODUCTION

Zn(II) compounds are widely used in galvanization, textiles, glasswork, accumulators, corrosion inhibitors, and other fields of production. There are industries such as galvanoplastics where both heavy metal salts and nonionic surfactants are used for the formulation of the same plating batch composi-

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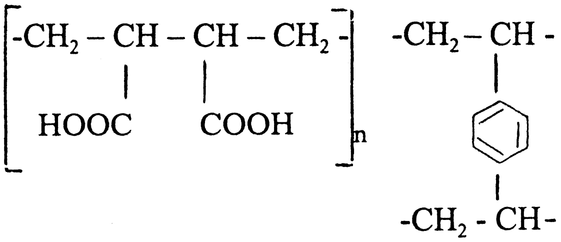
tion. Nonionic surfactants including oxyethylated alcohols (OS-20) and alkylmonoethers (ALM-10) are added into plating solution as antipitting agents (1). The toxicity of both heavy metal(II) and nonionic surfactants requires that the concentration of these contaminants in industrial sewage effluents be controlled. Control can be achieved by the purification and recycling of purified plating rinsewater. Sewage purification from heavy metal(II) and nonionic surfactant contaminants has been widely investigated separately and is used in practice. The simultaneous removal of heavy metal(II) and nonionic surfactants from the same solution is complex because the cation exchangers used for sewage purification for metal cations are not effective for the purification of nonionic surfactants. In this study the possibility of the simultaneous elimination of both nonionic surfactants and Zn(II) by the hydrogen-containing form of the carboxylic acrylcationic exchanger Purolite C 106 from separate solutions and from equimolecular mixtures was investigated for the control of both nonionic surfactants and Zn(II) in sewage effluents.

The possibility of controlling both metal(II) [Ni(II) (2), Pb(II) (3)] and nonionic surfactants (ALM-10, OS-20) by Purolite C 106 has been established.

The purpose of this study was to determine the reciprocal effect of Zn(II) and nonionic surfactants (oxyethylated alcohols OS-20, alkylmonoethers ALM-10) on the kinetics and the equilibrium of their take-up by the hydrogen-containing form of Purolite C 106 cation exchanger and to estimate Zn(II) take-up in its various forms.

Nonionic surfactants OS-20 and ALM-10 are produced on an industrial scale [Russia (21)]. They were supplied by Reagentas UAB (Lithuania). OS-20 and ALM-10 represent oxyethylated higher fatty alcohols which differ by both the number of carbon atoms in the alkyl radical and by the number of C_2H_4O units in the ethylene oxide chain. The structure of OS-20 and ALM-10 corresponds to the formula $C_nH_{2n+1}O(C_2H_4O)_mH$, where n is from 12 to 14 for ALM-10 and ~18 for OS-20; m is ~10 for ALM-10 and ~20 for OS-20; the mean molecular mass is ~643 for ALM-10 and ~1148 for OS-20. Wetting, emulsifying, degreasing, and other surface-active properties are inherent to OS-20 and ALM-10 due to the ethylene oxide active chain. As universal surfactants, OS-20 and ALM-10 are widely used not only as antipitting agents in galvanoplastics but also in many technological processes; OS-20 is also used as a disperser and antistatic agent (4).

Purolite C 106 carboxylic acrylcationic exchanger is produced by Purolite International Ltd. on an industrial scale (5). It represents a copolymer of the methylester of acrylic acid with divinylbenzene. A paired fixation of a carboxylic group —COOH at nearby carbon atoms in the matrix of the cation exchangers is inherent to the structure of cation exchangers like Purolite C 106:



Take-up of nonionic surfactants by carboxylic acrylcationic exchangers is much higher when compared to take-up by sulfonic, iminodiacetic, and other types. This is presumably due to the differences in the distances between the oxygen atoms in the chain of C_2H_4O units present in the surfactant with the distances between —COOH groups in the cation exchanger. Carboxylic cation exchangers are used for the removal of transition metal(II) (6); due to the complex (ionic + coordinate) bond with carboxylic groups, transition metals(II) are held stronger in carboxylic cation exchangers than in sulfonic ones.

The concentration of carboxylic functional groups (—COOH), determined with 0.1 N NaOH in the fraction of granules with diameters from 0.2 to 0.5 mm, is 7.3 mmol per gram of Purolite C 106. The sorption isotherms were measured as follows (7): The samples of the cation exchanger (0.5 g by dry weight) were equilibrated at 20°C with 100 mL of solution. The range of the concentration (from 1 to 10 $\text{mmol}\cdot\text{dm}^{-3}$) in the series of solutions investigated corresponds to the concentration of contaminants in sewage purified by ion exchangers. The concentration of Zn(II) was determined complexometrically with EDTA disodium salt using xylene orange (8). The spectrophotometric method was used for the determination of the nonionic surfactant (9).

Column investigation of sorption kinetics was carried out following Ref. 7. Effective coefficients for the intraparticle diffusion (D, $\text{cm}^2\cdot\text{s}^{-1}$) were calculated as described in Refs. 10 and 11.

Repetitive measurements of isotherms yielded reproducibility at a mean relative deviation (d/x) of $100 \leq 2$ and a standard relative deviation (s/x) of $100 \leq 2.5$ calculated in accordance with Ref. 12.

Distribution coefficients (K_d, $\text{cm}^3\cdot\text{g}^{-1}$) were calculated following Ref. 5.

RESULTS AND DISCUSSION

The presence of a nonionic surfactant contributes to an increase in the degree (F) of saturation of the cation exchanger with Zn(II). The effect of OS-

20 on the *F* value (Fig. 1, Curve 3) is considerably greater than that of ALM-10 (Curve 2). Besides other factors, this could be due to the more complex structure of the former than that of the latter, and consequently a greater influence of the steric factor against the diffusion of Zn(II) bonded to OS-20 compared to that against the diffusion of Zn(II) bonded to ALM-10. The number of carboxylic groups accessible to the sorbate diminishes due to the steric factor. In spite of Zn(II) bonded to RCO_2^- (here R is the matrix of the cation exchanger), taking up of Zn(II) bonded to nonionic surfactant also takes place due to the surfactant acting as an intermediate species. According to one explanation (13), taking up of a nonionic surfactant proceeds on the basis of hydrogen bonding between the oxygen atoms in C_2H_4O units and the hydrogen atoms in un-ionized —COOH groups. *D* values for the diffusion of both Zn(II) and nonionic surfactants are compared with *D* values for the diffusion of other contaminants in the ion exchangers used for sewage purification in Table 1. Consequently the sorber filled with Purolite C 106 cation exchanger would not

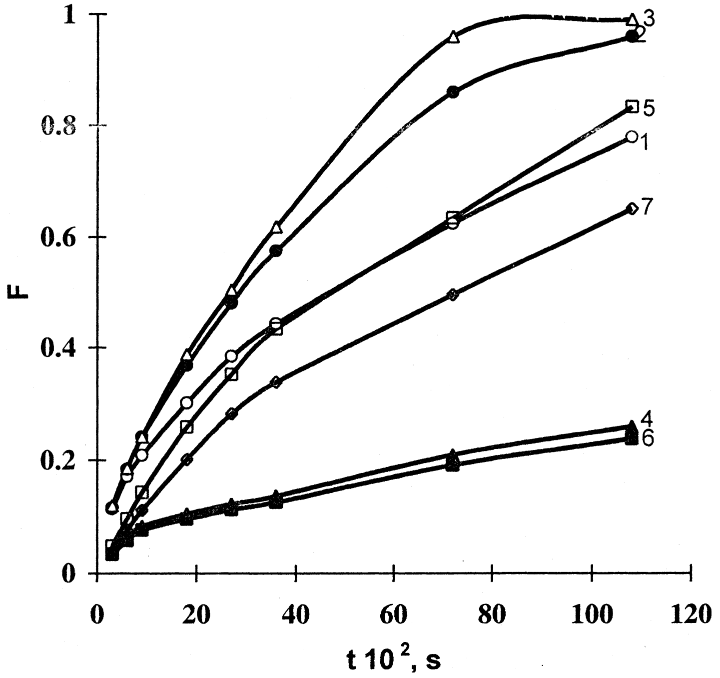


FIG. 1 The degree (*F*) of saturation of the cation exchanger with Zn(II) and nonionic surfactant vs duration of interaction. Curve 1: Zn(II) without nonionic surfactant (a_m = 0.077 mmol·g^{-1}). Curve 2: Zn(II) in the presence of ALM-10 (a_m = 0.063 mmol·g^{-1}). Curve 3: Zn(II) in the presence of OS-20 (a_m = 0.061 mmol·g^{-1}). Curve 4: ALM-10 without Zn(II) (a_m = 0.653 mmol·g^{-1}). Curve 5: ALM-10 in the presence of Zn(II) (a_m = 0.564 mmol·g^{-1}). Curve 6: OS-20 without Zn(II) (a_m = 0.303 mmol·g^{-1}). Curve 7: OS-20 in the presence of Zn(II) (a_m = 0.205 mmol·g^{-1}). The concentration of Zn(II) and nonionic surfactant in the initial solution was 0.006 mol·dm^{-3}; pH 5.

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TABLE 1

Dependence of the Coefficients (D) for Zn(II) and Nonionic Surfactant Intraparticle Diffusion in Purolite C 106 Cation Exchanger on the Duration of Interaction (t)

	$D \times 10^9$ ($cm^2 \cdot s^{-1}$)						
	Zn(II)			OS-20		ALM-10	
t (10^2 s)	$a_m = 0.077$ $mmol \cdot g^{-1}$	With ALM-10: $a_m = 0.063$ $mmol \cdot g^{-1}$	With OS-20: $a_m = 0.061$ $mmol \cdot g^{-1}$	$a_m = 0.303$ $mmol \cdot g^{-1}$	With Zn(II): $a_m = 0.205$ $mmol \cdot g^{-1}$	$a_m = 0.653$ $mmol \cdot g^{-1}$	With Zn(II): $a_m = 0.564$ $mmol \cdot g^{-1}$
3	2.66	2.66	3.0	0.1	0.2	0.02	0.03
6	2.80	3.10	3.0	0.2	0.4	0.04	0.06
9	2.56	3.10	3.1	0.3	0.6	0.07	0.07
18	2.71	3.59	3.7	0.3	1.3	0.15	0.20
27	2.62	4.26	4.9	0.3	1.5	0.29	0.31
36	2.71	5.78	6.1	0.3	1.5	0.29	0.49

[a] Diameter of granules: 0.2–0.5 mm. Initial concentration of Zn(II) and nonionic surfactant: 6 $mmol \cdot dm^{-3}$, pH 5.

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be the limiting stage if it was integrated into a conventional system of sewage treatment by ion exchangers.

The take up of transition metal cations in a carboxylic cation exchanger by ion exchange follows the transformation of its electronic envelope leading to the formation of a carboxylate complex on the basis of both ionic and coordinate bonds. The bond formation is explained as follows. The carboxylic group, —COOH, contained in the cation exchanger consists of two groups: carbonyl (═CO) and hydroxyl (—OH). The oxygen atoms in the carbonyl groups contain undivided pairs of electrons able to introduce themselves into the orbitals of transition metal cation-forming coordinate bonds (14). The ionization of carboxylic group is followed by the displacement of electrons from the oxygen atom in the hydroxyl group to the oxygen atom in the carbonyl group so that both oxygen atoms become uniform with respect to the density of their electron envelopes. The interaction between oxygen atoms in the carboxylic group and cations of the transition metal(II) leads to the formation of a stable four-membered cyclic compound on the basis of both ionic and coordinate bonding.

Taking into account the decrease in the solution pH due to the sorption of Zn(II) (Fig. 2, Curve 1) on one hand and that Zn(II) cation corresponds to two hydrogen ions

$$2RCH_2COOH + Zn^{2+} \rightleftarrows (RCH_2COO)_2Zn + 2H^+ \qquad (1)$$

on the other hand, Zn(II) sorption taking place by ion exchange on the basis of complex (ionic + coordinate) bonding (a_1, mmol·g^{-1}) can be calculated by

$$a_1 = \frac{1}{2}\Delta[H^+] \qquad (2)$$

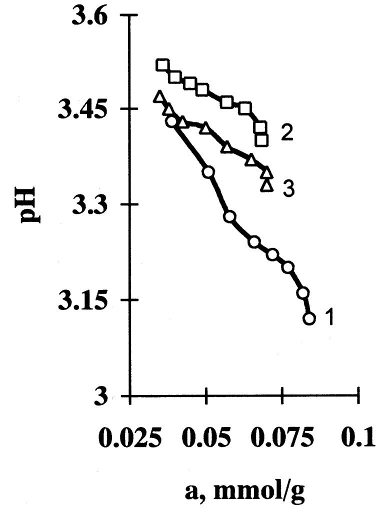

FIG. 2 pH dependence on Zn(II) sorption. Curve 1: Without nonionic surfactant. Curve 2: In the presence of ALM-10. Curve 3: In the presence of OS-20. Initial pH: 5.

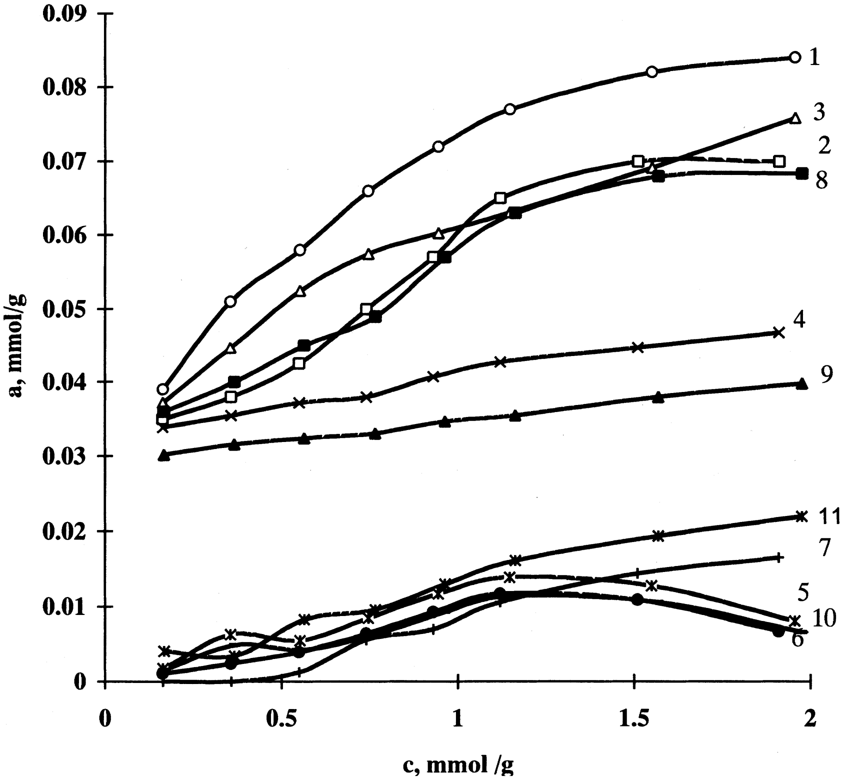

FIG. 3 Isotherms of Zn(II) sorption. Curve 1: Total without nonionic surfactant. Curve 2: Total in the presence of OS-20. Curve 3: In the form of Zn(II) free cation without nonionic surfactant. Curve 4: In the form of Zn(II) free cation in the presence of OS-20. Curve 5: By coordinate bonding without nonionic surfactant. Curve 6: By coordinate bonding in the presence of OS-20. Curve 7: In the form of Zn(II) cations bonded to OS-20. Curve 8: Total in the presence of ALM-10. Curve 9: In the form of Zn(II) free cations in the presence of ALM-10. Curve 10: By coordinate bonding in the presence of ALM-10. Curve 11: In the form of Zn(II) cations bonded to ALM-10. Initial pH: 5.

where $\Delta[H^+]$ is the increment of hydrogen ions concentration due to the substitution of Zn(II) cations for hydrogen ones (mmol·g^{-1}). The total sorption of Zn(II) (Σa, mmol·g^{-1}) determined experimentally should correspond to the sorption (a_1) calculated from the change in pH if the sorption had proceeded exclusively by ion exchange. Although the data obtained indicate that $\Sigma a > a_1$ (Fig. 3, Curves 1 and 3), this discrepancy may be due to the supplementary sorption of Zn(II) complexing proceeding exclusively by coordinate bonding without any ionic bonding. Sorption proceeding exclusively on the basis of coordinate bonding (a_2, mmol·g^{-1}) can be calculated by

$$a_2 = \sum a - a_1 \tag{3}$$

In the presence of a nonionic surfactant the change in pH is less significant (Fig. 2) and total sorption is lower than without a nonionic surfactant (Fig. 3,

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TABLE 2

Dependence of ALM-10, OS-20, and Zn(II) Distribution Coefficient (K_d) on Both the Concentration and the Composition of the Initial Solution

	Initial concentration (mmol·dm^{-3})							
	1	2	3	4	5	6	8	10
Composition	K_d (cm^3·g^{-1})							
ALM-10 + H_2O	729	516	526	400	300	215	137	103
ALM-10 + Zn(II) + H_2O	521	406	393	287	222	175	118	89
OS-20 + H_2O	380	146	107	89	74	65	50	42
OS-20 + Zn(II) + H_2O	252	107	73	58	45	37	27	25
Zn(II) + H_2O	48	29	21	18	15	13	11	9
Zn(II) + ALM-10 + H_2O	43	22	16	13	12	11	9	7
Zn(II) + OS-20 + H_2O	43	21	15	13	12	11	9	7

Curves 1, 2, and 8). The decrease in Σa arises from the decrease in a_1 which is due to the solubilization/dispersion of Zn(II) by nonionic surfactants. While a supplementary sorption of Zn(II) (except $a_1 + a_2$) was observed to be due to the presence of a surfactant, it may be related to the sorption of Zn(II) bonded to nonionic surfactant taking place by hydrogen bonding across —C_2H_4O— units as connecting species without a change in pH. Assuming that a_2, calculated with respect to the corresponding value of Σa in the presence of a surfactant could be in proportion to a_2 without a surfactant, the sorption of Zn(II) bonded to a surfactant (a_3, mmol·g^{-1}) can be approximated by

$$a_3 = \sum a - a_1 - a_2 \tag{4}$$

where a_1 is the sorption of Zn(II) by ion exchange in the presence of a surfactant (mmol·g^{-1}) and a_2 is the sorption of Zn(II) by coordinate bonding (mmol·g^{-1}). The sorption of Zn(II) bonded to a surfactant (Fig. 3, Curves 7 and 11) is higher in most cases when compared to sorption proceeding exclusively by coordinate bonding (Fig. 3, Curves 6 and 10). The sorption of a surfactant is predominant in determining the distribution coefficients regardless of the fact that Zn(II) is taken up in several forms (Table 2). The presence of Zn(II) leads to a decrease in K_d for a surfactant while the presence of a surfactant leads to a decrease in K_d for Zn(II). A decrease in K_d values for both the surfactant and Zn(II) is also observed when the initial solution concentration is increased.

CONCLUSIONS

In the presence of a nonionic surfactant (alkylmonoethers ALM-10, oxyethylated alcohols OS-20) the simultaneous sorption of Zn(II) cations, surfactant molecules, and products of their interaction takes place simultaneously in the hydrogen-containing form of Purolite C 106 carboxylic acrylcationic exchanger. The reciprocal action of Zn(II) and the surfactant leads to an increase in the rate of both their intraparticle diffusion and the degree of saturation of the cation exchanger, although it also leads to a decrease in the equilibrium sorption of both Zn(II) and the surfactant. The take-up of the free molecules of the surfactant is predominant.

The take-up of Zn(II) takes place in the following forms: 1) the take-up of the free cations proceeds by complex (ionic + coordinate) bonding; 2) the take-up of the free cations proceeds exclusively by coordinate bonding; 3) the take-up occurs by cations bonding to the molecules of a nonionic surfactant.

The simultaneous separation of nonionic surfactants and Zn(II) by using the hydrogen form of Purolite C 106 cation exchanger could be suitable for water recovery and for the control of both Zn(II) and surfactants in sewage effluents.

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