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SELECTIVE FLOTATION OF ZINC(II) AND CADMIUM(II) IONS FROM DILUTE AQUEOUS SOLUTIONS IN THE PRESENCES OF HALIDES

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An experimental investigation is presented of the batch ion flotation of zinc(II) and cadmium(II) ions from dilute aqueous solutions with sodium dodecylbenzenesulfonate (DBSNa) as an anionic surfactant and cetylpyridinium chloride (CPCl) as a cationic surfactant. The effect of halides, i.e. fluorides, chlorides, bromides, and iodides, on the selectivity of cadmium(II) over zinc(II) is established. Separation of Cd(II) and Zn(II) ions by DBSNa is not occurred. The separation of Cd(II)/Zn(II) by CPCl in presence of halides at concentration range of 0.001 M to 1.0 M increases in sequence: $F^- < Cl^- < Br^- < I^-$.

Key words: zinc, cadmium, halides, ion flotation, and separation

INTRODUCTION

Zinc and cadmium are removed from dilute aqueous solutions with different methods such as solvent extraction, ionic exchange, ion flotation, sorption or liquid membranes. Among these methods, ion flotation has special position for the removal of ions from very dilute solutions, i.e. at the concentration below $1.0 \cdot 10^{-4}$M. Ion flotation involves the removal of surface inactive ions from aqueous solutions by the introduction of a surfactant and the subsequent passage of gas bubble through the solution.

The ion flotation selectivity for inorganic cations has been presented in several papers. Jurkiewicz (1984-85) investigated foam separation of Cd(II) ions by lauryl sulfate and sodium dodecanoate from aqueous solutions. The presence of electrolyte in the solutions has a negative influence on Cd^{2+} foam separation. Also, Jurkiewicz (1985) investigated separation of thiocyanate and iodide complexes of cadmium(II) in

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acidic aqueous solutions using cetylotrimethylamonium bromide (CTMABr). In the presence of acids, the zinc thiocyanate complex removal increases in following sequence: $HClO_4 < HI < HNO_3 < H_2SO_4 < H_3PO_4 < CH_3COOH$. The influence of chloride, bromide, iodide and thiocyanate ions on the separation of zinc(II) and cadmium(II) ions with CTMABr Jurkiewicz (1990) also conducted. For anionic surfactants (sodium dodecylbenzenesulfonate and sodium dodecylsulfonate) Walkowiak (1991) found the following cations foam separation selectivity sequences toward: $Mn^{2+} < Zn^{2+} < Co^{2+} < Fe^{3+} < Cr^{3+}$, and $Ag^+ < Cd^{2+} < In^{3+}$. For the flotation of cations where no sublate was formed in the bulk solution, the good correlation between selectivity sequences of studied metal ions with anionic surfactant and the ionic potentials of those cations was found. The selective flotation of zinc(II), cadmium(II), mercury(II) and gold(III) ions using of cetyltrimethylamonium chloride in presence of chlorides and cyanides was also investigated by Walkowiak et al. (1976, 1979, 1992). The selectivity order of foam fractionation was as follows: $Au(CN)_4^- > Hg(CN)_4^{2-} > Cd(CN)_4^{2-} > Zn(CN)_4^{2-}$ (Walkowiak and Grieves 1976). The effect of inorganic ligands, i.e. thiosulfates, thiocyanates, and cyanides on the selectivity of ion flotation of Zn(II) and Ag(I) was investigated by Charewicz et al. (1999). The affinity of cyanide complexes to cetylpyridinium chloride follows the order: $[Ag(CN)_2]^- < [Zn(CN)_4]^{2-} + [Zn(CN)_3]^-$. The influence of zinc and cadmium ion concentrations on the effectiveness of flotation removal with potassium oleate was studied by Sinkova (1998). Zinc(II) and cadmium(II) ions are removed effectively from aqueous solution using this collector. Also, Scorcelli et al. (1999) was studied the removal of cadmium(II) using sodium dodecylsulfate as a collector. The best removal (99 %) was obtained for a metal cations to collector ratio equal to 1:3. Preliminary research of cadmium(II) over zinc(II) ions separation by cetyltrimethylamonium chloride was conducted by Kozłowski et al. (2000).

This paper concerns the selective removal of zinc(II) and cadmium(II) ions from dilute aqueous solutions in competitive ion flotation. Anionic complexes of Zn(II) and Cd(II) from aqueous solutions were floated with cetylpyridinium chloride. The competitive ion flotation of Zn^{2+} and Cd^{2+} by sodium dodecylbenzenesulfonate was also studied.

EXPERIMENTAL

The flotation experiments were carried out in a glass column 45.7 cm high and 2.4 cm in diameter. The nitrogen gas was saturated with water, and the flow rate was maintained at 12 ml/minute through a sintered glass sparger of 20-30 μm, of nominal porosity. The initial volume of each feed solution was 100 ml. The temperature was maintained at 20 ± 2 °C. The concentration of zinc(II) and cadmium(II) was $1.0 \cdot 10^{-5}$M. All aqueous solutions were prepared by using double distilled water of conductivity 0.1 μS/m at 25 °C. Inorganic ligands, i.e. F^-, Cl^-, Br^-, and I^- were investigated in range of the concentrations of $5.0 \cdot 10^{-5} \div 1.0$ M. Reagent grade inorganic chemical: NaF, NaCl, NaBr, NaI, $ZnSO_4$, $CdSO_4$, NaOH and H_2SO_4 were obtained from POCh

(Gliwice, Poland). Typical ionic surfactants were applied, i.e. sodium dodecylbenzenesulfonate (DBSNa, BHD reagent) as an anionic surfactant, and cetylpyridinium chloride (CPCl, Loba-Chemie reagent) as a cationic surfactant. Both surfactants were purified by recrystalization from ethanol. The concentration of surfactants in the aqueous solutions was $2.0 \cdot 10^{-4}$ M.

The dependence of metal ions concentration versus time of each metal in the bulk solution (c) was recorded continuously during an ion flotation experiment by means of radioactive analytical tracers and gamma radiation spectrometry following a procedure described previously by Charewicz and Niemiec (1969) and improved by Walkowiak and Ulewicz (1999). A single channel, gamma radiation spectrometer was used as the detector of radiation intensity of specific energy. The gamma radioactive isotopes, i.e., Zn-65 and Cd-115m, were from the Atomic Energy Institute „POLATOM" (Świerk near Otwock, Poland). They were of sufficiently high specific activity to neglect the effect of carrier concentration (9.2 MBq/mg for Zn-65 and 2.26 MBq/mg for Cd-115m).

The maximal percent removal (M) is described by an equation:

$$M = 1 - c_r / c_i \tag{1}$$

where c_i – the initial ion concentration,

c_r – metal ion concentration in the residual solution after foam ceased.

Selectivity coefficient (S) is described by an equation:

$$S_{Me1/Me2} = \frac{M_{Me1}}{M_{Me2}} \tag{2}$$

where M_{Me1} – the maximal percent removal of the first metal,

M_{Me2} – the maximal percent removal of the second metal.

The first order equation describing the dependence of floated ion concentration vs. time is applied to the flotation kinetics studies (Walkowiak and Ulewicz 1999):

$$\frac{dc}{dt} = -\frac{c_i}{c_i - c_r} k(c - c_r) \tag{3}$$

where k – kinetic rate constant,

t – time of flotation process,

c – metal ion concentration at a given time.

The Statistica Program (Version 5.0) was applied to calculate values of *k*. The program also allows to find the determination coefficient (r^2), which is from 0.0000 to 1.0000 and can be treated as a measure of data fitting to a first order kinetic equation (3).

The total concentration of metal in solutions can be described by an equation (4) and the formation ratio of metal complexes was calculated by an equation (5). In table 1 are given values of the stability constants of halide complexes of Zn(II) and Cd(II).

$$c_M = [M] + [ML] + [ML_2] + ... + [ML_n] \tag{4}$$

$$\alpha_n = \frac{\beta_n [L]^n}{1 + \beta_1 [L] + \beta_2 [L]^2 + ... + \beta_n [L]^n} \tag{5}$$

where [L] – ligand concentration not complexed by a metal,
β_n – overall stability constants of metal complex.

Table 1. Stability constants of zinc(II) and cadmium(II) for halide complexes (Stability constants, 1982)
Tabela 1. Stałe trwałości jonów kompleksowych Zn(II) i Cd(II) z halogenkami

System		$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$
F^-	Zn(II)	0.95	-	-	-
	Cd(II)	0.76	0.60	-	-
Cl^-	Zn(II)	0.72	0.49	-0.19	0.18
	Cd(II)	1.32	2.22	2.31	1.86
Br^-	Zn(II)	-1.46	0.47	-2.24	-
	Cd(II)	1.57	2.26	2.93	-
I^-	Zn(II)	0.70	1.18	-	-
	Cd(II)	1.91	3.34	4.65	5.86

RESULTS AND DISCUSSION

The study of batch ion flotation first involved the flotations of zinc(II) and cadmium(II) ions from aqueous solutions containing single metal ions, at the concentrations of metals equal to $1.0 \cdot 10^{-5}$ and $2.0 \cdot 10^{-5}$ M. The flotations of zinc(II) and cadmium(II) ions from equimolar mixture of both metals were also conducted. The kinetic curves for flotation of the studied Zn^{2+} and Cd^{2+} cations with DBSNa as the anionic surfactant are shown in Fig. 1. The maximal flotation percent of Zn(II) and Cd(II) cations was 92.1 and 89.0, respectively. Zinc(II) ions are removed better than cadmium(II) ions from solutions containing single metals and from equimolar mixture. However, comparing process rate, i.e. values of ***k***, the cadmium(II) ions are removed faster then zinc(II) ions. The results of the kinetic calculations for these flotations are shown in table 2. The determination coefficients were high, i.e. from 0.9789 to 0.9963, respectively. This means that the fitting of experimental points to the equation (3) is statistically very good.

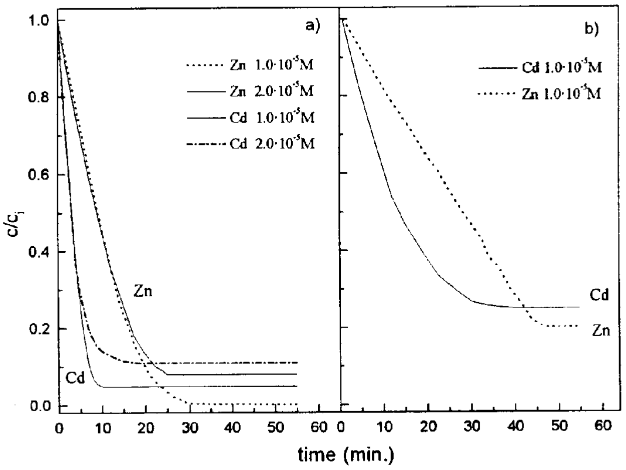

Fig. 1. Flotation curves for the Zn(II) and Cd(II) ions from solutions containing single metal (a) and equimolar metal mixture (b) by $2.0 \cdot 10^{-4}$ M DBSNa

Table 2. The maximum percent removal of zinc(II) and cadmium(II) ions and results of the kinetic calculations

Concentration of ions, [mol/dm^3]		The maximal flotation percent	Rate constant, [min^{-1}]	Determination coefficients
Zn^{2+}	$1.0 \cdot 10^{-5}$	0.993	0.369	0.9928
	$2.0 \cdot 10^{-5}$	0.921	0.369	0.9939
Cd^{2+}	$1.0 \cdot 10^{-5}$	0.951	0.481	0.9963
	$2.0 \cdot 10^{-5}$	0.890	0.488	0.9925
$\underline{Zn^{2+}} + Cd^{2+}$	$1.0 \cdot 10^{-5}$	0.800	0.329	0.9789
$\underline{Cd^{2+}} + Zn^{2+}$	$1.0 \cdot 10^{-5}$	0.752	0.356	0.9907

The influence of inorganic ligands, i.e. F^-, Cl^-, Br^-, and I^- on the separation of zinc(II) and cadmium(II) ions was examined. The removal of zinc(II) and cadmium(II) ions decreases with increasing of ligands concentration in aqueous solution using anionic collector, i.e. DBSNa. The separation of Zn(II) and Cd(II) in of fluorides, chlorides, bromides and iodides media aqueous solution with DBSNa is not possible, since the removal of both metals was comparable (Ulewicz, 2000). The separation of both metals occurs when a cationic collector, i.e. CPCl, was applied. In Fig. 2 flotation kinetics curves of Zn(II) and Cd(II) for competitive ion flotation of those metal from 1.0 M bromide (a) and iodide (b) aqueous solutions with CPCl is presented. As can be seen from this figure cadmium(II) is floated much better than zinc(II).

The maximal percent removal of Zn(II) and Cd(II) ions in presence of chloride, bromide and iodide ions are shown in Fig. 3. In this figure, the calculated percent formation of metal complexes for chlorides, bromides and iodides is also shown. Floatation of Zn(II) and Cd(II) in with cationic collector does not occur. Using this collector it is possible to remove of Zn(II) and Cd(II) existing in anionic forms from aqueous solutions. The differences of predomination range for anionic forms of Zn(II) and Cd(II) allow to separate cadmium(II) over zinc(II). With the increase of halides concentration a removal of Cd(II) ions increase, whereas the removal of Zn(II) is not excited of 10 %. The maximal percent removal of Cd(II) and Zn(II) is comparable with the halides complex anions of the investigated metals.

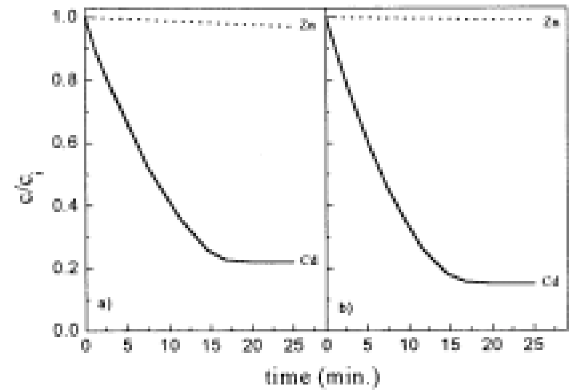

Fig. 2. Kinetic curves of the Zn(II) and Cd(II) ions from aqueous solutions containing 1.0 M bromide (a) and 1.0 M iodide (b) ions in solution by CPCl, $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5}$ M, $[CPCl] = 2.0 \cdot 10^{-4}$ M, pH = 4.0

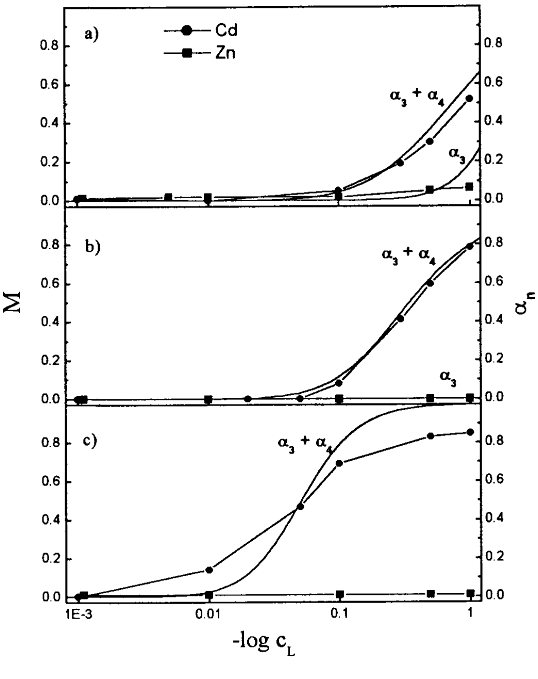

Fig. 3. Influence of analytical concentration of chloride (a), bromide (b) and iodide (c) on removal of Zn(II) and Cd(II) ions with CPCl , and molar fractions of anionic metal complexes, pH = 4.0

The selectivity coefficients of cadmium(II) over zinc(II) separation in presence of investigated ligands are shown in Fig. 4. The selectivity separation of investigation metals by CPCl in halides media aqueous solution at the concentration range of 0.01 to 1.0 M increases in the following sequence: Cl^- « Br^- < I^-. The selectivity coefficients of Cd(II)/Zn(II) at the concentration of 0.5 and 1.0 M for chloride, bromide and iodide are: 7.3; 59.2; 82.0 and 6.0; 67.3, 85.0, respectively. Separation of Cd(II) and Zn(II) ions using CPCl is the best in the presence of iodides and bromides. In the presence of chlorides we observed only a partial separation of Cd(II)/Zn(II) from aqueous solutions. The values of rate constants increase with halides concentration increasing, when CPCl was used (Table 3). As can be seen from this table, the kinetic rate constants for cadmium(II) are much higher than for zinc(II). The rate constant ratios of Cd(II)/Zn(II) for Cl^-, Br^-, and I^- are equal: 1.95; 18.7 and 19.2, respectively.

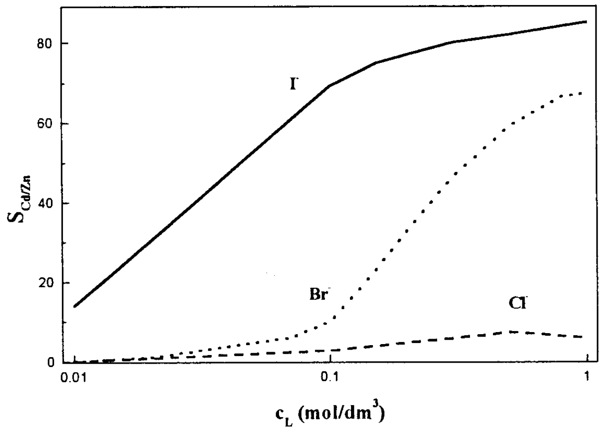

Fig. 4. Selectivity coefficients ($S_{Cd/Zn}$) vs. concentration of ligands, [CPCl] $=2.0\cdot10^{-4}$ M

Table 3. Rate constant of Zn(II) and Cd(II) by CPCl in presence of halides at concentration of 1.0 M

Lignads	***k*** [min^{-1}] Zn(II)	r^2	***k*** [min^{-1}] Cd(II)	r^2
Cl^-	0.040	0.9907	0.078	0.9972
Br^-	0.010	0.9914	0.187	0.9893
I^-	0.005	0.9897	0.096	0.9924

CONCLUSIONS

Separation of Cd(II) and Zn(II) ions using anionic collector, i.e. DBSNa, in halides media aqueous solution at the concentrations range of $5.0\cdot10^{-5} \div 1.0$ M is not possible, since the removal of both metals is comparable. This is caused by the fact, that zinc(II) and cadmium(II) form cation complexes possess comparable values of stability constants. In the presence of chlorides, bromides, and iodides in the range of concentrations of $5.0 \cdot 10^{-5}$ to 1.0 M the separation of Cd(II) over Zn(II) using a cationic collector, i.e. CPCl, is possible. The selectivity coefficient of Cd(II)/Zn(II) in the presence of studied ligands at the range concentrations of 0.5 to 1.0 M increases in the sequence: $F^- < Cl^- \ll Br^- < I^-$. The separation-ability for Cd over Zn are the highest at halides concentration range of 0.5 to 1.0 M. Selectivity coefficients of Cd/Zn reaches the values of: 67.3 and 85.0 for 1.0 M aqueous solutions of Br^- and I^-, respectively.

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Zbadano wydzielanie oraz selektywne rozdzielanie jonów cynku i kadmu w postaci Zn^{2+} i Cd^{2+} oraz jako aniony kompleksowe z wybranymi ligandami nieorganicznymi z roztworów wodnych zawierających zarówno pojedyncze metale jak i z roztworów zawierających równomolową mieszaninę obu metali przy użyciu kolektora kationowego - chlorku cetylopirydyniowego (CPCl) oraz kolektora anionowego - dodecylobenzenosulfonianu sodu (DBSNa). Ponieważ cynk i kadm tworzą kationowe formy kompleksowe o podobnych wartościach stałych trwałości rozdzielenie jonów Zn(II) i Cd(II) przy użyciu kolektora anionowego nie jest możliwe. Separacja jonów kadmu(II) od cynku(II) jest natomiast możliwa przy zastosowaniu kolektora kationowego, tj. chlorku cetylopirydyniowego. Separacja badanych jonów metali przy użyciu CPCl w obecności halogenków o stężeniu 0,5 i 1,0 M wzrasta w szeregu: $F^- < Cl^- << Br^- < I^-$. Współczynniki selektywności Cd(II)/Zn(II) dla stężenia ligandów równego 0,5 M wynoszą odpowiednio: 7,3; 59,2; 82,0 i dla stężenia 1,0 M odpowiednio: 6,0; 67,0; 85,0. Tak więc, niezależnie od stężenia halogenków, najlepsze rozdzielenie jonów Cd(II) od Zn(II) uzyskano w obecności jonów jodkowych i bromkowych w roztworze wodnym.