This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Mechanism of Selective Ion Flotation. 1. Selective Flotation of Transition Metal Cations

Wladyslaw Walkowiak[a]
[a] INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS TECHNICAL UNIVERSITY OF WROCLAW, WROCLAW, POLAND

To cite this Article Walkowiak, Wladyslaw(1991) 'Mechanism of Selective Ion Flotation. 1. Selective Flotation of Transition Metal Cations', Separation Science and Technology, 26: 4, 559 — 568

To link to this Article: DOI: 10.1080/01496399108050490

URL: http://dx.doi.org/10.1080/01496399108050490

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **26**(4), pp. 559–568, 1991

Mechanism of Selective Ion Flotation. 1. Selective Flotation of Transition Metal Cations

WLADYSLAW WALKOWIAK
INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS
TECHNICAL UNIVERSITY OF WROCLAW
50-370 WROCLAW, POLAND

Abstract

An experimental investigation is presented of the batch ion flotation of the transition metal cations Cr^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, and In^{3+} from acidic aqueous solutions with sodium dodecylsulfonate and sodium dodecylbenzenesulfonate as anionic surfactants. The selectivity sequences $Mn^{2+} < Zn^{2+} < Co^{2+} < Fe^{3+} < Cr^{3+}$ and $Ag^{+} < Cd^{2+} < In^{3+}$ are established, both from data for single and multi-ion metal cations solutions, where sublate was not formed in the bulk solution. Good agreement between the selectivity sequences and the values of ionic potential of metal cations was found. An experimental investigation was also performed on the solubility of sublates. The sublates solubility values are discussed in terms of ionic potentials of metal cations as well as of the surfactant size.

INTRODUCTION

Ion flotation involves the interaction of an ionogenic surfactant with oppositely charged ions in solution and at solution–gas bubble interfaces to produce a most significant enrichment of selected ions in a foam formed above an aqueous bulk solution. Ion flotation processes have been included in recent reviews of adsorptive bubble separation techniques (*1–4*).

The ion flotation selectivity of anionic surfactants for inorganic cations has been studied in several investigations (*5–9*). Walling et al. (*5*) found that the orders of increased selectivity of foam separation process are $H^{+} < Na^{+} < K^{+} < NH_4^{+}$ and $Ca^{2+} < Mg^{2+}$. Wace and Banfield (*6*) determined values of the selective adsorption coefficients in foam separation:

$$\alpha_{Sr^{2+},Cs^{+}} = 58, \qquad \alpha_{Ca^{2+},Cs^{+}} = 38.5, \qquad \alpha_{Ce^{3+},Cs^{+}} = 3.3$$

The low value of $\alpha_{Ce^{3+},Cs^{+}}$ was explained by the possibility of high hydration number of Ce(III) cations which reduces the effect of the high valency. Jorne and Rubin (*7*) compared their experimental data on the separation of Sr^{2+} and UO_2^{2+} ions with the proposed theory based on the diffuse layer model with the restriction of different closest approach to the surface for each ion.

Huang and Talbot (*8*) investigated the continuous flow foam fractionation of Pb^{2+}, Cd^{2+}, and Cu^{2+} cations with sodium dodecylsulfonate. They found that the order of increased selectivity is $Cu^{2+} < Cd^{2+} < Pb^{2+}$, which is the order of decreased ionic radii. Their results are in good agreement with a theory based on the Gouy-Chapman model of double layer (*7*). Kubota and Hayashi (*9*) carried out experiments of continuous flow foam fractionation of Na^{+}, Cd^{2+}, and Cr^{3+} cations with sodium dodecylbenzenesulfonate. Their selectivity order, $Na^{+} < Cd^{2+} < Cr^{3+}$, is in accordance with the Gouy-Chapman diffuse layer theory. Grieves and coworkers (*10*) recently investigated the continuous flow foam fractionation of each of the colligents Li^{+}, K^{+}, Rb^{+}, and Cs^{+} versus Na^{+}. The selectivity coefficients were determined to be 0.92, 1.10, 1.51, and 1.65, respectively. These coefficients were correlated with the absolute partial molal entropy of the studied cations in an aqueous solution, which increases as the degree of cation hydration decreases, for a series of monoatomic cations of like charge.

The objective of this investigation is to establish the selectivity of anionic surfactants, i.e., sodium dodecylsulfonate and sodium dodecylbenzenesulfonate, for transition metal cations with different ionic radii and electrical charge. In addition, the solubilities of sublates formed between metal cations and anionic surfactants are determined, and the results are interpreted in terms of the ionic potentials of the metal cations as well as the surfactant sizes.

EXPERIMENTAL

Reagents

Reagent Grade inorganic chemicals $Mn(NO_3)_2$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, $CO(NO_3)_3$, $Zn(NO_3)_2$, $AgNO_3$, $Cd(NO_3)_2$, $In(NO_3)_3$, and HNO_3 were obtained from POCh (Gliwice, Poland). All aqueous solutions were prepared by using double distilled water of conductivity 1.4 μmho/cm at 25°C. Sources of anionic surfactants include BHD Reagent (England) for sodium dodecylbenzenesulfonate (DBSNa), and Fisher Scientific Co. (USA) for sodium dodecylsulfonate (DSNa). Both surfactants were Reagent Grade and were purified by recrystallization from ethanol. Reagent Grade ethanol for preparing surfactant solutions was obtained from POCh (Gliwice, Poland).

Sources of gamma radioactive isotopes include Atomic Energy Institute (Swierk, Poland) for ^{51}Cr, ^{58}Co, ^{59}Fe, ^{65}Zn, ^{111}Ag, and ^{114m}In, Rotop (DDR) for ^{54}Mn, and Amersham (England) for ^{109}Cd. They were either carrier free (^{54}Mn, ^{58}Co, ^{109}Cd, ^{111}Ag) or of sufficient high specific radioactivity (^{59}Fe) to neglect the effect of carrier concentration. Only for ^{51}Cr, ^{65}Zn, and ^{114m}In was the specific radioactivity not high enough to neglect the carrier concentration. This concentration was subtracted from the floated ions concentration.

Apparatus and Procedure

The batch ion flotation experiments were carried out in a glass column 45.7 cm in height and 2.4 cm in diameter. The nitrogen gas was saturated with water, and the flow rate was maintained at 4 mL/min (at 25°C and 760 mmHg) through a sintered glass sparger of 20–30 μm nominal porosity. The volume of each initial solution, prior to ion flotation, was 100 mL, and the temperature was kept at 21 ± 2°C. The surfactants were utilized as 0.02 *M* standard solutions in ethanol. The surfactant concentration in the initial solutions was maintained at 2×10^{-4} *M* throughout this investigation. Measurements of pH were performed with an Elpo Model N512 pH meter using an Energopomiar Model SAgP-209 glass body combination electrode. pH in the initial solutions was kept constant at 2.0 throughout this study.

The time dependance of the concentration of each metal in the bulk solution (c_t) was recorded continuously during each ion flotation experiment by means of radioactive analytical tracers and gamma-radiation spectroscopy, following a procedure described previously (*11*). A single-channel, gamma-radiation spectrometer was used as the detector of radiation intensity of specific energy. The c_t versus time curves enabled the calculation of the percent removal, $[(1 - c_t)/c_i]100$, in which c_i is the initial metal concentration. The maximal percent removal is $[(1 - c_r)/c_i]100$, in which c_r is the metal concentration in the residual solution when foaming has ceased.

The determination of the solubility of sublates was carried out by the measurement of aqueous solution turbidity. For this, a photoelectrical colorimeter of the Specol type with titration equipment of the Ti type and with an amplifier of the Specol ZV type were used. To 20 mL of an aqueous solution of adequate nitrate placed in a 30-mL cell with a magnetic stirrer, the surfactant solution was dropped from a burette. The solution was stirred after each surfactant dropping. The composition and concentration of the studied solutions, as well as the temperature, were the same as in the ion flotation measurements. The turbidity measurements were stopped when the transmission of the aqueous solution reached a value of 15%. All measurements were carried out at a wavelength of 450 nm. From plots of transmission vs $-\log I_i$, where I_i is the ionic product, the solubility products were calculated by extrapolating the transmission to zero value.

RESULTS

In the first series of experiments the sublate solubilities of the chosen transition metal cations with sodium dodecylsulfonate and sodium dodecylbenzenesulfonate were determined. The Ag^+ cation did not form sublates with the surfactants studied. The sublate solubilities for other metal cations with DSNa and DBSNa are illustrated in Fig. 1. According to Fig. 1, the sublate solubilities depend on the kind of metal cation and the surfactant. The solubility values are the lowest for trivalent cations. Solubilities are higher for DSNa than for DBSNa in all cases.

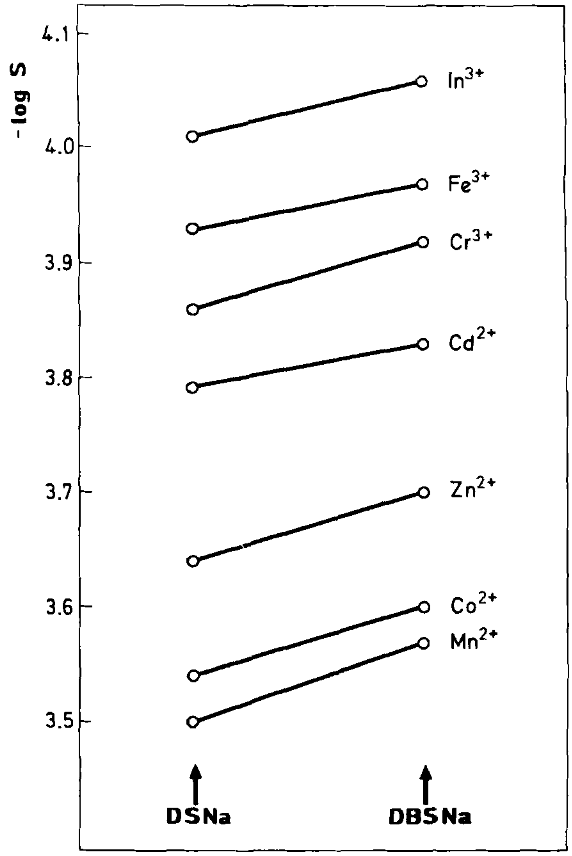

FIG. 1. Sublates solubility for transition metal cations with anionic surfactants.

In the next series of experiments the percent removal of two metal cations with different electrical charges, i.e., Co^{2+} and Fe^{3+}, from single and multi-ion aqueous solutions by DSNa and DBSNa was investigated. The results are shown in Fig. 2. Removal of Co^{2+} cations from dilute aqueous solutions

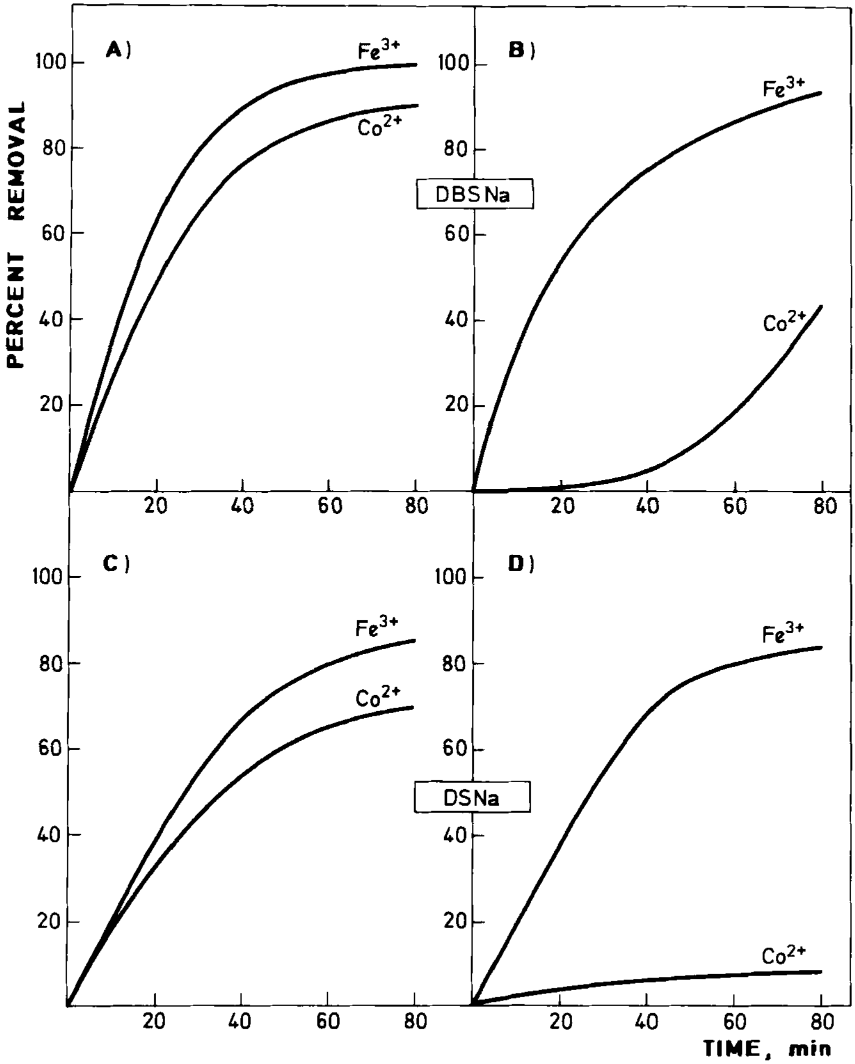

FIG. 2. Percent removal vs time for Co^{2+} and Fe^{3+} cations from single (A, C) and multi-ion (B, D) aqueous solutions by sodium dodecylbenzenesulfonate and sodium dodecylsulfonate at an initial metal concentration of 5×10^{-5} *M*.

containing only single metal cations is lower than Fe^{3+} cations removal (Fig. 2A, C). This also occurs in multi-ion systems, but removal of Co^{2+} cations is much lower in comparison with single metal ion systems (Fig. 2B, D). During the first 30 minutes of the flotation process, practically only Fe^{3+} cations are removed from an aqueous multi-ion system.

The next investigation dealt with removing Fe^{3+} and Co^{2+} cations from multi-ion aqueous solutions at different initial metal concentrations. The results are illustrated in Fig. 3. When the Co^{2+} concentration is lower than the Fe^{3+} concentration, almost all the iron(III) cations are removed into foam while the cobalt(II) cations remain in aqueous solution. Flotation of both metals is less selective when the Co^{2+} concentration is higher than the Fe^{3+} concentration. When the Fe^{3+} concentration is 100 times lower than the Co^{2+} concentration, the reverse selectivity is observed.

In Fig. 4 the percent removal of five metal cations (Cr^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+}, and Mn^{2+}) is shown. Flotation removal for solutions containing single metal cations at the stoichiometric concentration is not very efficient, and

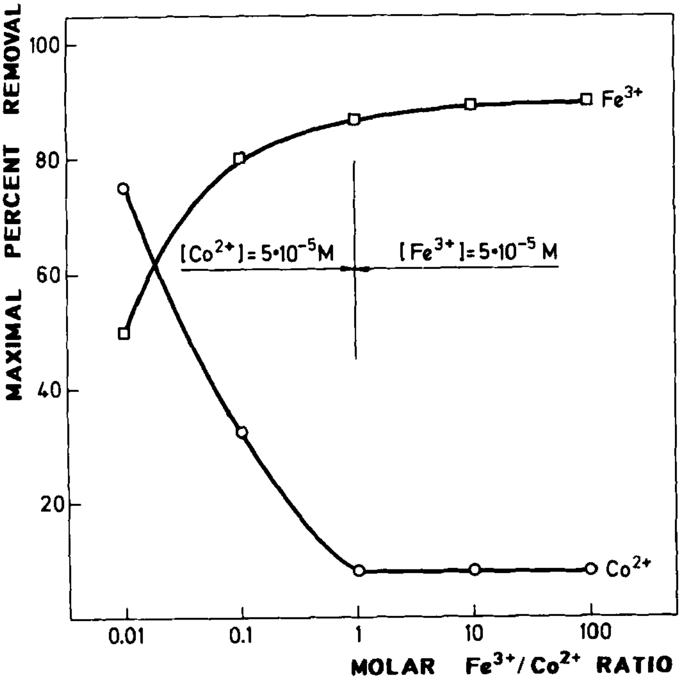

FIG. 3. Maximal percent removal vs molar Fe^{3+}/Co^{2+} ratio from multi-ion aqueous solutions by sodium dodecylsulfonate.

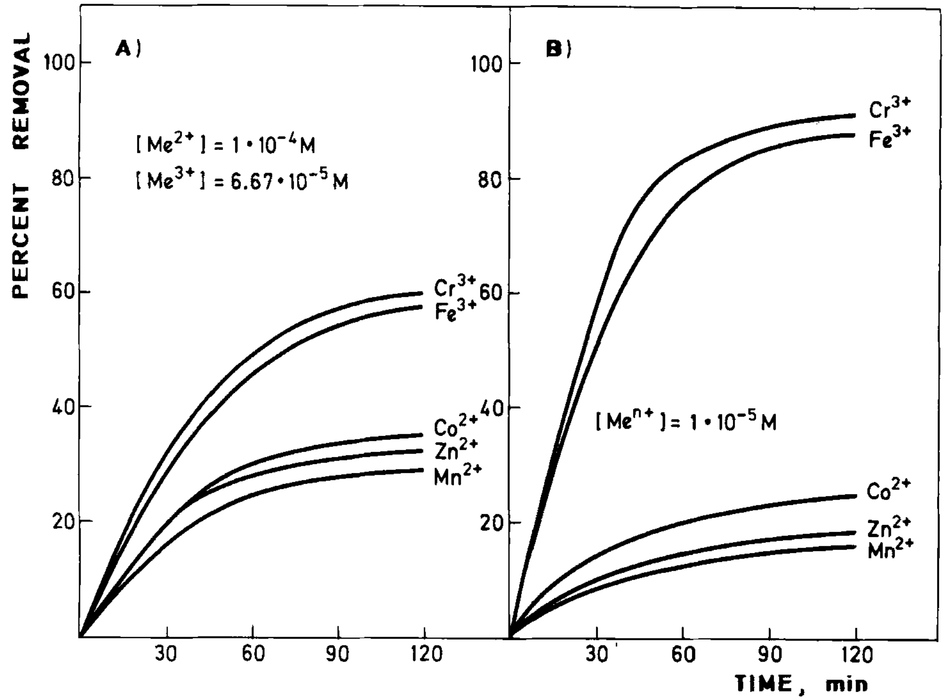

FIG. 4. Percent removal vs time for Cr^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+}, and Mn^{2+} cations from single (A) and multi-ion (B) aqueous solutions by sodium dodecylbenzenesulfonate.

trivalent cations are floated better than divalent cations (Fig. 4A). Removal of divalent cations from multi-ion systems is lower than of trivalent cations.

The final series of experiments was conducted to determine the flotation removal of three metal cations having the same $4d^{10}$ electron configuration but different electrical charges, i.e., Ag^+, Cd^{2+}, and In^{3+}. The results are given in Fig. 5, where it is seen that the flotation removal of metal cations is the highest for trivalent cations and the lowest for monovalent cations. Flotation from a multi-ion system allows removal of In^{3+} cations while the Ag^+ and Cd^{2+} cations remain in the residual aqueous solution.

DISCUSSION

According to the stability constant values of metal ions in dilute aqueous solutions, all the metal cations studied were 99–100% in their mentioned form when the pH of the aqueous solution was 2.0 (*12*, *13*). Only in the case of Fe(III) at pH 2.0 was the percent formation of Fe^{3+} cations equal to 90%. Sulfonates, used as the anionic surfactants, were in the form of

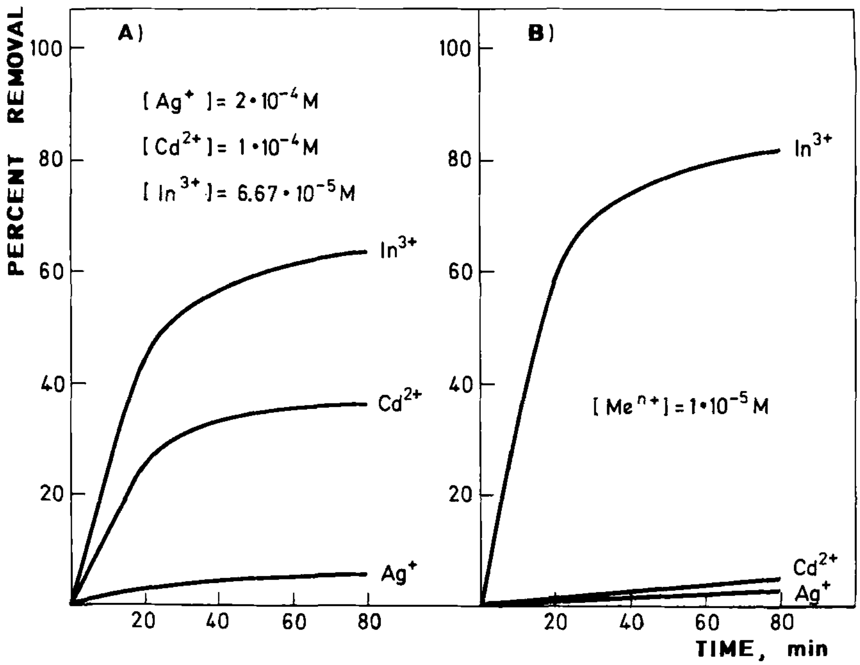

FIG. 5. Percent removal vs time for Ag^+, Cd^{2+}, and In^{3+} cations from single (A) and multi-ion (B) aqueous solutions by sodium dodecylbenzenesulfonate.

real solutions since their concentrations in aqueous solutions were lower than their critical micelle concentration values (*14*).

Table 1 shows the ionic radii and ionic potentials of the metal cations studied. The ionic potential is the ratio between the ionic charge and the ionic radius. According to Fig. 1, the solubility of sublates is influenced by the size and charge of the metal cations as well as by the size of the surfactant. The lowest sublate solubilities are for those sublates formed by metal cations with the highest ionic potential values. On the other hand, the solubility of sublates decreases with an increase of the number of carbon atoms in the surfactant molecule.

By knowing the sublate solubility and concentration of the floated cation as well as the surfactant concentration, it is possible to calculate whether the sublate can be precipitated in the bulk solution. For the ion flotation experiments, for which data are presented in Figs. 2–5, no sublate was formed in the bulk solution.

The ion flotation results illustrated in Figs. 2, 4, and 5 show that the highest affinity to ionic surfactants is by trivalent metal cations, while the lowest affinity to surfactants is by monovalent metal cations. The sequence

TABLE 1
Ionic Radii and Ionic Potentials of Studied Metal Cations

Cation	Ionic radii (Å) (*15*)	Ionic potentials ($Å^{-1}$)
Cr^{3+}	0.76	3.95
Fe^{3+}	0.79	3.80
Mn^{2+}	0.96	2.08
Co^{2+}	0.88	2.27
Zn^{2+}	0.89	2.25
Ag^{+}	1.29	0.78
Cd^{2+}	1.09	1.83
In^{3+}	0.93	3.23

of growing affinity of metal cations to anionic surfactants is the same as the sequence of ionic potential values:

$$\begin{array}{ccccccccc} Mn^{2+} < & Zn^{2+} < & Co^{2+} < & Fe^{3+} < & Cr^{3+}, & \quad Ag^{+} < & Cd^{2+} < & In^{3+} \\ 2.08 & 2.25 & 2.27 & 3.80 & 3.95, & \quad 0.78 & 1.83 & 3.23 \end{array}$$

Our data confirm the selective foam fractionation model proposed by Jorne and Rubin (*7*), which is based on the Gouy-Chapman diffused double layer theory with the restriction that the closest approach to the surface is determined by the size of the hydrated ions. The ion flotation results illustrated in Fig. 3 show that the above selectivity sequences can be observed only when the concentration of floated metal cations is equimolar. In the case of excess metal cations with a lower affinity for the anionic surfactant, the selectivity is reversed.

CONCLUSIONS

Experimental data on the ion flotation of Cr^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, and In^{3+} metal cations with sodium dodecylsulfonate and sodium dodecylbenzenesulfonate, where no sublate was formed in the bulk solution, were compared with the ionic potentials of these metal cations. From the good agreement between the selectivity sequences for the affinity of metal cations to anionic surfactants and the ionic potentials of those cations, it is concluded that a theory based on the Gouy-Chapman diffuse double layer model enables the ion flotation selectivity of metal cations to be predicted.

The sublate solubilities determined here are influenced by the size and charge of the metal cations as well as by the size of the surfactant. The lowest solubility is for the sublate formed by the metal cation with the highest ionic potential value. The solubility of sublates decreases with an increase of surfactant size.

REFERENCES

1. R. B. Grieves, in *Treatise on Analytical Chemistry*, 2nd ed., Vol. 5 (P. J. Elving, ed.), Wiley-Interscience, New York, 1982.
2. D. J. Wilson and A. N. Clarke, *Topics in Foam Flotation*, Dekker, New York, 1983.
3. A. M. Golman, *Ionnaja Flotacija*, Nedra, Moscow, 1982.
4. A. I. Rusanov, S. A. Levicer, and V. T. Zarov, *Poverchnostnoje radelene vercestv*, Izd. Chimija, Leningrad, 1981.
5. C. Walling, E. E. Ruff, and J. L. Thornton, *J. Phys. Chem.*, *67*, 486 (1957).
6. P. E. Wace and D. C. Banfield, *Chem. Process. Eng.*, *47*, 70 (1966).
7. J. Jorne and E. Rubin, *Sep. Sci.*, *4*, 313 (1969).
8. R. C. H. Huang and F. D. Talbot, *Can. J. Chem. Eng.*, *51*, 709 (1973).
9. K. Kubota and S. Hayashi, *Ibid.*, *55*, 286 (1977).
10. R. B. Grieves, K. Burton, and J. A. Craigmyle, *Sep. Sci. Technol.*, *22*, 1597 (1987).
11. W. Walkowiak and A. Bartecki, *Nukleonika*, *18*, 131 (1973).
12. *Stability Constants*, Special Publication No. 17, The Chemical Society, London, 1964.
13. *Stability Constants of Metal-Ion Complexes*, Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971.
14. K. Shinoda, T. Nakagawa, B. I. Tamamushi, and T. Isemura, *Colloidal Surfactants, Some Physicochemical Properties*, Academic, New York, 1963.
15. J. Burgess, *Ions in Solution: Basic Principles of Chemical Interactions*, Wiley, New York, 1989.

Received by editor March 5, 1990