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Solvent Extraction and Bulk Liquid Membrane Transport of Co(II) and Ni(II) Ammine Cations by Proton-Ionizable Crown Ethers★

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Abstract. Separation efficiencies and selectivities in solvent extraction of Co(II) and Ni(II) ammine cations from aqueous solutions into chloroform and toluene and in transport through bulk toluene membranes by proton-ionizable crown ethers have been determined. Six proton-ionizable crown ethers with differing lipophilicities, polyether cavity sizes and ionizable groups (carboxylic and sulfonic acid functions) were examined. Higher selectivity and efficiency for Co(II) ammine cation extraction was observed for the more lipophilic, proton-ionizable crown ethers. Highly lipophilic crown carboxylic acids provided effective and selective transport of Co(II) ammine cations through bulk toluene membranes.

Key words. Crown ether, membrane transport, solvent extraction, metal ammine cation

1. Introduction

Previously, we reported results for the single ion and competitive extraction of Co(II) and Ni(II) ammine cations from aqueous solutions into chloroform by 2-[(*sym*-dibenzo-14-crown-4)oxy]decanoic acid (**1**), 2-[(*sym*-dibenzo-16-crown-5)oxy]decanoic acid (**2**), and 2-[(*sym*-dibenzo-19-crown-6)oxy]decanoic acid (**3**) [1]. In strongly alkaline solutions, a much higher extractability of Co(II) ammine cations than Ni(II) ammine cations into the organic phase was observed which produced good separation of Co(II) from Ni(II). The ratios of metal to crown carboxylic acid in the organic phases indicated a $M(NH_3)_x^{2+} \cdot 2$(crown carboxylate) stoichiometry for the extraction complex. By analogy with reported crystal structures for complexes of crown ethers with transition metal ammine cations [2–6], a sandwich type of extraction complex was proposed in which a Co(II) or Ni(II) ammine cation is situated between two crown carboxylate anions with hydrogen bonding of the ammine ligands to the cyclic polyethers.

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** All extraction and transport experiments were conducted at this location.

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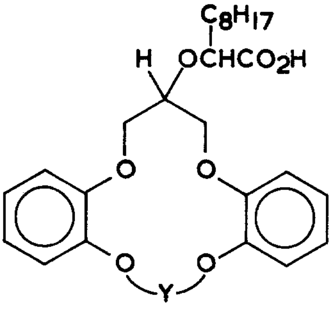
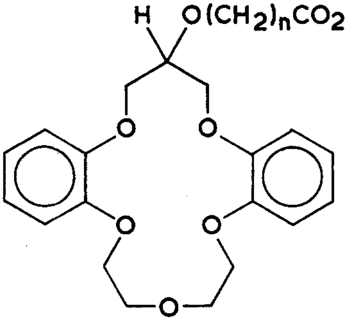
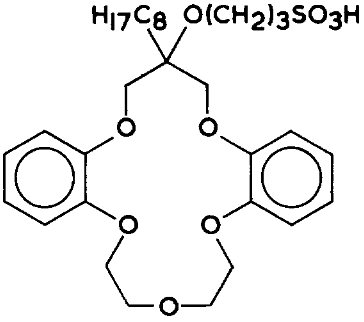


Y	
$CH_2CH_2CH_2$	**1**
$CH_2CH_2OCH_2CH_2$	**2**
$CH_2CH_2OCH_2CH_2OCH_2CH_2$	**3**



n = 1 **4**
n = 4 **5**



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In the present paper, results are presented for single and competitive solvent extractions of Co(II) and Ni(II) ammine cations from aqueous solutions into chloroform by the less lipophilic crown carboxylic acids **4** and **5** and the lipophilic crown sulfonic acid **6**, as well as from aqueous solutions into toluene by proton-ionizable crown ethers **1**–**6**. In addition, results from the competitive transport of Co(II) and Ni(II) ammine cations through bulk toluene membranes by proton-ionizable crown ethers **1**–**6** are described.

2. Experimental

2.1. MATERIALS AND REAGENTS

Crown carboxylic acids **1**–**5** were prepared by the published procedures [7, 8]. Reagent grade dimethylglyoxime, chloroform, toluene, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, hydrochloric acid, ammonium hydroxide, ammonium chloride, ammonium citrate, and iodine were obtained from POCh (Gliwice, Poland) and SLX-31 liquid scintillation cocktail was obtained from Tesla (Prague, Czechoslovakia). All aqueous solutions were prepared using doubly-distilled water. Radioactive isotopes ^{58}Co and ^{63}Ni (as aqueous chlorides) were carrier-free or of sufficiently high specific radioactivity.

2.2. PREPARATION OF 3-[*sym*-(*n*-OCTYL)-DIBENZO-16-CROWN-5-OXY]PROPANESULFONIC ACID (**6**)

After washing 0.63 g (1.5 equiv.) of sodium hydride with dry pentane to remove the protecting mineral oil, the solid was added to a solution of *sym*-(*n*-octyl)-hydroxydibenzo-16-crown-5 (4.00 g, 9.7 mmol) [8] in 40 mL of tetrahydrofuran. After stirring for 20 min, 1,3-propanesulfone (1.22 g, 1.2 equiv) in 5 mL of tetrahydrofuran was added, producing a white precipitate within 5 min. After stirring for 2.5 h, the reaction mixture was filtered. The collected solid was heated in 500 mL of hot *n*-hexane and the hot suspension was decanted. When allowed to cool to room temperature, an off-white solid crystallized from the hexane solution. To the material which remained undissolved after the first treatment with hot *n*-hexane, another 500 mL portion of *n*-hexane was added followed by heating, decanting and cooling as before. This procedure was performed a third time. The total yield of off-white solid was 4.65 g (88%). Decolorization with activated charcoal in chloroform gave a white solid with mp 85–90°C. Analysis: Calcd. for $C_{30}H_{43}SO_9Na$: C, 59.80; H, 7.14. Found: C, 59.55, H, 7.23.

A solution of the sodium salt of **6** in chloroform was shaken with several portions of 6N hydrochloric acid, dried over magnesium sulfate, and evaporated *in vacuo* (3 Torr for 6 h) to give an off-white solid with mp 55°C. ^1H NMR ($CDCl_3$): $\delta = 0.65$–2.3 (m, 19H), 2.85–3.3 (br m, 2H), 3.5–4.5 (m, 14H), 6.89 (s, 8H), 9.30 (br s, 1H).

2.3. APPARATUS

Concentrations of cobalt in the aqueous and organic phases were determined radiometrically (^{58}Co) with a Nuclear Data Model 1200 multichannel spectrometer and a Canberra Industries Model 7228 Ge/Li semiconductor γ-radiation probe while concentrations of nickel in those phases were determined by a liquid scintillation radiometrical technique (^{63}Ni) with a ZZUJ 'Polon' (Warsaw) single channel counting system. Equilibrium pH measurements in the aqueous phases were made with an Elpo Model N512 pH meter and an Energopomiar Model SAgP–209W glass body combination electrode (Gliwice). The pH of the source aqueous phase in the bulk liquid membrane systems was kept constant using a pH-controller of our own construction and a Domet Model S-31 peristaltic pump (Pruszkow). Absorption spectral of the organic phases were measured with a Hitachi Model 356 ultraviolet spectrophotometer and a Zeiss Specord 75 infrared spectrophotometer (Jena).

2.4. PROCEDURE FOR SOLVENT EXTRACTION EXPERIMENTS

Solvent extractions were conducted at room temperature (20–23°C). The organic phase (5.0 mL) containing a crown ether (0.010M) in chloroform (or toluene) and the aqueous solution (5.0 ml) of $CoCl_2$ and/or $NiCl_2$ (0.0050 M each, labeled with ^{58}Co and ^{63}Ni radioisotopes) were placed into a set of separatory funnels. To adjust the equilibrium pH of the aqueous phase, NH_4Cl and NH_4OH were added at various molar ratios to give a total ammonium salt concentration of 2.40M. The separatory funnels were shaken vigorously for 15 min and then allowed to stand for

20 h to provide for complete separation of the organic and aqueous phases. Samples (1.0 mL) of each phase were removed for the γ-spectrometric determination of cobalt concentrations. Samples (0.025 mL) of each phase were also removed for determination of nickel concentration by liquid scintillation counting. Additional samples (0.50 mL) of the aqueous phases were removed for colorimetric determination of the nickel concentrations. For the extractions into chloroform, the absorbance of the organic phases were measured at 273–274 nm after dissolving 0.50 mL of the organic phase in 9.50 mL of chloroform. Finally, the equilibrium pH of the aqueous phase was measured. Values of percent metal extracted were found to be reproducible within ±5% of the stated value.

2.5. INFRARED SPECTRAL DETERMINATION OF ORGANIC PHASE CONSTITUENTS IN SOLVENT EXTRACTIONS

Special extractions were conducted in which the aqueous phase (5.0 mL) contained 0.20M $CoCl_2$ (or $NiCl_2$) without radioisotope and 2.4M NH_4OH. The organic phase (5.0 mL) was a 0.10M solution of the proton-ionizable crown ether. After vigorous shaking of the two solutions for 15 min, they were allowed to stand for 20 h to provide for complete separation of the two phases. The chloroform phase was separated and its infrared spectrum in the region of 4000–2000 cm^{-1} was determined.

2.6. PROCEDURE FOR BULK LIQUID MEMBRANE TRANSPORT EXPERIMENTS

Bulk liquid membrane experiments were conducted at room temperature (20–23°C) in a beaker-in-beaker cell (Figure 1). The organic phase (50 mL) was a 0.0010M solution of the crown ether in toluene. The source phase (190 mL) was an aqueous solution of $NiCl_2$ and $CoCl_2$ (0.005M each) and NH_4OH (2.4M). The source phase pH was kept constant (pH 12.0) by adding a 2.4M solution of NH_4OH. The receiving phase (25 mL) was 3.0M aqueous hydrochloric acid. The source/organic and organic/receiving phases contact areas were 21.1 and 13.2 cm^2, respectively. Each of the three phases was stirred at 120 rpm. Samples of each phase were periodically removed for metal concentration determination. After the γ-spectrometric determination of the cobalt concentrations was completed, samples were returned back into the respective solutions. Bulk membrane transport experiments were also conducted with chloroform as the membrane solvent in a suitable experimental cell [9]. Metal concentrations in the various phases were found to be reproducible within ±10% of the stated values.

3. Results and Discussion

Compounds **1**–**6** form a series of proton-ionizable crown ethers in which the structure of the complexing agent is systematically varied. For crown carboxylic acids **1**–**3**, the crown ether ring size is varied from 14-crown-4 to 16-crown-5 to 19-crown-6, respectively. Crown carboxylic acid **4** has the same dibenzo-16-crown-5 unit as **2**, but the lipophilic *n*-octyl group is absent in the side arm of **4**. The crown carboxylic acids **4** and **5** have the same crown ether ring, but differing lengths for

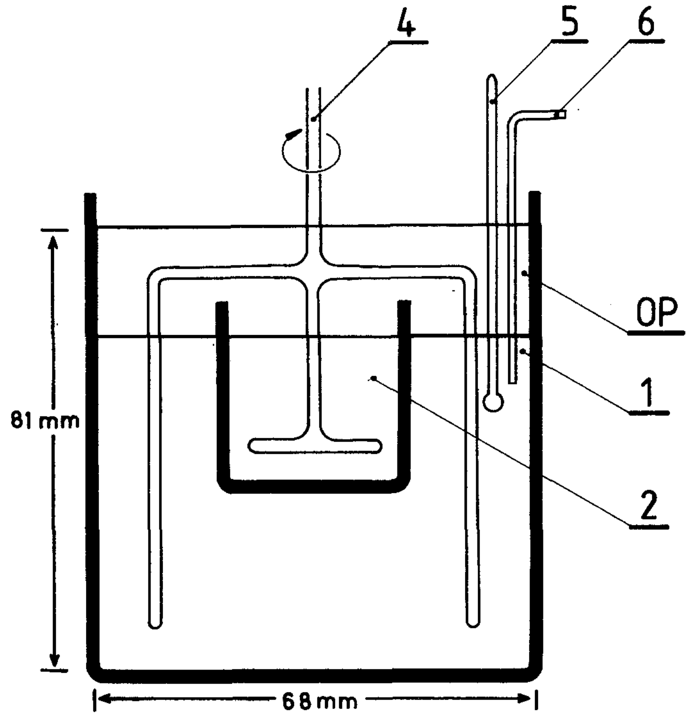

Fig. 1. Experimental cell for bulk liquid membrane transport measurements. (1 – aqueous source phase, 2 – aqueous receiving phase, OP – organic membrane phase, 4 – glass stirrer, 5 – combination electrode, 6 – glass tube for adding NH_4OH solution).

the unit which joins the ionizable group to the cyclic polyether framework. Proton-ionizable crown ether **6** is different from previously-prepared **1–5** in that it is a crown sulfonic acid. Compared with the structurally-similar crown carboxylic acid **2**, the crown sulfonic acid **6** has the same crown ether unit (dibenzo-16-crown-5), but a different attachment site for the lipophilic group and a longer arm joining the ionizable group to the crown ether unit.

3.1. SOLVENT EXTRACTION

Results for single ion extractions of 0.0050M aqueous solutions of Co(II) or Ni(II) ammine cations with 0.010M chloroform solutions of proton-ionizable crown ethers **4**, **5** and **6** are presented in Figure 2. Results for the corresponding competitive extractions in which the aqueous solution was 0.0050M in both Co(II) and Ni(II) ammine cations are shown in Figure 3 together with previously-reported results for crown carboxylic acid **2** [1] which has the same polyether ring unit as **4**, **5** and **6**. The data contained in Table I provide a comparison of competitive extraction results in chloroform and in toluene for proton-ionizable crown ethers **1–6**.

For single ion extractions of Co(II) and Ni(II) ammine cations into chloroform, crown carboxylic acid **5** provided better extraction of the former than did **4**. Maximum extractabilities were 18% at pH 12.2 for **4** and 40% at pH 11.6 for **5**

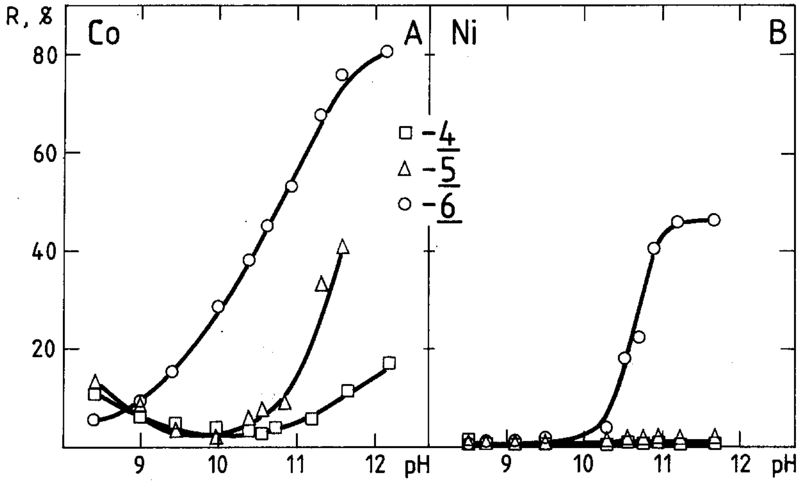

Fig. 2. %(R) of metal extracted into the chloroform phase vs. the equilibrium pH of the aqueous ammonia phase for single ion extractions of 0.0050M Co(II) chloride (A) and 0.0050M Ni(II) chloride (B) with 0.010M solutions of proton-ionizable crown ethers **4–6**.

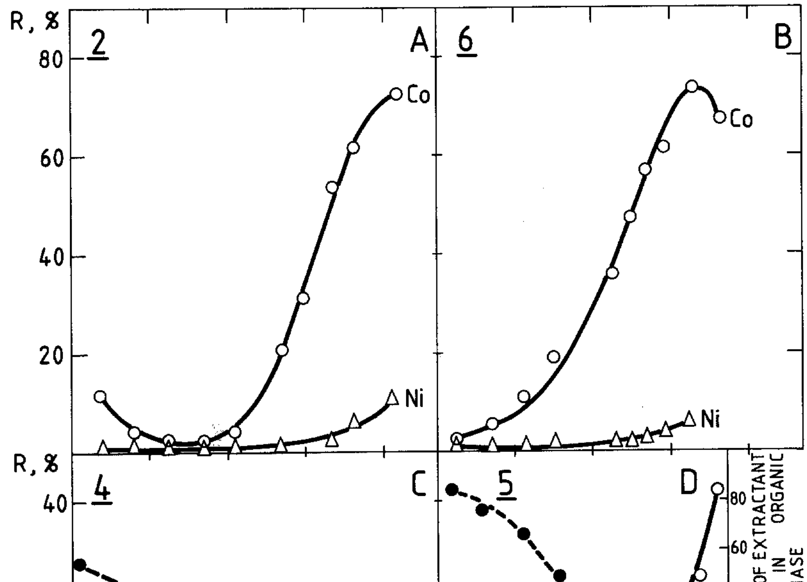

Fig. 3. %(R) of metal extracted into the chloroform phase vs. the equilibrium pH of the aqueous ammonia phase for competitive extractions of 0.0050M Co(II) and 0.0050M Ni(II) chlorides with 0.010M solutions of proton-ionizable crown ethers **2** [1] and **4–6**. (Broken lines and filled circles illustrate % of crown carboxylic acids which remained in the organic phase after extraction).

Table I. Results from competitive extractions of 0.0050M $CoCl_2$ and 0.050M $NiCl_2$ from 2.4M aqueous ammonia solution (pH = 12.0) with 0.010M proton-ionizable crown ethers **1**–**6** in chloroform and in tolune

	%(*R*) of metal extracted into			
	Chloroform		Toluene	
Crown Ether	Co	Ni	Co	Ni
1	73[a]	8.1[a]	69	ND[b]
2	73[a]	11[a]	76	9.3
3	56[a]	7.0[a]	89	18
4	12	1.0	3.6[c,d]	1.0[c,d]
5	42[c]	1.5[c]	4.8[c,d]	ND[b,c,d]
6	68[c]	5.0[c]	90[c]	3.5[c]

[a] From reference [1]. [b] ND = not detected. [c] pH = 11.6. [d] The organic phase was 5% chloroform–95% toluene (v/v).

(Figure 2A). For both **4** and **5**, only very small amounts of Ni(II) ammine cation were transferred into the organic media.

The extractabilities and apparent selectivities which were observed in the single ion extractions into chloroform by crown carboxylic acids **4** and **5** (Figure 2) were reflected in the competitive extraction results (Figures 3C and 3D). In the competitive systems, the Ni(II) ammine cation extraction was very low while the Co(II) ammine cation extraction efficiency resembled that in the single ion extractions. For competitive extractions with **5** as the complexing agent (Figures 3D), high selectivity for Co(II) ammine extraction (Co/Ni concentration ratio of 28 at pH 11.6) was observed. For both crown carboxylic acids **4** and **5**, which do not possess pendant lipophilic groups, losses of the complexing agent to strongly alkaline aqueous phases were considerable (see filled circles in Figures 3C and 3D). Such losses explain the relatively low extraction efficiencies for **4** and **5** compared with the more lipophilic 16-crown-5 carboxylic acid **2** (Figure 3A) [1].

Efficiencies of Co(II) and Ni(II) ammine cation extractions into chloroform in single ion extractions were markedly enhanced when the lipophilic crown sulfonic acid **6** was utilized as the extractant (Figure 2). In competitive extractions using **6**, the selectivity for Co(II) ammine cations was high with a Co/Ni concentration ratio in the organic phase of 13.4 when the aqueous phase pH was 11.2 (Figure 3B). Results for competitive extractions of Co(II) and Ni(II) into chloroform by the lipophilic dibenzo-16-crown-5 sulfonic acid **6** (Figure 3B) and lipophilic dibenzo-16-crown-5 carboxylic acid 2 [1] (Figure 3A) are very similar with the exception that the extraction curves for **6** are shifted to somewhat lower (< 1 pH unit) pH values. By analogy to **4** and 3-(*sym*-dibenzo-16-crown-5-oxy)propanesulfonic acid for which dissociation constants have been determined in aqueous methanol [10], the lipophilic crown sulfonic acid **6** is anticipated to be a considerably stronger acid than the lipophilic crown carboxylic acid **2**. Presumably this is responsible for the shifted extraction curves.

To provide additional information about the chemical species present in the organic phases, extractions were conducted with more concentrated aqueous and chloroform phase solutions (see Experimental) and infrared spectra were taken of the separated organic phases for the region of 4000–2200 cm^{-1} (Table II). The organic phases were found to contain $Ni(NH_3)_6^{2+}$ or $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$, NH_4^+ and ammonia [11]. Presumably the ammonia was simply dissolved in the chloroform and $Co(NH_3)_6^{3+}$ was produced by facile air oxidation of $Co(NH_3)_6^{2+}$ [12]. The presence of two different cobalt species was also indicated by stripping experiments in which one portion of the cobalt could be easily stripped from the chloroform phase by contact with dilute aqueous hydrochloric acid while another portion was removed only slowly even with 6M hydrochloric acid.

To investigate the influence of organic solvent upon extraction efficiency and selectivity, competitive extractions of 0.0050M Co(II) and 0.0050M Ni(II) ammine cations into 0.010M toluene solutions of crown ethers **1–3** and **6** were performed. Since crown ethers **4** and **5** had insufficient solubility in pure toluene, extractions were conducted with 5% chloroform–95% toluene as the organic solvent. Results are recorded in Table I.

For extractions performed with the lipophilic dibenzo-14-crown-4 carboxylic acid **1**, the selectivity for Co(II) over Ni(II) ammine cation extraction at pH 12 was found to be much higher in toluene than chloroform and the fraction of metal ions extracted (*R*) was only slightly lower. For the dibenzo-16-crown-5 analog **2**, both the extraction selectivity and efficiency were constant for this solvent change. However, for the analogous dibenzo-19-crown-6 carboxylic acid **3**, the extraction efficiency increased appreciably but the selectivity diminished when chloroform was replaced by toluene as the extraction solvent.

Table II. Data from infrared spectral measurements of chloroform phases containing proton-ionizable crown ethers after equilibration with $CoCl_2$ (or $NiCl_2$) in 2.4M NH_4OH

Metal and crown ether in chloroform phase	Absorption maxima, cm^{-1}, and assignments[a]
Ni and **1**	3390[b], 3330 and 3230[c], 3160[d]
Ni and **2**	3390[b], 3330 and 3230[c], 3150[d]
Ni and **3**	3390[b], 3330 and 3215[c], 3145[d]
Ni and **4**	3390[b], 3330 and 3230[c], 3140[d]
Ni and **5**	3395[b], 3330 and 3230[c], 3155[d]
Ni and **6**	3400[b], 3330 and 3230[c], 3148[d]
Co and **1**	3388[b], 3280[e], 3245[f], 3158[g], 3110[d]
Co and **2**	3388[b], 3295[e], 3198 and 3165[g]
Co and **3**	3390[b], 3265[e], 3198[g], 3145[d]
Co and **4**	3385[b], 3285[e], 3175[g]
Co and **5**	3385[b], 3395[e], 3245[f], 3165[g], 3140[d]
Co and **6**	3390[b], 3262[e], 3235[f], 3162[g]

[a] Characteristic frequencies of N—H vibrations in uncomplexed species: $Ni(NH_3)_6^{2+}$ (3345 and 3190 cm^{-1}); $Co(NH_3)_6^{2+}$ (3300 and 3250 cm^{-1}), $Co(NH_3)_6^{3+}$ (3250 and 3160 cm^{-1}); NH_4^+ (3145 cm^{-1}); NH_3 (3414 and 3336 cm^{-1} for gas, 3378 and 3223 cm^{-1} for solid) [11]. [b] NH_3. [c] $Ni(NH_3)_6^{2+}$. [d] NH_4^+. [e] $Co(NH_3)_6^{2+}$. [f] $Co(NH_3)_6^{2+}$ and/or $Co(NH_3)_6^{3+}$. [g] $Co(NH_3)_6^{3+}$.

Crown carboxylic acids **4** and **5**, which do not possess lipophilic groups, were found to be considerably poorer extractants when the solvent was changed from chloroform to 5% chloroform–95% toluene presumably due to lower solubility of the extracted metal complexes in the less polar solvent mixture. The lipophilic dibenzo-16-crown-5 sulfonic acid **6** gave enhanced extraction efficiency and selectivity when chloroform was replaced by toluene as the extraction solvent.

3.2. BULK LIQUID MEMBRANE TRANSPORT

To further explore the potential for use of proton-ionizable crown ethers to separate Co(II) and Ni(II) ammine cations, liquid membrane transport processes were investigated.

Initially, the possibility for Co(II) and Ni(II) ammine cation transport through chloroform solutions of crown ether carboxylic acids **2** and **4** was examined using a suitable cell [9]. Although no metal cation transport was observed, the acidic aqueous receiving phase was rapidly neutralized due to permeation of ammonia from the source phase through the chloroform membrane. A control experiment conducted without any crown ether in the organic phase also gave neutralization of the acidic aqueous receiving phase which demonstrated that the solubility of ammonia in chloroform was too high for chloroform to be used as the bulk liquid membrane solvent.

When toluene was utilized as the bulk liquid membrane solvent in the cell shown in Figure 1, Co(II) and Ni(II) ammine cations were transported from the alkaline aqueous source phase, through the toluene membrane, and into the acidic aqueous source phase by crown ethers **1–6**. This system provides an important addition to the metal ion species for which proton-coupled transport across liquid membranes by proton-ionizable crown ethers has been reported [13–16].

Highly lipophilic crown carboxylic acids **1–3** were found to be very selective carriers of Co(II) ammine cations in competitive transport processes (Figure 4). The selectivity was found to vary with the crown ether ring size in the order **3**(19-crown-6) > **2**(16-crown-5) > **1**(14-crown-4) and appears to result from depression of the Ni(II) ammine cation transport rate as the polyether ring size is expanded. For **3**, the Co(II)/Ni(II) transport selectivity exceeds 10^2.

When lipophilic crown sulfonic acid **6** was employed as the ion carrier (Figure 5), the overall transport rate was similar, but the selectivity for Co(II) ammine cation transport plummeted, compared with lipophilic crown carboxylic acids **1–3**. Both proton-ionizable crown ethers **3** and **6** have a common 16-crown-5 ring size. However, they have differing ionizable groups, numbers of methylene groups in the spacers which separate the ionizable group from the cyclic polyether framework, and attachment sites for the lipophilic groups. Although variation of either the side arm length [17] or lipophilic group attachment site [18] would be anticipated to alter the transport selectivity somewhat, the striking difference between the selectivities observed with **3** and **6** suggests that the identity of the ionizable group plays an important role.

For the lipophilic proton-ionizable crown ethers **1–3** and **6**, the amounts of cobalt ion transported into the toluene layer from the aqueous source phase were usually

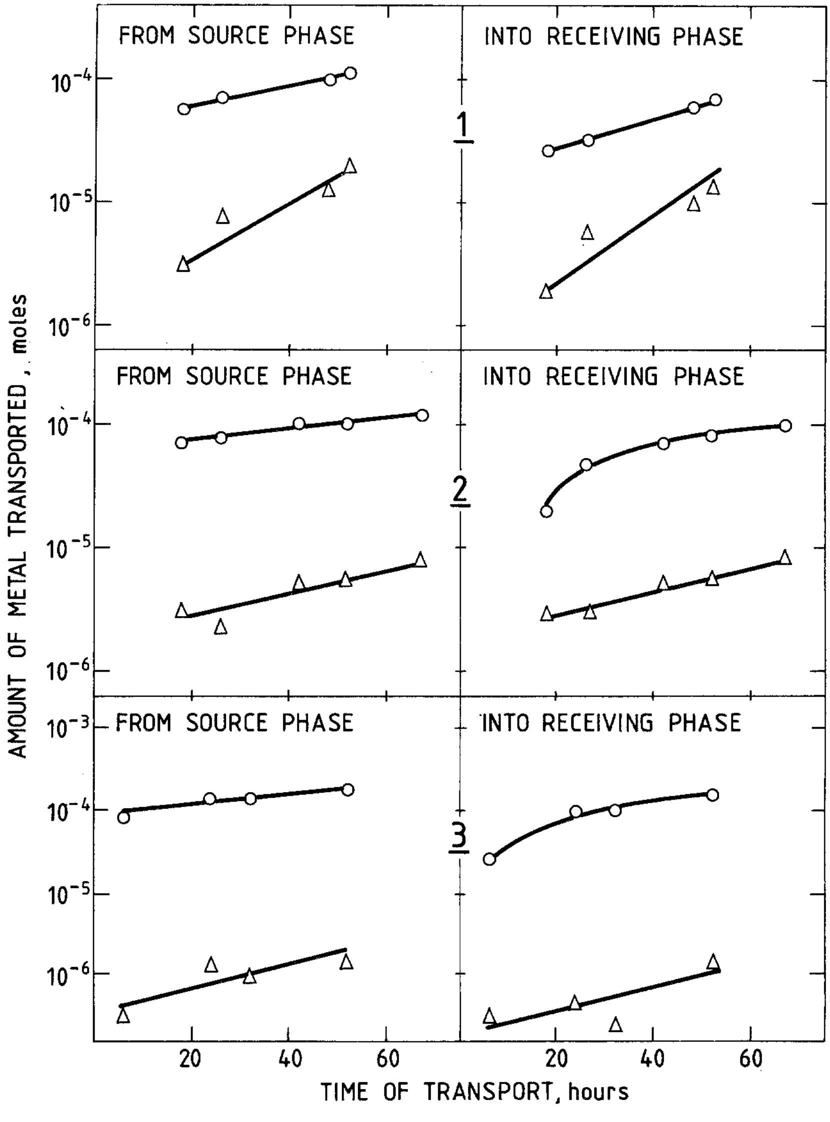

Fig. 4. Amounts of cobalt (○) and nickel (△) removed from the source phases and transported through 0.0010M toluene solutions of 1–3 into the receiving phases. (Initial source phase: 0.0050M $NiCl_2$ and 0.0050M $CoCl_2$, 2.4M NH_4OH, pH = 12.0. Initial receiving phase: 3.0M aqueous hydrochloric acid).

higher than those transported from the toluene membrane into the aqueous receiving phase (Figures 4 and 5). On the other hand, the amounts of nickel ion removed from the source phase and transported into the receiving phase were very similar. Therefore, cobalt ammine complex was accumulating in the membrane solution. One explanation for this observation is that some Co(II) was being oxidized to Co(III) [12] and that Co(III) ammine cations are complexed more strongly by the crown ethers than Co(II) ammine cations. Such strongly-bound

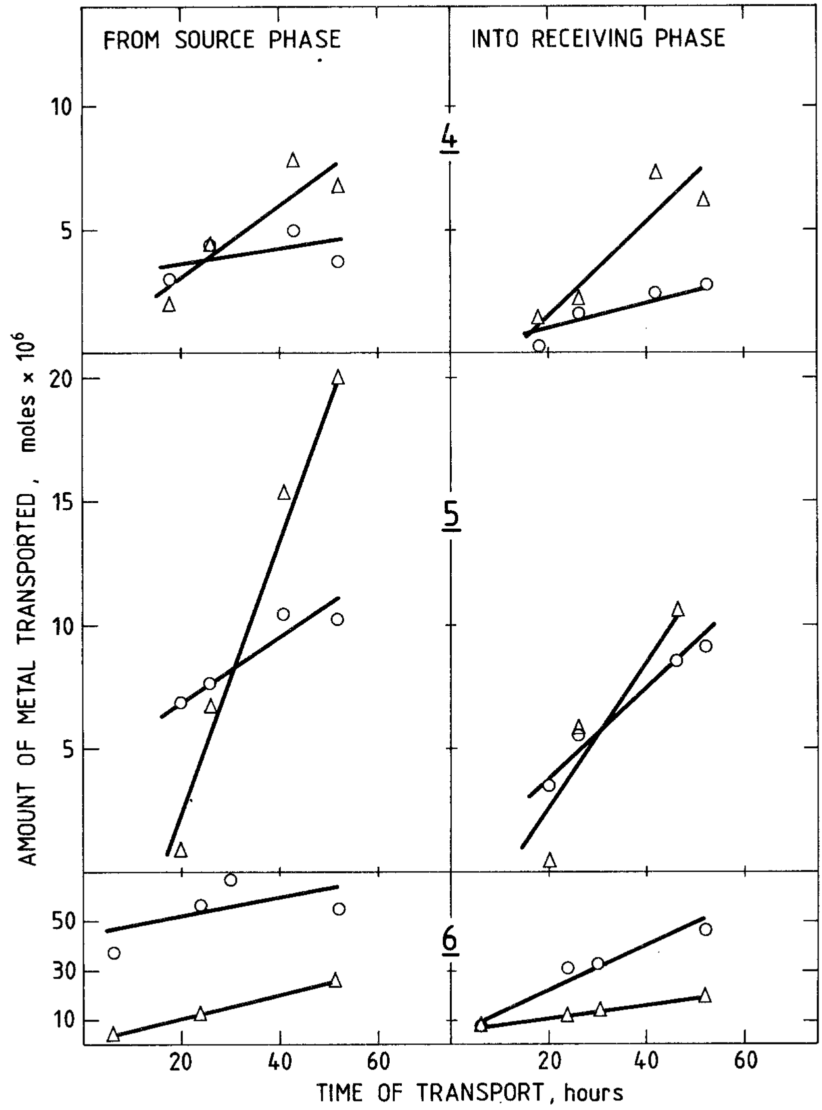

Fig. 5. Amounts of cobalt (○) and nickel (△) removed from the source phases and transported through 0.0010M toluene solutions of **4**–**6** into the receiving phases. (Initial source phase: 0.0050M $NiCl_2$ and 0.0050M $CoCl_2$, 2.4M NH_4OH, pH = 12.0. Initial receiving phase: 3.0M aqueous hydrochloric acid).

Co(III) ammine cations would be more difficult to release from the toluene solution into the acidic aqueous receiving phase and would accumulate in the organic membrane. In agreement with this proposal is the detection of $Co(NH_3)_6^{3+}$ ions in chloroform phases after solvent extraction of aqueous Co(II) solutions (Table II) and the indication of two organic-phase cobalt species in stripping experiments (*vide supra*).

When crown carboxylic acids **4** and **5** were utilized as ion carriers, the transport efficiency was much lower than that observed with the lipophilic proton-ionizable crown ethers **1–3** and **6** (Figure 5). The selectivity noted with **4** and **5** was poor and some preference for Ni(II) ammine cation transport was found.

It should be recalled that the selectivity for solvent extraction of Co(II) and Ni(II) cations by crown carboxylic acids **4** and **5** was in the order Co(II) > Ni(II) (Table I). This reversal in selectivity for solvent extraction, a system under thermodynamic equilibrium, and liquid membrane transport, a kinetically controlled process, suggests that interaction kinetics of the metal ammine cation with the polyether ring and the carboxylate group may be different. In support of this contention are the different selectivities in alkali metal cation solvent extraction and transport across liquid membranes by crown carboxylic acids which were proposed to arise from differing extraction kinetics of the metal cation with the polyether and carboxylate units of the complexing agent [19]. Kinetic studies of Na^+ complexation by **4** in 99% methanol–water indicate more rapid interaction of the cation with the carboxylate unit [10].

4. Conclusions

The efficiency and selectivity of Co(II) and Ni(II) ammine cation extractions into chloroform and toluene by **1–6** is influenced by structural variation within the proton-ionizable crown ethers. Crown carboxylic acids **4** and **5** had insufficient lipophilicity to function as good extractants. The extraction curve for lipophilic crown sulfonic acid **6** was shifted to somewhat lower pH values than the analogous crown carboxylic acid **2**. Although all of the proton-ionizable crown ethers **1–6** exhibited preferential extraction of Co(II) ammine cations, the selectivity was highest for extraction with crown carboxylic acid **1** in toluene.

Proton-ionizable crown ethers **1–6** also function as carriers in proton-coupled transport of Co(II) and Ni(II) ammine cations across bulk toluene membranes. Efficiency and selectivity of cation transport are strongly influenced by the structure of the carrier. Very high selectivity for transport of Co(II) ammine cations by lipophilic crown carboxylic acid **3** was obtained.

The separations of Co(II) from Ni(II) ammine cations achieved in this study apparently result from the differing stereochemical flexibilities of the cations and their abilities to adjust to the field imposed by the polyether ring and carboxylate group of the complexing agent. A strong preference for octahedral coordination is exhibited by Ni(II). On the other hand, Co(II) readily shifts from octahedral to tetrahedral (or intermediate) coordination geometries. Stereochemical flexibility of the Co(II) ammine cation should enhance hydrogen-bonding interactions of first-sphere ammine ligands with second-sphere crown carboxylate ligands.

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