Edward SOCZEWIŃSKI, Regina MAŃKO

Partition Chromatography of Metals in Oxo Solvent Systems.
II. Alcohols as Extractants of Thiocyanate Complexes of Metals

Chromatografia podziałowa metali w układach oksoniowych. II. Alkohole jako
ekstrahenty kompleksów rodankowych metali

Распределительная хроматография металлов в оксониевых системах.
II. Спирты в качестве экстрагентов роданидных комплексов металлов

Alcohols, ketones, esters and ethers form an individual group of
extractants called oxo solvents, which according to the classification
proposed by F o m i n [1] belong to chemically neutral extractants.
Their extraction properties are due to the formation of extractable
coordination compounds with simple complexes of metals; e.g. with
thiocyanate complexes. Solvent systems composed of oxo solvents and
aqueous solutions of thiocyanates are often employed for chromato-
graphic and extraction methods of separation of metals [2—13].

In recent years the search for selective partition systems is mainly
focused on multicomponent solvents, composed of mixtures of oxo sol-
vents [14—17] or mixed extractants in which alcohols, ketones or
esters are diluents for active solvents which extract metal ions or their
simple complexes by the liquid ion exchange mechanism [18—20] or as
neutral high-molecular weight extractants (e.g., tributylphosphate)
[17, 21]. In all these cases it is useful to understand the effect of the
diluting solvent on the partition behaviour of metals during extraction
with mixed organic solvents.

In the previous part [22] it was demonstrated that in the "moist
paper" technique, in solvent systems of the type oxo solvent/aqueous
electrolyte solution, the decisive process in chromatography is liquid/
/liquid partition. These results, as well as data reported in other pa-
pers [23], seem to indicate that paper chromatographic results may

provide information on the distribution behaviour of metals in analogous solvent systems.

The present paper is an attempt of examining the effect of the molecular structure of oxo solvents of the alcohol type on the distribution behaviour of thiocyanate complexes of metals. The variation of the R_F values with concentration in the range of 0.2 to 6.8 M NH$_4$SCN was investigated.

EXPERIMENTAL

Whatman No 4 paper was impregnated with fresh solutions of NH$_4$SCN acifified to $pH = 3.0$ to avoid hydrolysis of metals; the use of nitric acid instead of usually employed hydrochloric acid was preferred in view of the lower stability of nitrate complexes of metals. The impregnated paper strips were air dried until the moisture content dropped to 50% (0.5 g of aqueous solution per 1 g of dry paper) whereupon the strips were immediately transferred to glass chromatographic tanks for descending development. The development was carried out at room temperature (23 ± 1° C), using as the mobile phase the following alcohols pre-saturated with aqueous solutions of NH$_4$SCN of suitable concentration:

1) n–butyl alcohol (Estron, Warsaw),
2) n–amyl alcohol (import, Moscow),
3) 3-methyl-butyl alcohol (Kutno,Poland),
4) n-hexyl alcohol (BDH, England),
5) n-octyl alcohol (BDH, England),
6) n-nonyl alcohol (BDH, England),
7) cyclohexanol (Nitrogen Works, Tarnów, Poland),
8) Benzyl alcohol ("Xenon" Łódź, Poland).

The use of higher alcohols and a controlled degree of humidity of the paper secured the partition mechanism of the chromatographic process. The chromatographic behaviour of 35 metal ions was investigated and the experimental results are presented in Figs. 1—14.

RESULTS AND DISCUSSION

In Fig. 1 the effect of the concentration of the ligands (thiocyanate ions) in the aqueous phase on R_F values of the metals is presented as R_F vs. log [SCN⁻] relationships. Four metals, Tl (I), Ge (IV), V (V), and Sc (III) remained on the line of start over the whole range of the ligand concentration examined and are omitted from the plot. All metals gave well defined, elliptical spots except for Zr (IV) and Ti (IV). It can

be seen that only As (III) has a constant R_F coefficient in the whole concentration range; Se (IV), Ag (I), Sb (III), W (VI) and Pb (II) have low R_F values. On the other hand, the R_F values of Fe (III), Zn (II), Mo (VI), In (III) Au (III) and Sn (IV) are high, which indicates good extraction of their thiocyanate complexes by hexanol.
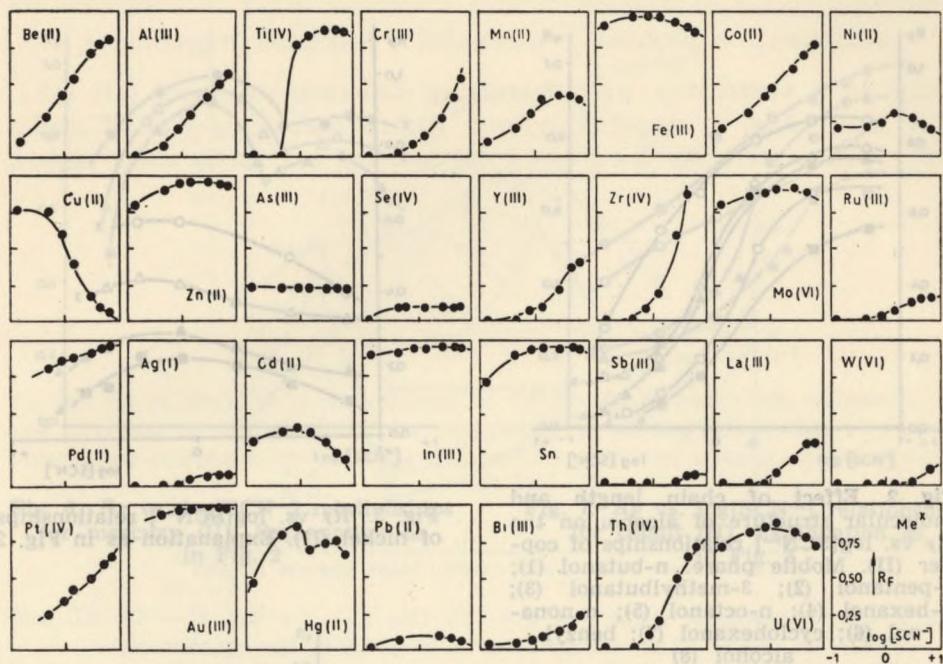

Fig. 1. Relationship between R_F values of metal ions and log concentration of ligand in the aqueous phase for the system n-hexanol/aqueous solution of NH₄SCN acidified with HNO₃ to $pH = 3$

Hg (II) shows a peculiar shape of the R_F vs. log [SCN⁻] relationship, as in the system n-pentanol/aqueous NH₄SCN (cf. [22]). The remaining metals can be subdivided into three groups.

A. Be (II), Al (III), Ti (IV), Cr (III), Co (II), Y (III), Zr (IV), Ru (III), La (III), Pd (II), Pt (IV), Bi (III) and Th (IV) are better extracted from aqueous solutions at highest concentrations of SCN⁻.

B. Mn (II), Ni (II), Cd (II), Hg (II), and U (VI) show maximal R_F value at ca. 1 M concentration of thiocyanate in the aqueous phase; this presumably corresponds to the maximal extraction of the metals.

C. Only Cu (II) is better extracted at low concentrations of thiocyanates in the aqueous phase.

The differentiated behaviour of various metals permits to choose optimal solvent systems for their separation.

In Figs. 2 to 6 the R_F vs. log [SCN$^-$] relationships of some metals are presented for a few members of the homologous series of alcohols. R_F vs. log [SCN$^-$] curves for the alcohols are almost parallel for a given metal ion, their sequence being also generally identical; the highest R_F values were obtained for butanol and the lowest ones for n-nonyl
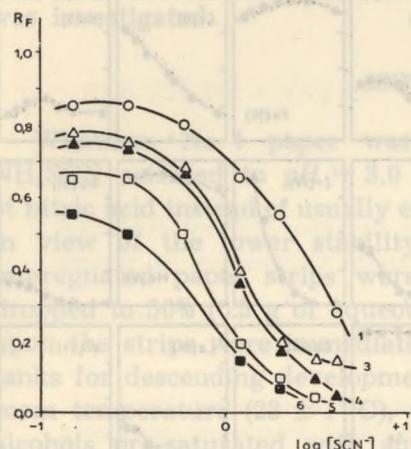

Fig. 2. **Effect of chain length and** molecular structure of alcohol on the R_F vs. log[SCN$^-$] relationships of copper (II). Mobile phase: n-butanol (1); n-pentanol (2); 3-methylbutanol (3); n-hexanol (4); n-octanol (5); n-nonanol (6); cyclohexanol (7); benzyl alcohol (8)
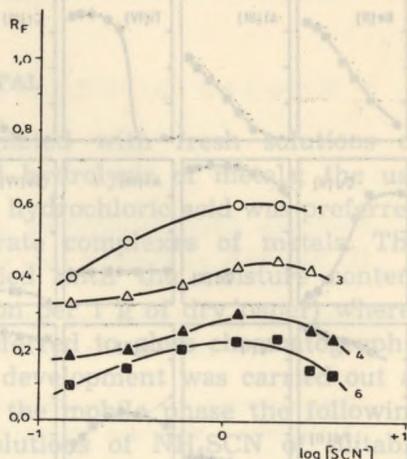
Fig. 3. R_F vs. log[SCN$^-$] relationships of nickel (II). Explanation as in Fig. 2
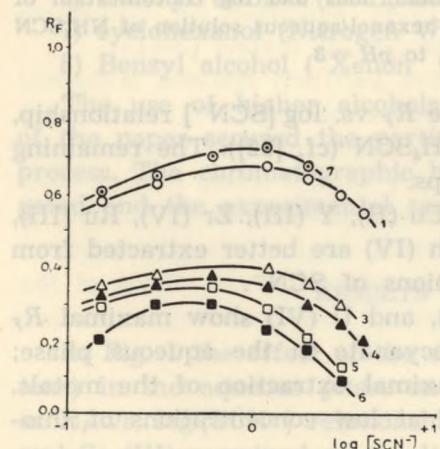
Fig. 4. R_F vs. log[SCN$^-$] relationships of cadmium (II). Explanation as in Fig. 2
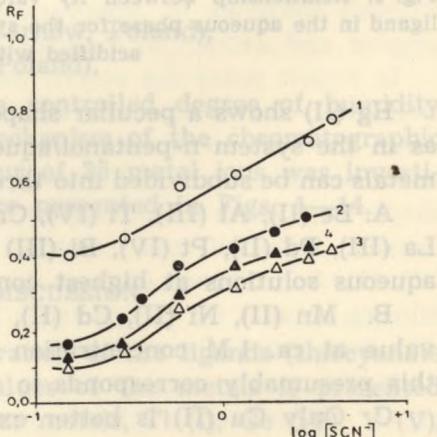
Fig. 5. R_F vs. log[SCN$^-$] relationships for manganese (II). Explanation as in Fig. 2

alcohol. The parallel course of the relationships seems to indicate that the mechanism of partition in the systems with higher alcohols is analogous. The R_F values of the various metals investigated are weakly differentiated which is in agreement with earlier reports about the low selectivity of oxo solvents [8, 15].
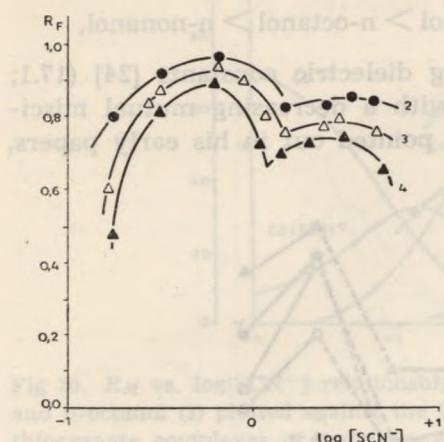
Fig. 6. R_F vs. log[SCN−] relationships for mercury (II). Explanation as in Fig. 2
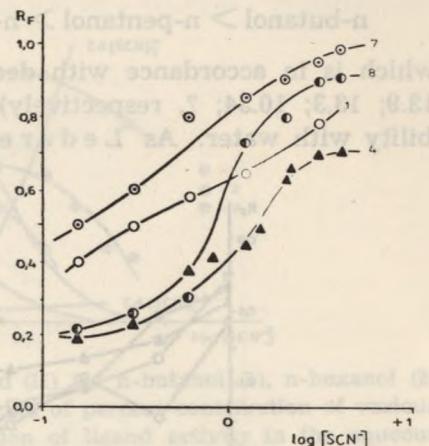
Fig. 7. R_F vs. log[SCN−] relationships for cobalt (II). Explanation as in Fig. 2
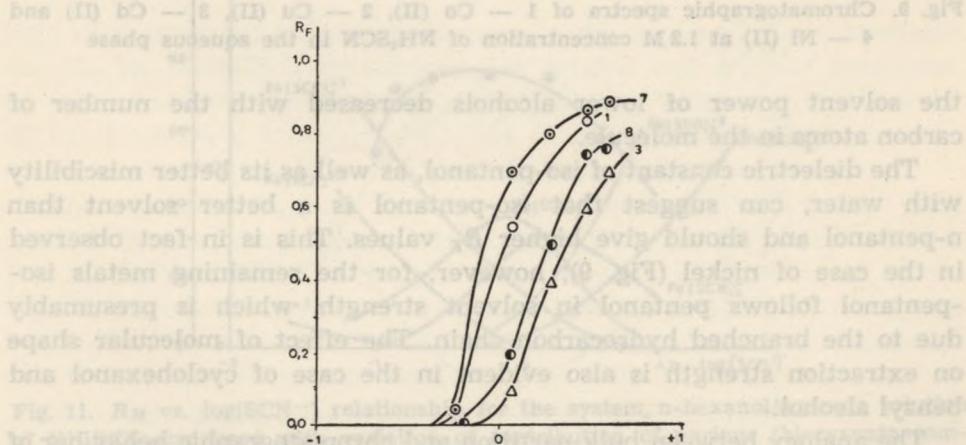
Fig. 8. R_F vs. log[SCN−] relationships of zircon (IV). Explanation as in Fig. 2

Two further oxo solvents investigated, cyclohexanol and benzyl alcohol (Figs. 7, 8) show more individual behaviour in comparison with that of the straight-chain aliphatic alcohols.

In order to demonstrate the effect of the chain length of n-alcohols and that of the presence of an alicyclic or aromatic ring in the alcohol molecule, the R_F vs. solvent spectra of some metals are presented for 1.2 M concentration of NH_4SCN in the aqueous phase (Fig. 9). It is evident that the R_F values of the metals decrease in the following sequence:

$$n\text{-butanol} > n\text{-pentanol} > n\text{-hexanol} > n\text{-octanol} > n\text{-nonanol},$$
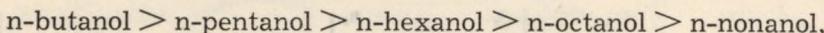
which is in accordance with decreasing dielectric constants [24] (17.1; 13.9; 13.3; 10.34; ?, respectively) and with a decreasing mutual miscibility with water. As L e d e r e r [9] pointed out in his early papers,
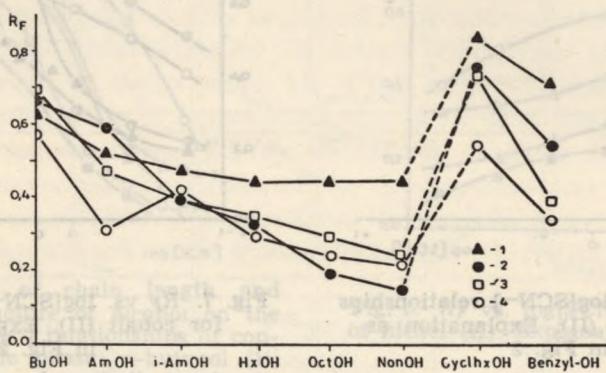
Fig. 9. Chromatographic spectra of 1 — Co (II), 2 — Cu (II), 3 — Cd (II) and 4 — Ni (II) at 1.2 M concentration of NH_4SCN in the aqueous phase

the solvent power of lower alcohols decreased with the number of carbon atoms in the molecule.

The dielectric constant of iso-pentanol, as well as its better miscibility with water, can suggest that iso-pentanol is a better solvent than n-pentanol and should give higher R_F values. This is in fact observed in the case of nickel (Fig. 9); however, for the remaining metals iso-pentanol follows pentanol in solvent strength, which is presumably due to the branched hydrocarbon chain. The effect of molecular shape on extraction strength is also evident in the case of cyclohexanol and benzyl alcohol.

The analogy between bulk partition and chromatographic behaviour of metals in oxo solvents [22, 23] suggests that chromatographic data may provide certain information concerning the mechanism of partition between water and the solvent phase. Therefore, the R_M vs. log [SCN^-] plots of Cd, Co, Hg and Ni ($R_M = \log R_F/(1 - R_F)$) are compared with the corresponding formation equilibria of thiocyanate complexes (Figs. 10 to 14).

The comparison is unfortunately only approximate because the conditions of the chromatographic and static data are not strictly comparable (different ionic strength, the use of concentrations instead of activities
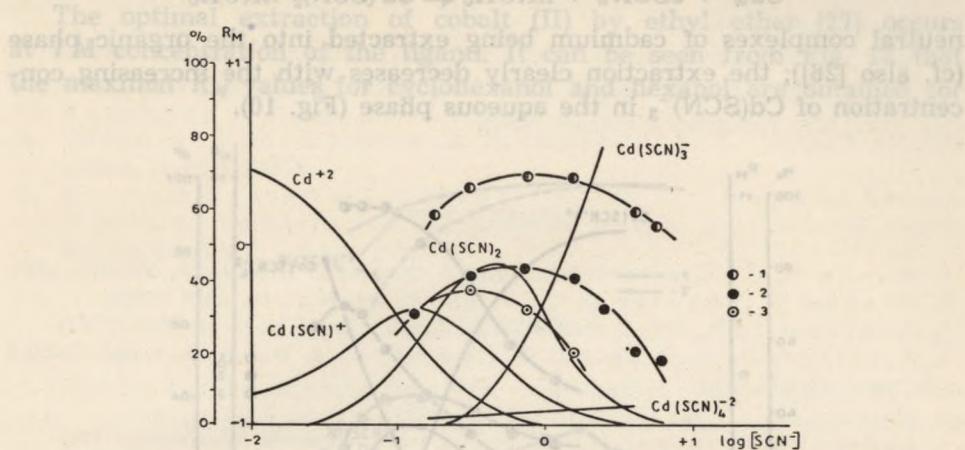
Fig 10. R_M vs. log[SCN$^-$] relationships of Cd (II) for n-butanol (1), n-hexanol (2) and n-octanol (3) plotted against the background of percent contribution of various thiocyanate complexes of cadmium as function of ligand activity in the aqueous solution [34]
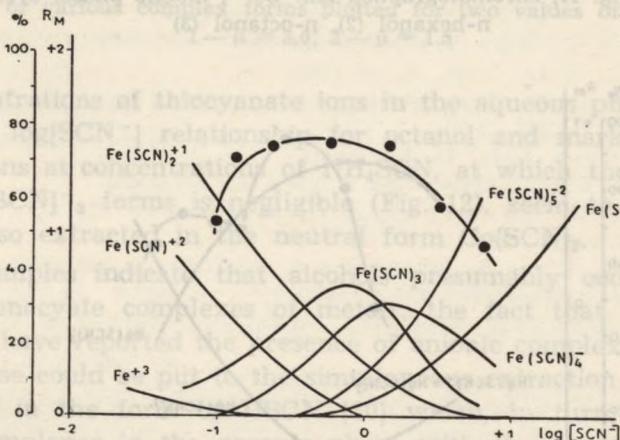
Fig. 11. R_M vs. log[SCN$^-$] relationship for the system, n-hexanol/aqueous solution of NH$_4$SCN compared with variation of contribution of various thiocyanate complexes of iron (III) as function of activity of SCN$^-$ in the aqueous phase

of thiocyanate ions in the solution). Nevertheless, the comparison seems to indicate that definite complex forms of metals are extracted by the organic solvents.

Presumably, the extraction of cadmium can be described by the following equation:

$$Cd_w^{+2} + 2SCN_w^- + nROH_o \rightleftarrows Cd(SCN)_2 \cdot nROH_o$$
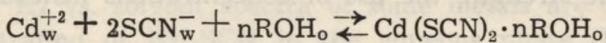
neutral complexes of cadmium being extracted into the organic phase (cf. also [26]); the extraction clearly decreases with the increasing concentration of $Cd(SCN)^-_3$ in the aqueous phase (Fig. 10).
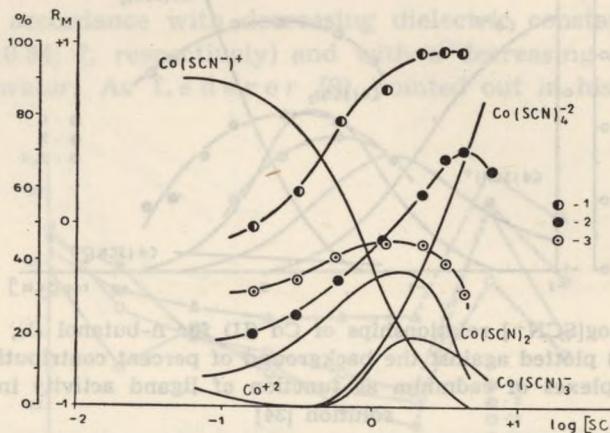
Fig. 12. As in Fig. 11, chromatographed ion: Co^{+2}; mobile phase: cyclohexanol (1), n-hexanol (2), n-octanol (3)
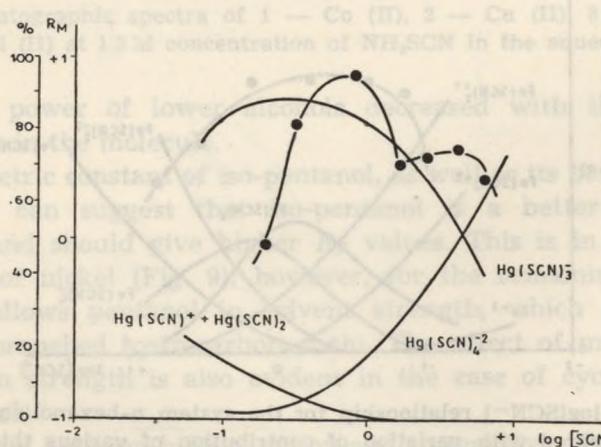
Fig. 13. As in Fig. 11; chromatographed ion: Hg^{+2}; mobile phase: n-hexanol

In the case of Fe (III) it is difficult to conclude which complex form is extracted. B o c k [27] reports that optimum extraction of iron ions from aqueous NH_4SCN by ethyl ether occurs at 0.5 M concentration of

NH₄SCN, which approximately corresponds to the maximum on the R_M vs. log[SCN⁻] plot for hexanol (Fig. 11). This seems to suggest that the equation of extraction is analogous to that of cadmium.

The optimal extraction of cobalt (II) by ethyl ether [27] occurs at 7 M concentration of the ligand. It can be seen from Fig. 12 that the maximal R_M values for cyclohexanol and hexanol are obtained for
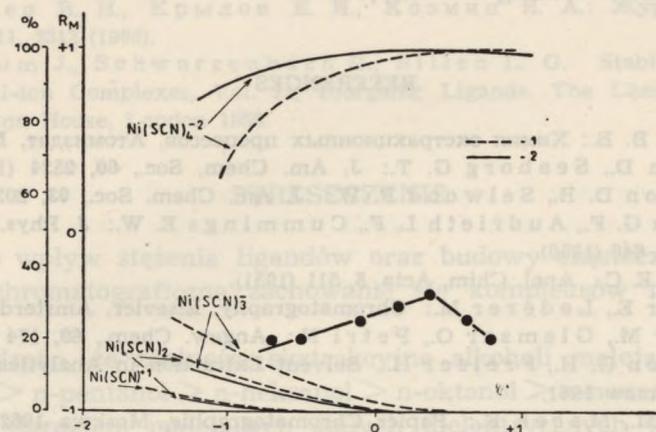
Fig. 14. As in Fig. 11; chromatographed ion: Ni⁺²; mobile phase: n-hexanol; contributions of various complex forms plotted for two values of ionic strength: $1 - \mu = 3.0$; $2 - \mu = 1.5$

high concentrations of thiocyanate ions in the aqueous phase; however, the R_M vs. log[SCN⁻] relationship for octanol and marked extraction of cobalt ions at concentrations of NH₄SCN, at which the contribution of the Co[SCN]⁻₃ forms is negligible (Fig. 12), seem to indicate that cobalt is also extracted in the neutral form Co(SCN)₂.

The examples indicate that alcohols presumably coordinate with neutral thionacyate complexes of metals; the fact that some authors [13, 28, 29] have reported the presence of anionic complex forms in the organic phase could be put to the simultaneous extraction of the ligand by alcohols in the form of HSCN [30] which, in turn, can produce negative complexes in the organic phase with the neutral forms.

However, taking into account the amphoteric character of alcohols (class AB according to the classification proposed by P i m e n t e l and M c C l e l l a n [31]) one cannot exclude the possibility of extraction of anionic thiocyanate complexes of metals. Data in Figs. 13 and 14 suggest the conclusion: Hg (II) and Ni (II) can presumably be extracted both as neutral as well as negative thiocyanate complexes. Similar opinions were reported for tributyl phosphate (TBP) systems which belong also

to oxo solvents. As some authors pointed out, TBP extracted some metals in neutral forms [32] and other metals as negative complexes [33]. Therefore, the mechanism of extraction of metals by oxo solvents remains an open problem.

Note. The contributions of the various complex forms of metal at varying activity of the ligand have been calculated from the literature (Ni, [13]; the remaining metals, [34].

REFERENCES

1. Фомин В. В.: Химия экстракционных процессов, Атомиздат, Москва 1960.
2. Graham D., Seaborg G. T.: J. Am. Chem. Soc., 60, 2524 (1938).
3. Appleton D. B., Selwood P. W.: J. Am. Chem. Soc., 63, 2029 (1941).
4. Asselin G. F., Audrieth L. F., Cummings E. W.: J. Phys. and Colloid Chem., 54, 640 (1950).
5. Martin E. C.: Anal. Chim. Acta, 5, 511 (1951).
6. Lederer E., Lederer M.: Chromatography, Elsevier, Amsterdam 1957.
7. Ziegler M., Glemser O., Petri N.: Angew. Chem., 69, 174 (1957).
8. Morrison G. H., Freiser H.: Solvent Extraction in Analytical Chemistry, PWN, Warsaw 1961.
9. Hais I. M., Macek K.: Papier Chromatographie, Moskwa 1962.
10. Елисеева Г. Д.: Тр. инст. геол. наук АН УССР. Сер. Петрограф. Минералог. Геохимия, 21, 121 (1964).
11. Chang C. C., Yang H. H.: C. A. 63, 3601 (1965).
12. Ющенко А. С., Ёфа Б. З.: Радиохимия, 8, 621 (1966).
13. Różycki C.: Chem. Anal., 11, 447 (1966).
14. Вдовенко В. М., Кривохатский А. С., Сизов А. В.: Журн. неорган. химии, 5, 2363 (1960).
15. Kuča L.: Chem. Listy, 58, 763 (1964).
16. Вдовенко В. М.: Украин. хим. журнал, 32, 284 (1966).
17. Гибало И. М., Алимарин И. П., Альбадри С., Еремина Г. В.: Радиохимия, 9, 118 (1967).
18. Deptuła C., Minc S.: Nukleonika, 3, 197 (1961); 6, 343 (1965).
19. Smułek W.: Nukleonika, 9, 547 (1962).
20. Mason G. W., Lewey S., Peppard D. F.: J. Inorg. Nucl. Chem., 26, 2271 (1964).
21. Таубе М.: Радиохимия, 4, 260 (1962).
22. Soczewiński E., Mańko R., Kuczyński J.: Ann. Univ. Mariae Curie-Skłodowska, sectio AA, this issue.
23. Елисеева Г. Д.: Тр. комиссии анал. химии, 6, 439 (1955).
24. Riddick J. A., Toops E. E., Jr.: Organic Solvents [in:] Weissberger J. A. [Editor]: Technique of Organic Chemistry, Vol. VII, Intersc. Publ. Inc., New York 1955.
25. Scheflan L., Jacobs M.: The Handbook of Solvents, D. Van Nostrand Comp. Inc., N. Y. — Toronto—London 1953.
26. Soczewiński E., Rojowska M., Przeszlakowski S.: Ann. Univ. Mariae Curie-Skłodowska, Lublin, sectio AA, XXI, 21 (1966).
27. Bock R.: Z. anal. Chem., 113, 110 (1951).

28. **Specker H., Werding G.**: Z. anal. Chem., **200**, 337 (1964).
29. **Specker H., Jackwerth E., Hovermann G.**: Z. anal. Chem., **177**, 10 (1960).
30. **Винаров И., Ковалева Е. И., Бык И. Г.**: Украин. хим. журнал, **34**, 62 (1968).
31. **Pimentel G. C., McClellan A. L.**: The Hydrogen Bond, Freeman, S. Francisco 1960.
32. **Никитина Г. П., Пушленков М. Ф.**: Радиохимия, **1**, 137 (1962).
33. **Старцев В. Н., Крылов Е. И., Козмин Я. А.**: Журнал неорган. химии, **11**, 2312 (1966).
34. **Bjerrum J., Schwarzenbach G., Sillen L. G.**: Stability Constants of Metal-ion Complexes, Vol. II, Inorganic Ligands. The Chemical Society, Burlington House, London 1958.

STRESZCZENIE

Badano wpływ stężenia ligandów oraz budowy cząsteczkowej alkoholu na chromatograficzne zachowanie się kompleksów rodankowych 35 metali.

Stwierdzono, że zdolności ekstrakcyjne alkoholi maleją w szeregu: n-butanol > n-pentanol > n-heksanol > n-oktanol > n-nonanol, co jest zgodne z szeregiem malejących stałych dielektrycznych tych alkoholi i malejącą ich wzajemną mieszalnością z wodą. Stwierdzono również wpływ budowy cząsteczkowej alkoholu (rozgałęzienia łańcucha węglowego i obecności pierścienia aromatycznego) na wartości R_F metali w badanych układach.

Wysunięto sugestie odnośnie mechanizmu podziałowego metali w układzie rozpuszczalnik oksoniowy (alkohol) — wodny roztwór NH_4SCN.

РЕЗЮМЕ

Исследовалось влияние концентрации лиганда и молекулярной структуры спирта на хроматографическое поведение роданидных комплексов 35 металлов.

Установлено, что коэффициенты R_F и экстракционная способность спиртов уменьшаются в следующем порядке: n-бутанол > n-пентанол > n-гексанол > n-октанол > n-нонанол, что соответствует уменьшающемуся ряду диэлектрических констант и взаимной растворимости с водой. Наблюдалось влияние молекулярной структуры спирта (разветвление углеводородной цепи, присутствие ароматического кольца) на величины R_F металлов в исследованных системах.

Авторы выдвигают несколько гипотез о механизме распределения ионов металлов в системах типа оксониевый растворитель (спирт) — водный раствор NH_4SCN.

31. Irving H., Rossotti H. S.: J. Chem. Soc.

32. Никитина Г. П., Пушленков М. Ф., Разумова Л. П. (1959)

33. Старик Б. Н., Крылов Б. К., Козин Н. А.: Журнал неорган. химии, 11, 311 (1966).

34. Bjerrum J., Schwarzenbach G., Sillen L. G.: Stability Constants of Metal-Ion Complexes, Vol. II Inorganic Ligands. The Chemical Society, Burlington House, London 1958

1. Фомин В. Б.: Химия экстракционных процессов, Атомиздат, Москва 1960.
2. Graham R. D., Sinha S. T.: J. Am. Chem. Soc., 90 (1931).
3. Appleton D. B., Selwood (1941).
4. Asselin G. F., Andrieth L. F., Cummings S. W.: J. Phys. and Colloid Chem. (1961).
5. Lederer E., Lederer M.: Chromatography, Elsevier, Amsterdam 1957.
6. Ziegler M., Glemser O., Petri N.: Angew. Chem. 68 (1956).

Badano wpływ stężenia ligandów oraz budowy rozpuszczalników alkoholi na chromatograficzne zachowanie się kompleksów rodankowych 35 metali.

Stwierdzono, że zdolność ekstrakcyjna alkoholi maleje w szeregu: n-butanol > n-pentanol > n-heksanol > n-oktanol > n-nonanol, co jest zgodne z szeregiem malejących stałych dielektrycznych tych alkoholi i malejącej ich wzajemnej mieszalności z wodą. Stwierdzono również wpływ budowy cząsteczkowej alkoholu (rozszczepienia łańcucha węglowego i obecności pierścienia aromatycznego) na wartości R metali w badanych układach.

Wysnuto sugestie odnośnie mechanizmu podziału tego metali w układzie rozpuszczalnik oksoniowy (alkohol) — wodny roztwór NH_4SCN.

РЕЗЮМЕ

Исследовалось влияние концентрации лиганда и многоуглеродных спиртов на хроматографическое поведение роданидных комплексов 35 металлов.

Установлено, что коэффициенты R экстракционная способность спиртов уменьшаются в следующем порядке: n-бутанол > n-пентанол > n-гексанол > n-октанол > n-нонанол, что соответствует уменьшающимся рядам диэлектрических констант и взаимной смешиваемости спиртов с водой. Наблюдалось влияние молекулярной структуры спирта (разветвление углеродной цепи, присутствие ароматического кольца) на величины R металлов в исследованных системах.