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# LIQUID-LIQUID EXTRACTION OF COBALT(II) WITH POLYETHYLENEGLYCOL AND ITS DERIVATIVES

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Polyethyleneglycol and its derivatives were found to be employed as new extracting reagents of trace amounts of Co(II) in liquid-liquid extraction. The extraction behavior of Co(II) with polyethyleneglycol alkylphenyl ether (Triton X-100) from thiocyanate solutions was studied, and the extracted chemical species was estimated to be $(NH_4)_2Co(NCS)_4$(Triton X-100)$_2$.

Recently polyethyleneglycol (PEG) and its derivatives have been widely used as nonionic surfactants in research and industry, but their application to analytical chemistry has been limited to the use of these compounds as an auxiliary reagent to dissolve some sparingly soluble chelate precipitates and/or to the increase of absorptivity of some chelates in the absorption spectrophotometry[1]. Various determination methods of these surfactants have been developed by many authors. Among them, a determination method by Brown and Hayes[2] is based on the extraction of the complexes, formed by the polyoxyethylene chain with diammonium tetrathioisocyanatocobaltate(II), in an organic phase, followed by spectrophotometric determination. More recently, a detailed report on the extraction of a small amount of nonionic surfactant into an organic solvent with Co(II) thiocyanate complex was published[3], but so far no examination has been carried out on the extraction of trace amounts of Co(II) into an organic solution of these surfactants. So we investigated the extraction of a small amount of Co(II) into 1,2-dichloroethane*) containing PEG isooctylphenyl ether (Triton X-100). Further we studied the extraction of Co(II) from thiocyanate solution into 1,2-dichloroethane with PEG's of various molecular weights and some of their related compounds. In the present paper we will briefly describe the effects of cencentration of thiocyanate in the aqueous phase and that of extractant in the organic phase on the extractability of Co(II). The chemical form of the extracted species will also be discussed.

The ratio of the concentration of Co(II) in the organic phase to that in the aqueous phase, distribution ratio D, was determined by measuring the radioactivity concentration of $^{60}Co$ in both phases; the radioactivity measurements were made with a well-type NaI(Tl) scintillation counter. Aqueous phases used for all the present extraction experiments had a concentration of 10 ppb in Co, and their radioactivity concentration was bout $10^4$ cpm/ml.

*) Unlike diethyl ether and methyl isobutyl ketone, 1,2-dichloroethane itself has no extractability of Co(II) thiocyanate complex from thiocyanate solution.

At first, the extraction of Co(II) was made for a system of Triton X-100 in 1,2-dichloroethane —— ammonium thiocyanate solution. The dependence of distribution ratio on the thiocynate concentration was investigated at a constant concentration (1%, w/v) of the extractant and the results are shown in Fig. 1. A marked increase in the distribution ratio D was observed in the thiocyanate concentration range of 0.1 - 1.0 M, and the value of D amounted to a maximum of 240 between 2 and 3 M thiocyanate.

The distribution ratio was also measured with varying concentrations of the extractant at a constant thiocyanate concentration of 1.0 M. Fig. 2 shows the log-log plot of distribution ratio to extractant concentration (0.01 - 1.0%, w/v) and this plot gave a straight line with a slope of about 2. As a result, the ratio of Co(II) to the extractant molecule in the extracted Co(II) complex was possibly expected to 1 : 2.

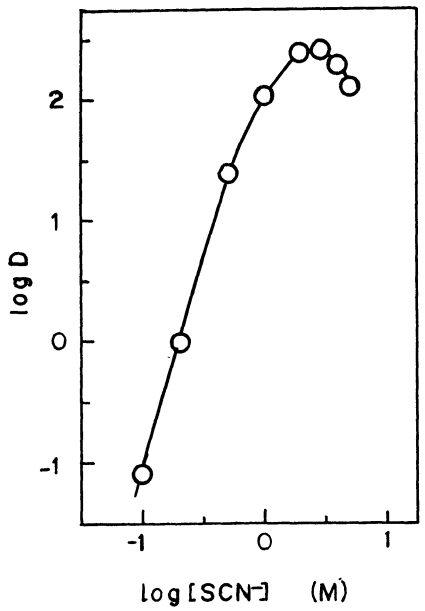


Fig. 1. Distribution ratio of Co(II) vs. concentration of thiocyanate
Organic phase: 1% (w/v) Triton X-100

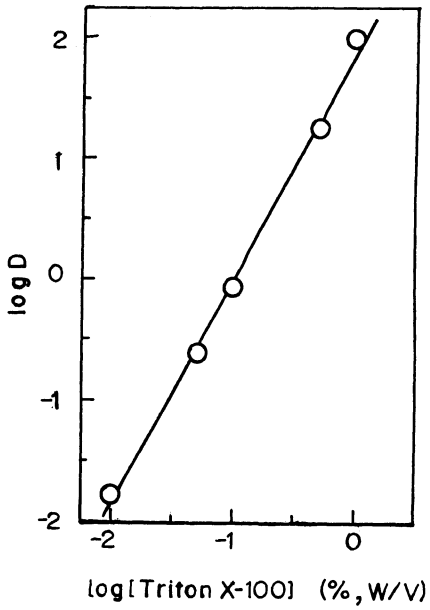


Fig. 2. Distribution ratio of Co(II) vs. concentration of Triton X-100 in 1,2-dichloroethane

The extraction of Co(II) with Triton X-100 in 1,2-dichloroethane (1%, w/v) was made from a constant ionic-strength solution of 1 M $NH_4(SCN, ClO_4)$. In Fig. 3 the log-log plot of distribution ratio vs. thiocyanate concentration is presented. Since this plot yielded a slope of 4, the chemical form of the extracted Co(II) thiocyanate complex was estimated to be $Co(NCS)_4^{-2}$. From these findings above obtained, the extracted chemical species was estimated to be $(NH_4)_2Co(NCS)_4 \cdot (\text{Triton X-100})_2$.

The effect of the hydrochloric-acid concentration in aqueous phase on the percentage extraction of Co(II) from 2.5 M thiocyanate into a 1,2-dichloroethane solution of Triton X-100 (1%, w/v) was investigated and the results are summarized in Table 1. From this table it will be clearly seen that the extractability was markedly reduced to a 60-percent level in the concentration range of more than

0.5 M; here it was observed that the extractant was almost kept in the organic phase at concentrations of more than 0.1 M HCl in the aqueous phase.

Secondly, various surfactants other than Triton X-100 were examined on the extractability of Co(II) from ammonium thiocyanate solution. They involved PEG's of various degrees of polymerization, polypropyleneglycols (PPG) and PEG alkyl ethers (Brij 35 and 58); the nominal degree of polymerization of oxyethylene group was 23 and 20 for Brij 35 (lauryl ether) and Brij 58 (cetyl ether), repectively.

The effect of the thiocyanate concentration on the distribution ratio of Co(II) with these surfactants (1%, w/v) was investigated at concentrations from 0.1 - 5.0 M. Some of these results are shown in Table 2. The extractability of Co(II) was dependent on the thiocyanate concentration in aqueous phase and exhibited a nearly similar trend with a maximum value between 2 and 4 M thiocyanate for the extractants other than PEG 1000. The extractability for PEG 1000 increased with increasing thiocyanate concentration in the range of thiocyanate concentration studied.

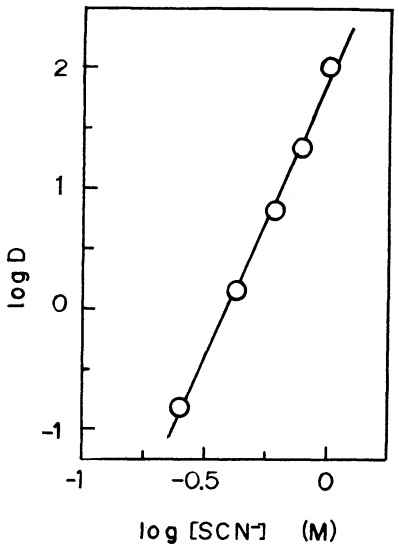


Fig. 3. Distribution ratio vs. thiocyanate concentration at a constant ionic strength
Aqueous phase:
1.0 M $NH_4$(SCN, $ClO_4$)

Table 1. Effect of acidity of aqueous phase on the extractability of Co(II) from 2.5 M thiocyanate solution

| Concentration of hydrochloric acid (N) | Percentage extraction (%) |
|---|---|
| 1.0 | 27.7 |
| 0.5 | 62.8 |
| 0.1 | 96.0 |
| 0.01 | 99.6 |

The extraction of Co(II) from 1 M thiocyanate solution into 1,2-dichloroethane containing PEG's of various molecular weights and some PPG's (1%, w/v) was carried out and the results are summarized in Table 3; here PPG 3000 and 4000 are of triol type. From this table it proved that an increasing trend in the percentage extraction of Co(II) was obviously found out with increasing molecular weight.

From the results shown in Tables 2 and 3, the percentage extraction for PPG 1000 (n=17) was found greater than that for PEG 1000 (n= 23), and hence it will be certainly expected that the extractability for PPG may be much higher than that for PEG, when both are of approximately the same degree of polymerization. Further, PEG alkyl (phenyl) ehters showed the highest extractability, as compared with those of PEG and PPG, when they have nearly the same degree of

polymerization. As a result, the order of the extractability of Co(II) from thiocyanate solution (1.0 M) with PEG, PEG derivatives and PPG was found as follows:

PEG alkyl ether ≃ PEG alkylphenyl ehter > PPG > PEG,

when their degrees of polymerization are of approximately the same.

Table 2. Effect of thiocyanate concentration on the percentage extraction of Co(II)

| Concentration of thiocyanate ( M ) | Percentage extraction PEG 1000* (n=23)*** | PPG 4000* (n=23) | Brij 58 (n=20) | Brij 35 (n=23) | Nonion NS** (n=20) |
|---|---|---|---|---|---|
| 5.0 | 93.5 | 99.7 | 99.7 | 99.8 | --- |
| 4.0 | 89.5 | 99.8 | 99.8 | 99.9 | --- |
| 3.0 | 86.1 | 99.7 | 99.8 | 99.9 | --- |
| 2.0 | 79.5 | 99.4 | 99.8 | 99.9 | --- |
| 1.0 | 58.8 | 99.2 | 99.6 | 99.7 | 99.7 |
| 0.5 | 19.2 | 68.7 | 98.4 | 98.3 | --- |
| 0.1 | 0.0 | 0.6 | 16.2 | 14.8 | --- |

*) These figures indicate "nominal average molecular weight".

**) Nonion NS: PEG nonylphenyl ether

***) The figures in parenthese (n) refer to the degree of polymerization of oxyethylene or oxypropylene group.

Table 3. Percentage extraction of Co(II) with PEG's and PPG's of various molecular weights from thiocyanate solution (1.0 M)

| Extractant | | Average degree of polymerization | Percentage extraction |
|---|---|---|---|
| PEG | 200* | 4.5 | 0.1 |
| PEG | 600 | 14 | 23.8 |
| PEG | 1000 | 23 | 58.8 |
| PEG | 2000 | 45 | 80.7 |
| PEG | 7500 | 170 | 83.4 |
| PEG | 20000 | 455 | 93.5 |
| PPG | 1000 | 17 | 96.7 |
| PPG | 2000 | 34 | 98.1 |
| PPG | 3000 | 17 | 98.1 |
| PPG | 4000 | 23 | 99.2 |

*) The figures in this column refer to "nominal average molecular weight".

## References

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