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ORIGINAL CONTRIBUTION

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Simultaneous sorption of nonionic surfactant (alkylmonoethers) and copper(II) in a weak acid polyacrylic cation exchanger

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Abstract The mutual influence of copper(II) cations and nonionic surfactant alkylmonoethers on their simultaneous sorption by the hydrogen form of Purolite C 106 polyacrylic acid functionalized cation exchanger was investigated considering the suitability for the prevention of environmental contamination. Sorption isotherms were measured and sorption equilibrium coefficients calculated. The modelling of copper(II) sorption and copper(II) carboxyl complex formation was carried out. The sorption of copper(II) proceeds predominantly by complex (ionic and coordinate) bonding followed by the change in pH, also by single coordinate bonding. The mutual action of copper(II) and alkylmonoethers leads to a decrease in the equilibrium sorption for both copper(II) and the surfactant. The sorption of copper(II) and alkylmonoethers could be applicable for the purification of sewage including copper plating rinsewater from both contaminants simultaneously for the control of copper(II) and the surfactant in sewage effluents.

Key words Copper(II) · Nonionic surfactant · Sorption · Cation exchanger

Introduction

The toxicity of heavy metals(II) in ionic form and nonionic surfactants is concerned with public health problems. The maximum allowed levels of these contaminants are regulated by legislation in each country. Therefore the sorption of copper cations and molecules of nonionic surfactants in the hydrogen-containing form of polyacrylic acid functionalized cation exchanger is of interest with respect to the prevention of environmental pollution. Both copper(II) and nonionic surfactants are often discharged simultaneously from a variety of industrial sources, including copper electroplating rinsewater. To avoid environmental pollution the rinsewater must be purified and recycled. Ion exchangers are used for the sorption of metals(II) including copper(II) to almost the detection limit [1]. The mechanism of the sorption of metals(II) by ion exchangers in the absence of nonionic surfactant has been widely investigated using potentiometric titration, IR spectroscopy, electron microscopy, X-ray structure analysis and other techniques [2–10]. The formation of a carboxylate complex during the sorption of transition-metal(II) cations by carboxyl-group-containing cation exchangers has been confirmed [10–13]. Because of the formation of complex compounds the sorption of transition metals(II) by carboxylic cation exchangers is governed by intraparticle diffusion in spite of the initial solution concentration.

The sorption of nonionic surfactants by ion exchangers in the absence of copper(II) has been investigated [14, 15]. One of the assumptions concerning the sorption of nonionic surfactants by unionized carboxyl-group-containing cation exchangers is that the taking up proceeds on the grounds of hydrogen bonding [15, 16]. On increasing either the degree of cross-linking in the matrix of the cation exchanger or the degree of the transformation of carboxyl groups to the sodium form (–COONa) a decrease in the sorption of nonionic surfactant was observed. When the concentration of the carboxyl groups in the sodium form amounted to

50%, the sorption of nonionic surfactant stopped; when it amounted to 100%, the desorption of nonionic surfactant took place. In previous work the sorption of nonionic surfactant alkylmonoethers (ALM-10) in the presence of cadmium(II) [17], lead(II) and nickel(II) was investigated [18]. It was determined that the sorption of metal(II) cations and surfactant molecules took place simultaneously. The total sorption of lead(II) was higher than that of nickel(II). Subsequently the action of lead(II) resulted in a decrease in the equilibrium sorption of surfactant, whereas the action of nickel(II) on the equilibrium sorption of surfactant was insignificant. The data concerning the simultaneous sorption of copper(II) and nonionic surfactant were not available.

The purpose of this study was to determine the mutual influence of ALM-10 and copper(II) cations on the equilibrium of their simultaneous sorption by Purolite C 106 polyacrylic acid functionalized cation exchanger and to estimate the forms of copper(II) sorption.

Experimental

A KFK spectrophotometer (Russia) with 5-cm path length cells was applied to determine the concentration of nonionic surfactant; the main absolute derivation of the measurement of the transmission coefficients was ±1%. A pH-673M model pH meter–millivoltmeter (Russia) supplied with glass and silver chloride electrodes and with an automatic thermocompensator was used for the measurement of the solution pH. Stirring was carried out with an R5 (Poland) magnetic stirrer adjusted to 400 rpm.

Purolite C 106 of industrial scale production was supplied by Purolite International [1]. It represents a copolymer of methylester of acrylic acid with divinylbenzene.

The sorption of nonionic surfactants by polyacrylic acid functionalized cation exchangers is much higher when compared to that by sulphonic, iminodiacetic and cation exchangers of other types, presumably because of the steric arrangement between adjacent functional groups of the cation exchanger and oxyethylene units in the surfactant.

Carboxylic cation exchangers, including polyacrylic acid functionalized ones, are also used for the removal of transition metals(II) [1]. Because of the complex (ionic and coordinate) bond with carboxyl groups transition metals(II) are held more strongly in carboxylic cation exchangers than in sulphonic ones.

A sample of the cation exchanger in the hydrogen-containing form was sieved with 0.2 and 0.5-mm sieves. The fraction containing the granules from 0.2 to 0.5 mm in diameter was dried in air. The concentration of the carboxyl groups was 7.3 $\mathrm{mEqg^{-1}}$ of the cation exchanger (dry weight).

ALM-10 produced on an industrial scale was provided by Reagentas UAB (Lithuania). ALM-10 represents oxyethylated higher fatty alcohols [19]. The structure of ALM-10 corresponds to the formula $C_nH_{2n+1}O(C_2H_4O)_mH$, where n is from 12 to 14, $m{\sim}10$ and the mean molecular mass is about 643. Wetting, emulsifying, degreasing and other surface-active properties are inherent to ALM-10 owing to the active chain of ethylene oxide and the alkyl radical. As a universal surfactant ALM-10 is widely used not only in galvanoplasty but also in many other technological processes. The surfactant was dried at 105 °C and held in a dessicator.

Copper chloride, sodium hydroxide, ethylenediaminetetraacetate (EDTA) disodium salt, hydrochloric acid and nitric acid were of reagent analytical grade. They were purchased from Reagentas UAB and were used without further purification. Deionized water was used for the preparation of all the solutions in all experiments.

The pH of the initial solutions was adjusted to 5 with 0.01 N sodium hydroxide or 0.01 N hydrochloric acid solutions. The sorption of copper(II) and ALM-10 proceeded without any adjustment of the pH. The final pH after the attainment of the equilibrium between the solution and the resin was measured. The acidification of the solution after the sorption of copper(II) was detected because the resin was in the hydrogen form.

The apparent ionization constant (pK_a) for Purolite C 106 cation exchanger was determined at half neutralization of the carboxyl groups ($\alpha = 1/2$) as described in Ref. [20].

The copper(II) concentration in solution was determined complexometrically with 0.05 N solution of EDTA disodium salt using murexide. The determination of copper(II) was also checked when titrating the solution of known concentration both in the absence and in the presence of the surfactant; the determination of copper(II) was not interfered with by the surfactant. A spectrophotometric method using chromazurol S [21] was applied for the determination of the nonionic surfactant. The method is selective for a nonionic surfactant: the formation of a chromazurol S surfactant complex leads to an increase in the solution optical density which is in proportion to the concentration of $-C_2H_4O$ units in the solution. The determination of the surfactant was also checked in the presence of copper(II). It was established that the formation of a copper(II)–chromazurol S complex did not proceed at given acidity (pH 6); consequently, the action of copper(II) did not interfere with the determination of the surfactant.

The measurement of the sorption isotherms was carried out as follows [22]. On the day of use the series of standard solutions of copper(II) containing from 1 to 10 $\mathrm{mmoldm^{-3}}$ (0.2–2 $\mathrm{mmolg^{-1}}$ cation exchanger) copper (II) was prepared. The solutions were equilibrated with 0.5 g cation exchanger (dry weight) at 20 ± 1 °C for 3 days with stirring at 400 rpm for 30 s, three times a day. Upon attainment of the equilibrium the samples of the supernatant liquids were taken and the determination of the copper(II) concentration was carried out in both the supernatant liquids (c_2) and in the series of copper(II) standard solutions without cation exchanger (c_1). The copper(II) sorption was calculated using Eq. (1):

$$a = V(c_1 - c_2)/m_1 \ , \tag{1}$$

where a is the copper(II) sorption (millimoles per gram), V the volume of solution taken for the equilibration with the cation exchanger (cubic centimetres), c_1 the initial copper(II) concentration (millimoles per cubic centimetre), c_2 the equilibrium concentration of copper(II) in solution (millimoles per cubic centimetre) and m_1 the dry mass of cation exchanger (grams).

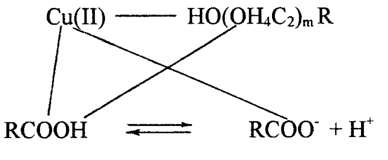
The measurement of the isotherms of ALM-10 sorption by the cation exchanger was carried out analogously using the series of ALM-10 solutions instead of copper(II) solutions. The ALM-10 uptake was calculated as that of copper(II) according to Eq. (1).

The series of standard mixtures containing from 1 to 10 $\mathrm{mmoldm^{-3}}$ (0.2–2 $\mathrm{mmolg^{-1}}$ cation exchanger) copper(II) and ALM-10 was also prepared. Upon attainment of the equilibrium with the cation exchanger the concentration of copper(II) and ALM-10 was determined in the mixtures of the series both without and with the cation exchanger.

Repeated measurements of the isotherms yielded the reproducibility with a mean relative deviation $d/x100 \leq 2$ and a standard relative deviation $s/x100 \leq 2.5$ calculated accordingly to Ref. [23].

Results and discussion

An aqueous solution containing copper(II) salt and nonionic surfactant in the presence of the cation exchanger represents a system which is too complex to evaluate all the interactions occurring in it. The most important of these can be expressed by the Scheme 1.



Scheme 1

Here *R* is the matrix of the cation exchanger (saponified copolymer of methylester of acrylic acid with divinylbenzene).

The interaction between H^+ ions and the cation exchanger depends on the acidic properties of the cation exchanger. The acidic properties may be characterized by the apparent constant (pK_a) of carboxyl groups ionization. pK_a for Purolite C 106 determined according to the modified Henderson–Hasselbach equation [24, 25] at half neutralization in 0.5 M KCl is of the order of 5.8; however carboxylic groups are almost completely non-ionized in mildly acidic or neutral conditions in the absence of salt and base and, consequently, the self-ionization of the ion exchanger can be neglected [26]. The interaction copper(II)-exchanger resulting in the sorption of copper(II) is followed by a decrease in the equilibrium solution pH referring to the transfer of hydrogen cations from the cation exchanger into the solution (Fig. 1). Consequently the action of copper(II) promotes the displacement of the carboxyl group deprotonation equilibrium to the right, resulting in an increase in the concentration of the deprotonated carboxyl groups:

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

It has been demonstrated previously [18] that in the sorption of nickel(II) and lead(II) cations the ion-exchange reactions between the hydrogen form of Purolite C 106 cation exchanger and metal(II) cations were stoichiometric. It was evident that the decrease in the pH of the equilibrium solution was in good agreement with the metal(II) sorption value in the initial concentration range 0-10 mmoldm^{-3}. It can therefore be stated that any pH changes produced during the copper(II) cation sorption may be attributed to the substitution of copper(II) cations for hydrogen ones.

Purolite C 106 cation exchanger acts as a chelating resin because of its ability to form coordinate bonds. The interaction between oxygen atoms in deprotonated carboxyl groups and the cation of transition metals, including copper(II), leads to the formation of stable four-membered cyclic compounds [22] (Scheme 2).

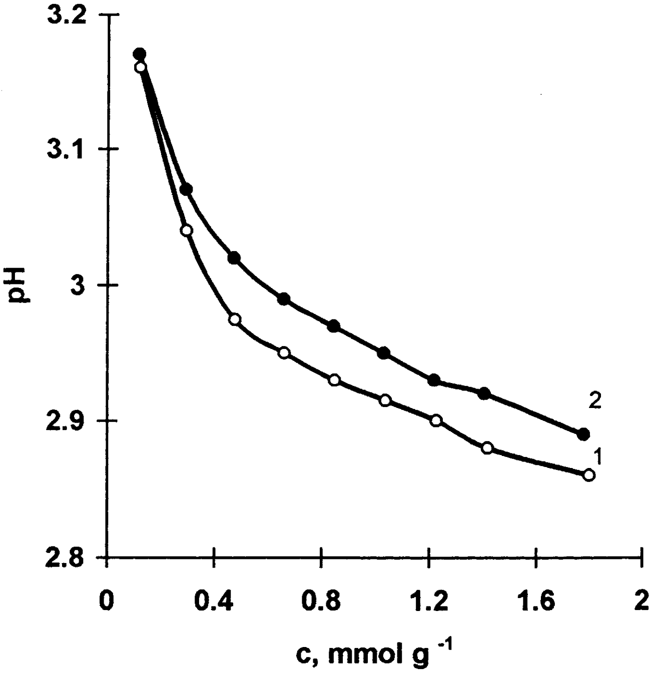
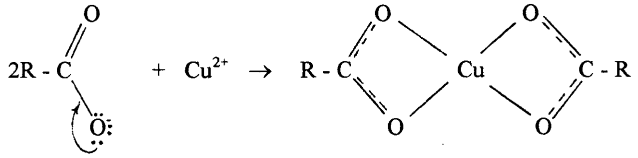


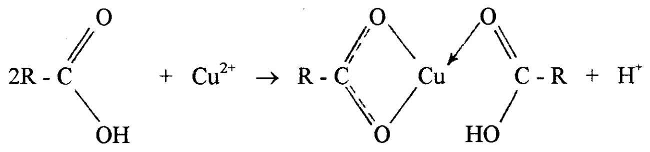
Fig. 1 Correlation between copper(II) equilibrium concentration in solution and the equilibrium solution pH: *1* in the absence of surfactant; *2* in the presence of nonionic surfactant alkylmonoethers (*ALM-10*). Initial pH 5



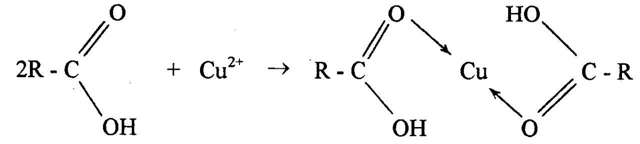
Scheme 2

The formation of these compounds is explained as follows [11, 12, 22]. The ionization of the carboxyl group is accompanied by the displacement of the electrons from the oxygen atom in the hydroxyl group to the oxygen atom in the carbonyl group so that both oxygen atoms in the ionized carboxyl group are equal with respect to the density of their electronic envelope. The interaction between the oxygen atoms in the carboxyl group and the transition-metal cation, including copper(II), leads to the formation of a stable compound on the grounds of a complex (ionic and coordinate) bond followed by a change in the solution pH.

The total sorption of copper(II) determined experimentally would have corresponded to the increment of the hydrogen ion concentration in the equilibrium solution if two deprotonated carboxyl groups were needed for the copper(II) cation; however the discrepancy is observed. The discrepancy between the total sorption of copper(II) and the change in pH may be due to the copper(II) complexing by partial substitution of copper(II) cations for hydrogen ones [27] (Scheme 3) or complexing by exclusively single coordinate bonding [22, 27] (Scheme 4). The coordinate bond arises from the introduction of undivided pairs of electrons from oxygen atoms of the carbonyl group into vacant orbitals of the transition-metal cations.



Scheme 3



Scheme 4

Three versions of the model can be used to describe the copper(II) sorption by the hydrogen form of Purolite C 106 cation exchanger:

1. The assumption that the sorption of copper(II) takes place by ion exchange in general (Scheme 2), by partial ion exchange (Scheme 3) and by exclusive coordinate bonding (Scheme 4).
2. The assumption that copper(II) sorption takes place by partial ion exchange and by ion exchange in general.
3. The assumption that copper(II) sorption takes place by ion exchange in general and by exclusive coordinate bonding.

Although it does not seem to be relevant here the third version enables the contribution of coordinate bonding to the total copper(II) sorption to be evaluated (Fig. 2). By taking into account that two ionized carboxyl groups are coordinated by one copper(II) cation, the sorption of copper(II) proceeding by complex (ionic and coordinate) bonding (a_1, millimoles per gram) can be calculated using Eq. (2)

$$a_1 = (1/2)\Delta[H^+] \ . \qquad (2)$$

The total sorption of copper(II) (Σa, millimoles per gram) determined experimentally should correspond to a_1 if all the sorption proceeded by only a complex (ionic and coordinate) bond according to Scheme (2), whereas the data obtained shows that $\Sigma a > a_1$. The discrepancy might be attributed to exclusive coordinate bonding accordingly to Scheme (4). The sorption by exclusive coordinate bonding is not followed by a change in the solution pH; therefore the sorption (a_2, millimoles per gram) proceeding by exclusive coordinate bonding (Fig. 2, curves 5, 6) can be calculated using equation (3)

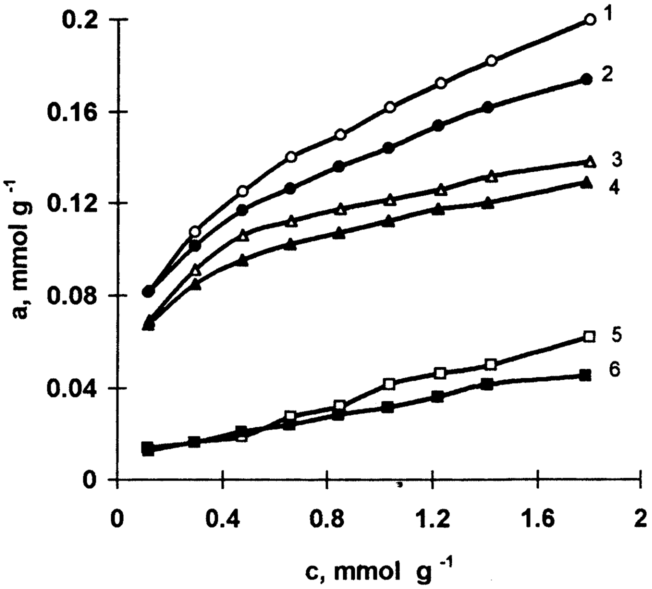


Fig. 2 Isotherms of copper(II) sorption: *1* the total sorption (Σa) in the absence of the surfactant; *2* Σa in the presence of ALM-10; *3* copper(II) sorption by complex (ionic and coordinate) bonding (a_1) in the absence of the surfactant; *4* a_1 in the presence of ALM-10; *5* copper(II) sorption by coordinate bonding (a_2) in the absence of surfactant; *6* a_2 in the presence of ALM-10. Initial pH 5

$$a_2 = \sum a - a_1 \ . \qquad (3)$$

In the presence of ALM-10 both the change in pH (Fig. 1) arising from copper(II) sorption, a_1, and Σa are lower than the corresponding values without the surfactant (Fig. 2, curves 2, 4).

Assuming that copper(II) sorption takes place by partial ion exchange and by ion exchange in general (Schemes 2, 3) the interaction between copper(II) and the hydrogen form of Purolite C 106 cation exchanger can be represented as follows:

$$\begin{array}{l} Cu^2 + RCOOH \rightleftharpoons (RCOOCu)^+ + \quad H^+ \\ Cu^{2+} + 2RCOOH \rightleftharpoons \underline{[(RCOO)_2Cu] + 2H^+} \\ \qquad\qquad\qquad\qquad\quad \sum a \qquad\quad \Delta[H^+] \end{array}$$

The increment of the hydrogen ion concentration, $\Delta[H^+]$, in the equilibrium solution and the total copper(II) sorption (Σa) allow the amount of both copper(II) and ionized carboxyl groups taking part in the formation of the $(RCOOCu)^+$ complex and the $[(RCOO)_2Cu]$ neutral complex to be evaluated separately.

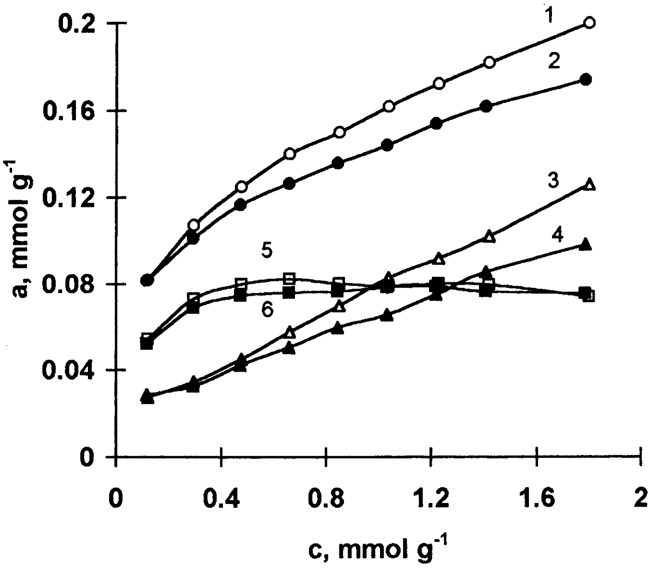


Fig. 3 Isotherms of copper(II) sorption in the absence of ALM-10 (*1*, *3*, *5*) and in the presence of ALM-10 (*2*, *4*, *6*): *1*, *2* the total copper(II) sorption; *3*, *4* copper(II) sorption through the formation of a $(R\mathrm{COOCu})^+$ complex; *5*, *6* copper(II) sorption through the formation of a $[(R\mathrm{COO})_2\mathrm{Cu}]$ complex. Initial pH 5

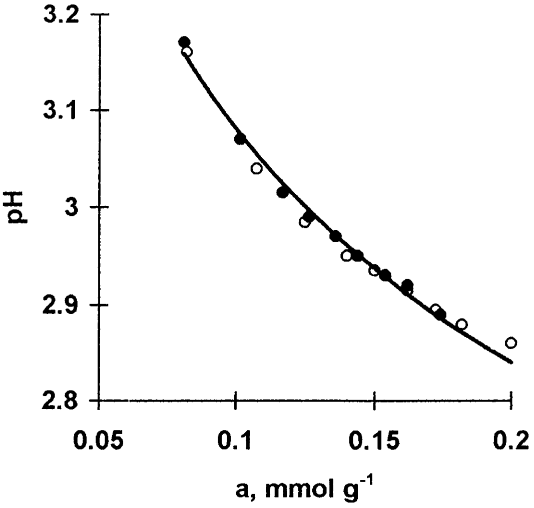


Fig. 4 Correlation between the total copper(II) sorption and the equilibrium solution pH: ○ in the absence of surfactant; ● in the presence of ALM-10. Initial pH 5

The total increment of the hydrogen ion concentration may be expressed as

$$\Delta[\mathrm{H}^+] = \Delta[\mathrm{H}^+]_\mathrm{p} + \Delta[\mathrm{H}^+]_\mathrm{g} \ , \tag{4}$$

where $\Delta[\mathrm{H}^+]_\mathrm{p}$ and $\Delta[\mathrm{H}^+]_\mathrm{g}$ are the increments of the hydrogen ion concentration because of the partial ion exchange and ion exchange in general, respectively.

The total copper(II) sorption can be expressed as

$$\begin{aligned}\sum a &= a_{\mathrm{CuL}} + a_{\mathrm{CuL2}} \\ &= \Delta[\mathrm{H}^+]_\mathrm{p} + (1/2)\Delta[\mathrm{H}^+]_\mathrm{g} \\ &= \Delta[\mathrm{H}^+] - (1/2)\Delta[\mathrm{H}^+]_\mathrm{g} = \Delta[\mathrm{H}^+] - a_{\mathrm{CuL2}} \ ,\end{aligned} \tag{5}$$

where CuL and CuL2 represent the complex containing 1 and 2 deprotonated carboxyl groups, respectively.

The sorption of copper(II) by ion exchange in general and by partial ion exchange can be calculated as follows:

$$a_{\mathrm{CuL2}} = \Delta[\mathrm{H}^+] - \sum a \ , \tag{6}$$

$$a_{\mathrm{CuL}} = \sum a - a_{\mathrm{CuL2}} \ . \tag{7}$$

The distribution of the copper(II) carboxyl complexes is shown to be dependent on the initial solution concentration in Fig. 3. On increasing the initial solution concentration the part of copper(II) sorbed through the formation of the $(R\mathrm{COOCu})^+$complex continually increases (curve 3) although curve 5 indicates that the part of copper(II) sorbed through the formation of the $[(R\mathrm{COO})_2\mathrm{Cu}]$ neutral complex is higher only at low initial solution concentration and approaches a nearly constant value at higher concentration. In the case of the $(R\mathrm{COOCu})^+$ complex formation the electroneutrality in the cation-exchanger phase is attained by the uptake of Cl^- coions.

The simultaneous sorption of both copper(II) and ALM-10 from their mixture leads to the diminution of copper(II) sorption. At a low initial solution concentration (1 mmoldm^{-3}) the influence of ALM-10 on the copper(II) sorption is negligible although it gradually increases on increasing the initial solution concentration. Figure 3 shows that in the presence of ALM-10 the total copper(II) sorption (curve 2) decreases mainly because of the diminution of copper(II) sorption proceeding through the formation of the $(R\mathrm{COOCu})^+$ complex (curve 4), although the formation of the $[(R\mathrm{COO})_2\mathrm{Cu}]$ complex seems almost unaffected by ALM-10 (curve 6). This is presumably because the complex (ionic and coordinate) bonding between copper(II) and the cation exchanger is more stable compared with coordinate bonding (Schemes 2, 3) and therefore the sorption of copper(II) following Scheme 2 is preferable under conditions of competitive sorption.

The experimental results concerning the sorption of lead(II), nickel(II) and zinc(II) in the presence of nonionic surfactant reported earlier [18, 28] led to the conclusion that a part of metal(II) was taken up in the form of ions attached to the nonionic surfactant molecules as connecting species between metal(II) cations and the cation exchanger; however, the present work suggests that the copper (II)–ALM-10 compounds can be sorbed only through the metal ions. This opinion is based on the results presented in Fig. 4: the sorption of the same amount of copper (II) from pure solution and from the mixture with ALM-10 is followed by almost the same change in the equilibrium solution pH. Therefore the influence of ALM-10 on the copper(II) sorption is insignificant and is relatively limited, presumably by screening of carboxyl groups in the cation exchanger.

The sorption of copper(II) by Purolite C 106 cation exchanger can be interpreted as a two-step complex formation process [22, 29]:

$$R\mathrm{COOH} + \mathrm{Cu}^{2+} \rightleftharpoons (\mathrm{RCOOCu})^{+} + \mathrm{H}^{+} \ , \qquad (8)$$

$$(R\mathrm{COOCu})^{+} + R\mathrm{COOH} \rightleftharpoons [(R\mathrm{COO})_2\mathrm{Cu}] + \mathrm{H}^{+} \ , \qquad (9)$$

where the second ligand-ionized carboxyl group can be involved in the complexation of copper(II) ion following the first step of complex formation. Supposing that the copper(II) sorption equilibria correspond to Eqs. (8) and (9) the equilibrium coefficients are

$$k_1 = [(R\mathrm{COOCu})^{+}][\mathrm{H}^{+}]/[\mathrm{Cu}^{2+}][R\mathrm{COOH}] \ , \qquad (10)$$

$$k_2 = [(R\mathrm{COO})_2\mathrm{Cu}][\mathrm{H}^{+}]/[(R\mathrm{COOCu})^{+}][R\mathrm{COOH}] \ , \qquad (11)$$

where $[\mathrm{H}^{+}]$ is the concentration of hydrogen ions (millimoles per cubic centimetre), $[\mathrm{Cu}^{2+}]$ the concentration of copper(II) ions (millimoles per cubic centimetre), $[(R\mathrm{COOCu})^{+}]$ the concentration of copper(II) carboxylate complex with one ionized carboxyl group (millimoles per gram), $[(R\mathrm{COO})_2\mathrm{Cu}]$ the concentration of copper(II) carboxylate complex with two ionized carboxyl groups (millimoles per gram) and $[R\mathrm{COOH}]$ the concentration of free carboxyl groups (millimoles per gram). The concentration of the free carboxyl groups in the resin was obtained by the difference from the total number of carboxyl groups in the resin (7.3 mmolg^{-1}) to that taking part in the copper(II) complex formation.

The equilibrium coefficients demonstrate (Table 1) that the presence of ALM-10 is the factor giving the decreased k_1 values. Otherwise the second step of the copper(II) complex formation is less sensitive to the effect of ALM-10. On increasing the initial solution concentration the copper(II) sorption equilibrium coefficients decrease in the presence as well as in the absence of ALM-10. It can be explained by no-uniform selectivity of the sorption sites in the cation exchanger for copper(II) ions. At a low degree of the cation exchanger saturation the sorption takes place preferentially at more selective sites.

Copper(II) sorption by the hydrogen form of the cation exchanger is considerably lower than that of lead(II) [18]. This could be explained on the basis of the theory of hard and soft acids and bases [30]. Although both lead(II) and copper(II) are on the borderline dividing Lewis acids into hard and soft ones, lead(II) as an acid is harder than copper(II) because lead(II) has $5d^{10}6s^{2}$ electrons in its external electronic envelope, whereas copper(II) has only $3d^{9}$ [31]. Since d electrons are more sensitive to the action of the ambient solution ingredients when compared to s ones, the presence of s^{2} electrons results in the diminution of the diffusiveness of d electrons by screening them. As hard acids bind strongly to hard bases (a rule of the theory of hard and soft acids and basis [30]), lead is attached to the cation exchanger $R\mathrm{CO}_2^{-}$ (a hard base) more strongly than copper(II); consequently, the equilibrium sorption of lead(II) is higher than that of copper(II).

With respect to the sorption of lead(II), nickel(II) [18] and zinc(II) [28] the affinity of Purolite C 106 cation exchanger towards copper(II) is Pb(II) > Cu(II) > Zn(II) ≥ Ni(II) both without and with the surfactant.

The action of copper(II) and the surfactant on their sorption is reciprocal. In the presence of copper(II) the sorption of ALM-10 is lower than that without cop-

Table 1 The effect of nonionic surfactant alkylmonoethers (*ALM-10*) on the equilibrium coefficients of copper(II) sorption at various initial solution concentrations

$[\mathrm{Cu}^{2+}]_{\mathrm{initial}}$ (mmolcm^{-3})	$\mathrm{p}k_1$		$\mathrm{p}k_2$	
	Without ALM-10	With ALM-10	Without ALM-10	With ALM-10
0.001	2.10	2.12	4.12	4.18
0.002	2.26	2.31	3.97	3.99
0.003	2.34	2.39	4.00	4.04
0.004	2.38	2.47	4.08	4.09
0.005	2.43	2.51	4.14	4.16
0.006	2.45	2.55	4.24	4.18
0.007	2.47	2.57	4.30	4.23
0.008	2.48	2.58	4.36	4.32
0.01	2.50	2.62	4.51	4.39

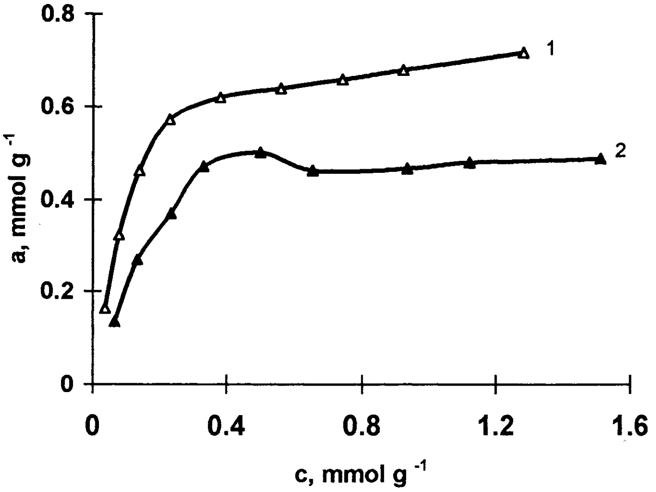


Fig. 5 Isotherms of ALM-10 sorption: *1* in the absence of copper(II); *2* in the presence of copper(II). Initial pH 5

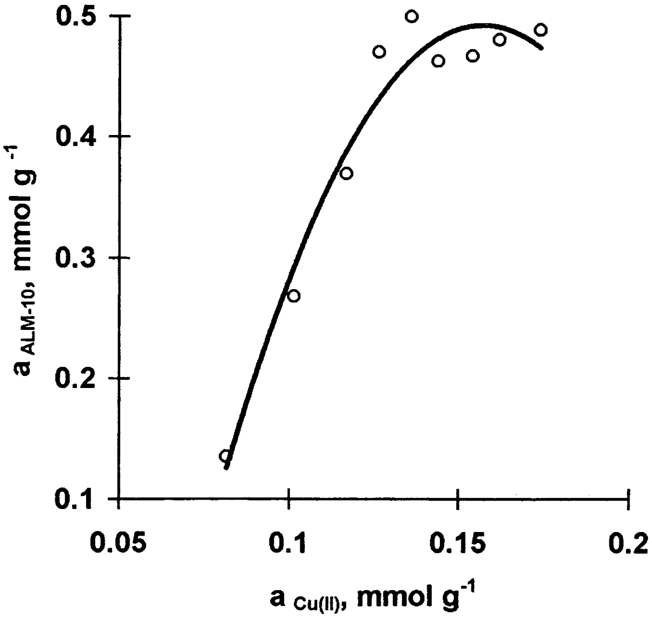


Fig. 6 Correlation between ALM-10 and copper(II) sorption. Initial pH 5

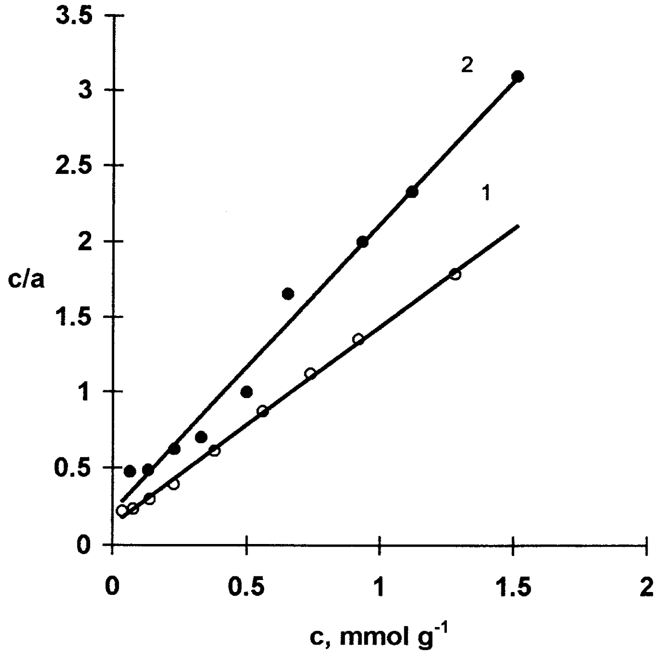


Fig. 7 Linear Langmuir isotherms of ALM-10 sorption in Purolite C 106 cation exchanger: *1* ALM-10 without copper(II); *2* ALM-10 in the presence of copper(II)

per(II) because of the simultaneous exhaustion of the sorptive capacity by not only the surfactant but also by copper(II) (Fig. 5). Consequently the isotherm of ALM-10 sorption from the mixture approaches a plateau. When the sorption of ALM-10 is 0.47 mmolg^{-1} it stops rising, whereas the sorption of copper(II) continues to grow, presumably because of steric factor (Fig. 6): the structure of the ALM-10 molecules is more complex than that of hydrated copper cations; consequently, the sorptive sites are more accessible for copper(II) cations than for ALM-10 molecules.

The ALM-10 sorption isotherms corresponding to Langmuir type can be presented (Fig. 7) and expresed by the linear form of Langmuir equation [32]:

$$c/a = 1/a_{\mathrm{m}}K + c/a_{\mathrm{m}} \quad , \tag{12}$$

where c is the equilibrium solution concentration (millimoles per gram), a_{m} the maximum sorption (millimoles per gram) and K the sorption equilibrium constant (grams per millimole). a_{m} determined from Eq. (12) is 0.769 and 0.527 mmolg^{-1} for ALM-10 sorption without and with copper(II); K is 9.551 and 8.587 gmmol^{-1} without and with copper(II), respectively.

The data obtained refer to the application of the hydrogen form of Purolite C 106 cation exchanger for the purification of copper(II) plating rinsewater from both copper(II) and ALM-10 simultaneously, preventing environmental contamination.

Conclusion

Mutual action of copper(II) and ALM-10 leads to a decrease in the equilibrium sorption of both copper(II) and ALM-10. Although the takeup of ALM-10 is overwhelming it is more affected by the presence of copper(II) compared with the action of ALM-10 on the sorption of copper(II). The isotherms of ALM-10 sorption could be attributed to the Langmuir type.

The sorption of copper(II) by the hydrogen form of Purolite C 106 cation exchanger can be described as a process of general or partial ion exchange followed by copper(II) carboxyl complex formation. The sorption of copper(II) proceeds by complex (ionic and coordinate) bonding and by single coordinate bonding.

The sorption of copper(II) presented as a two-step complex formation reaction is characterized quantitatively. The copper(II) sorption equilibrium coefficients depend on the initial solution concentration: on increasing the concentration of the solutes the equilibrium coefficients decrease. The presence of ALM-10 diminishes the coefficients of the first-step complexation equilibrium although the second step of the copper(II) carboxyl complex formation remains almost unaffected.

The hydrogen form of the Purolite C 106 cation exchanger can be applicable for the purification of sewage including copper plating rinsewater from both ALM-10 and copper(II).

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