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Separation of Cobalt by Liquid Surfactant Membranes

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Abstract

An experimental study is presented on the separation of cobalt(II) cations from an aqueous solution by means of liquid surfactant membranes containing the ion exchanger di(2-ethylhexyl)phosphoric acid. The process was studied at various emulsifier (Span 80) concentrations, membrane viscosities, pHs, and rates of stirring as well as at various KNO_3 and cobalt concentrations. Cobalt recovery over 99% was achieved with up to tenfold enrichment. A substantial difference of the process course for cobalt and copper was found which allowed for their effective separation.

INTRODUCTION

The hitherto published works on the separation of metals from aqueous solution by liquid surfactant membranes involve chromates (*1–3*), copper (II) (*4*, *5*), mercury(II) (*5*), and cadmium(II) (*5*) cations. This work, as a part of a research project on the separation of metal ions by liquid surfactant membranes, contains the results of studies on the separation of cobalt(II) cations from aqueous solution.

The system studied was similar to that for cupric cations (*4*) where two aqueous solutions, "internal" aqueous nitric acid and "external" aqueous copper(II), were separated by an organic liquid membrane to form a water-in-oil-in-water type emulsion. The liquid membrane con-

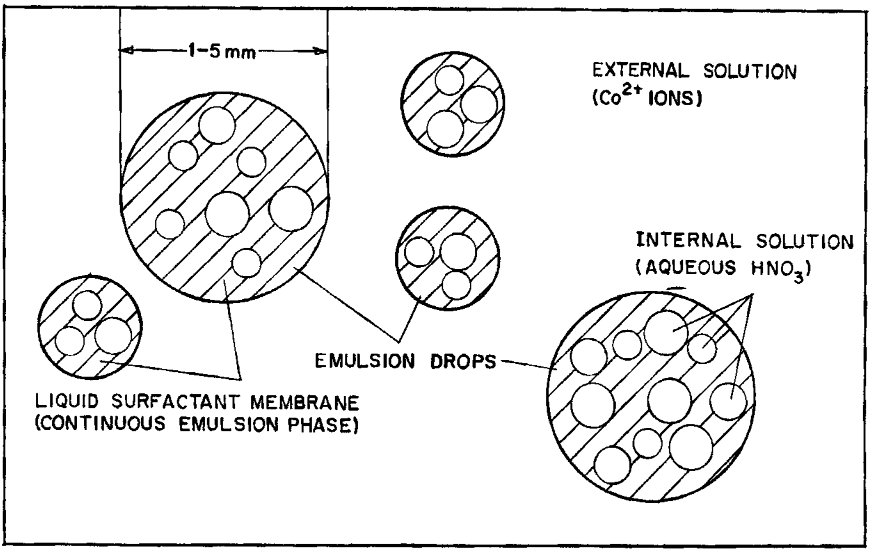

FIG. 1. Liquid surfactant membrane system for cobalt separation.

tained an emulsifier stabilizing the emulsion droplets and the liquid ion exchanger, di(2-ethylhexyl)phosphoric acid (D2EHPA), dissolved in an organic solvent. Cobalt(II) cations diffuse from the "external" solution through the liquid membrane as a Co–D2EHPA complex which decomposes at the internal interface of the membrane (Fig. 1).

EXPERIMENTAL

The water-in-oil type emulsion prepared from the aqueous nitric acid and the organic solution was stirred with aqueous cobalt(II) nitrate to form the water-in-oil-in-water type liquid membrane system according to the previous experimental procedure (*4*). Organic solution (liquid membrane) was prepared by dissolution of emulsifier (Span 80, International Enzymes Ltd.), the ion exchanger (D2EHPA, 98%), and polybutadiene of average molecular weight equal to 6000 in cyclohexane as a solvent. The initial concentration of nitric acid in the internal solution was maintained constant and equal to 2.0 *M*. The acidity of the external solution was controlled by a pH meter and maintained at a given level by the addition of 2.0 *M* aqueous potassium hydroxide. This acidity

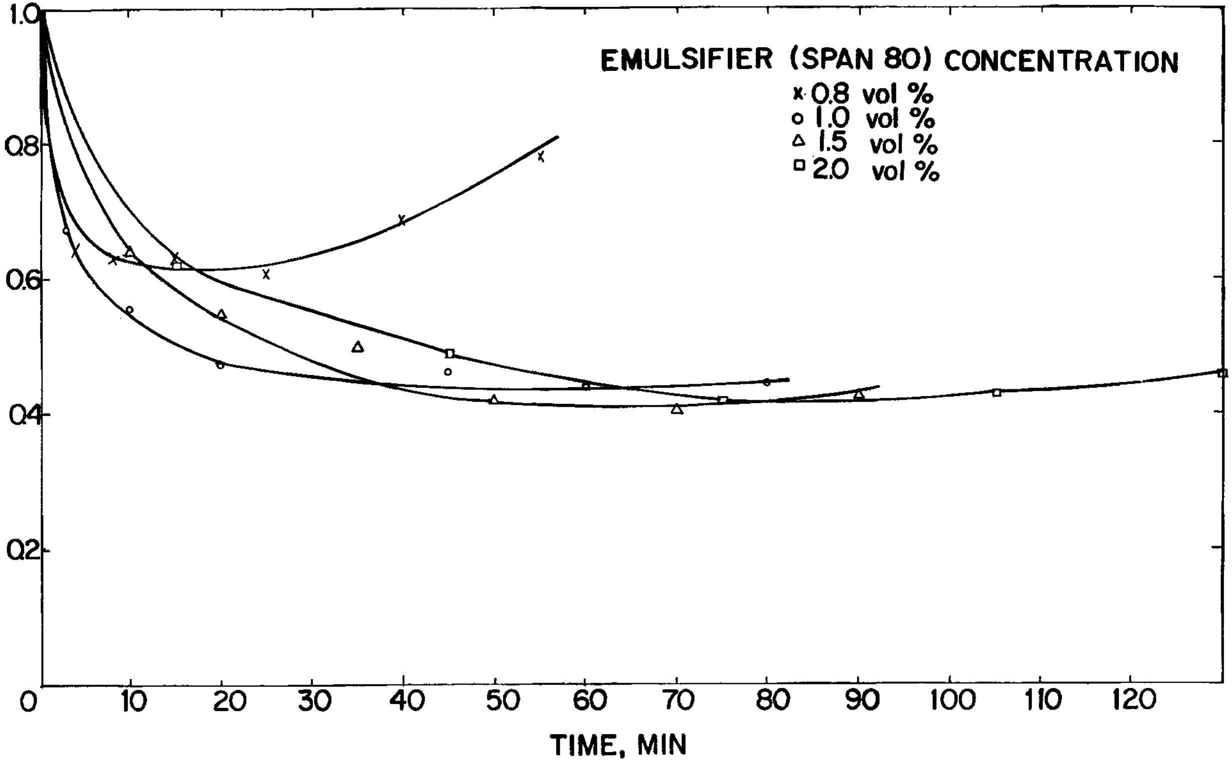

FIG. 2. Kinetics of cobalt separation by liquid membrane at various concentrations of emulsifier (Span 80). Membrane: 6.3% (vol) solution of D2EHPA in cyclohexane, polybutadiene added up to a viscosity of 3.1 cP. Stirring at 310 rpm. The pH of the external solution containing 0.5 *M* KNO_3 is equal to 3.1.

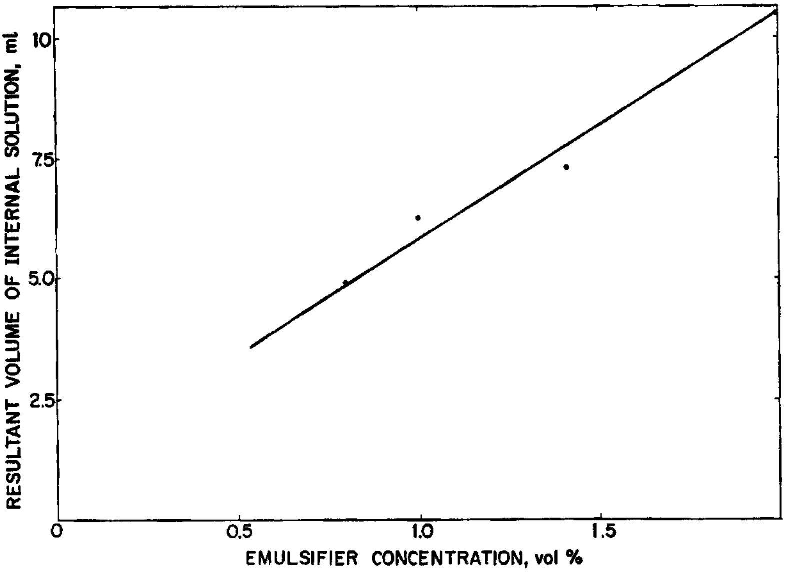

FIG. 3. The resultant volume of internal solution at various Span 80 concentrations. Membrane, stirring, and external solution as in Fig. 2.

was usually equal to pH 3.1, which corresponds to the $pH_{0.5}$ value for cobalt(II) liquid extraction with D2EHPA (*6*). The concentration of cobalt was determined by the radiotracer technique (Co-58) using the multichannel gamma radiation analyzer ND–1200 with a semiconductor (Ge/Li) probe.

RESULTS AND DISCUSSION

The effects on cobalt separation by the liquid surfactant membrane were studied through the external solution composition: the pH, the KNO_3 and Co^{2+} concentrations, the organic phase composition (concentration of the emulsifier and viscosity), as well as of the stirring.

The composition of the organic phase (membrane) influences the kinetics of cobalt separation. Consequently the increase of emulsifier concentration from 0.8 to 2.0% (vol) changes the cobalt recovery from 39 to 59% and increases the maximum recovery time from 20 to 80 min (Fig. 2) as well as the emulsion stability (Fig. 3). This stability was determined by comparision of the initial and final volumes of the internal emulsion solution. An increase of this volume shows the emulsion instability.

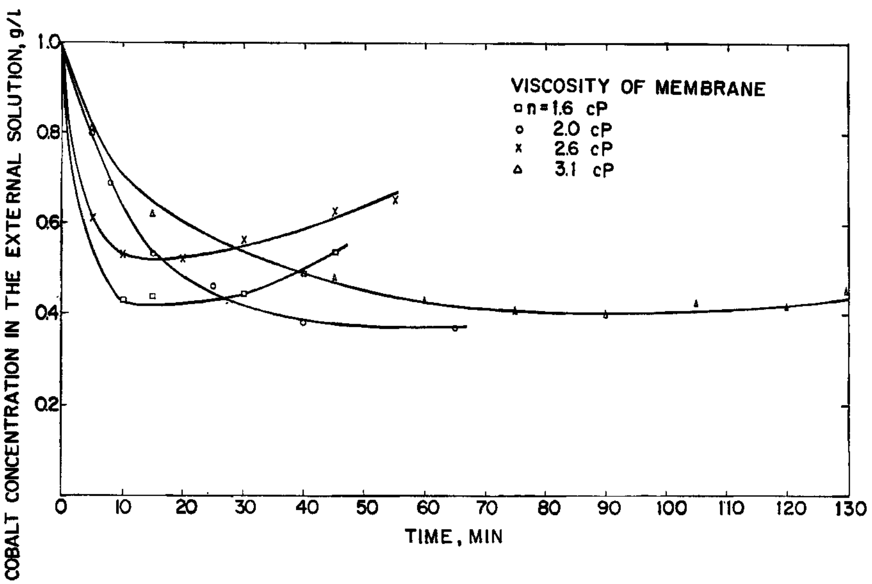

FIG. 4. Kinetics of cobalt separation at various viscosities of the liquid membrane. Membrane: 6.3% (vol) of D2EHPA; 2.0% (vol) of Span 80 solution in cyclohexane. Stirring at 310 rpm. The pH of the external solution containing 0.5 *M* KNO_3 is equal to 3.1.

Similar effects were observed for copper separation by the liquid surfactant membrane (*4*). A possible explanation lies in the growing membrane thickness and the saturation of membrane interfaces by emulsifier molecules.

The membrane viscosity also affects the cobalt recovery as well as the separation rate (Fig. 4). For viscosity changing from 1.6 to 3.1 cP, the highest cobalt recovery was achieved at 2.0 cP, and the maximum recovery time increases with the viscosity. These effects are most probably connected with varied membrane thicknesses, and thus with the diffusion distance.

The composition of the external solution substantially affects the liquid membrane separation process where a lowering of the acidity causes higher cobalt recovery and reduces the maximum recovery time (Fig. 5). At higher pH the cobalt(II) cations replace protons from the ion-exchanger molecules adsorbed on the membrane interface more easily and with a higher rate. For instance, when the pH of the external solution increases from 3.1 to 5.0, the cobalt recovery grows from 42 to 81% with the maximum recovery time decreasing from 25 to 15 min.

The cobalt recovery and liquid membrane separation process rate vary

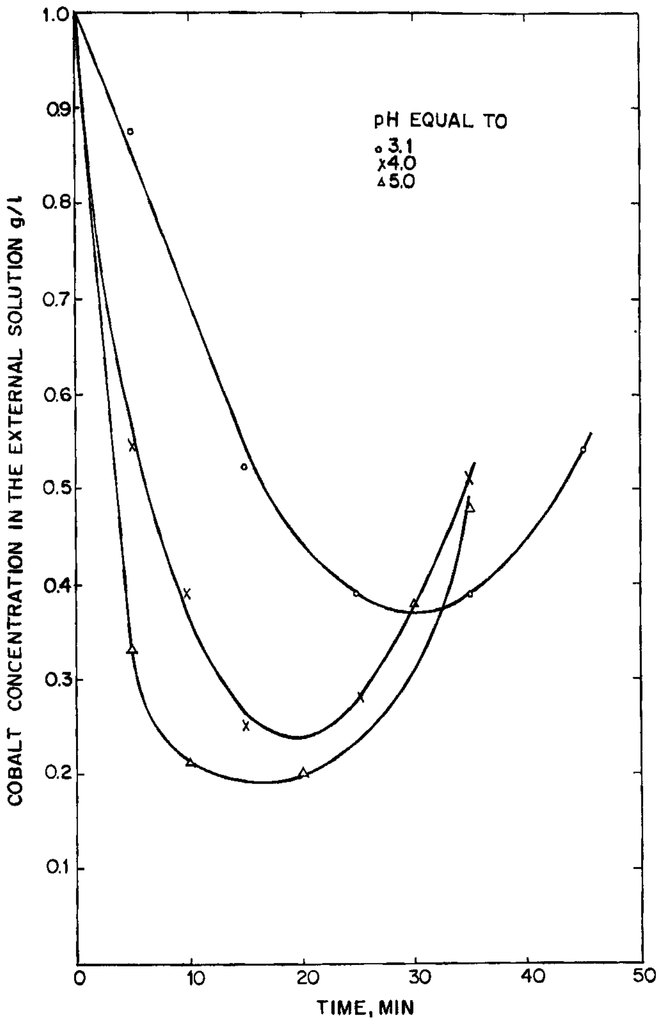

FIG. 5. Kinetics of cobalt separation at various pH values of the external solution. Membrane as for Fig. 4. Viscosity of 3.1 cP. Stirring at 650 rpm. The external solution contains 0.5 *M* KNO_3.

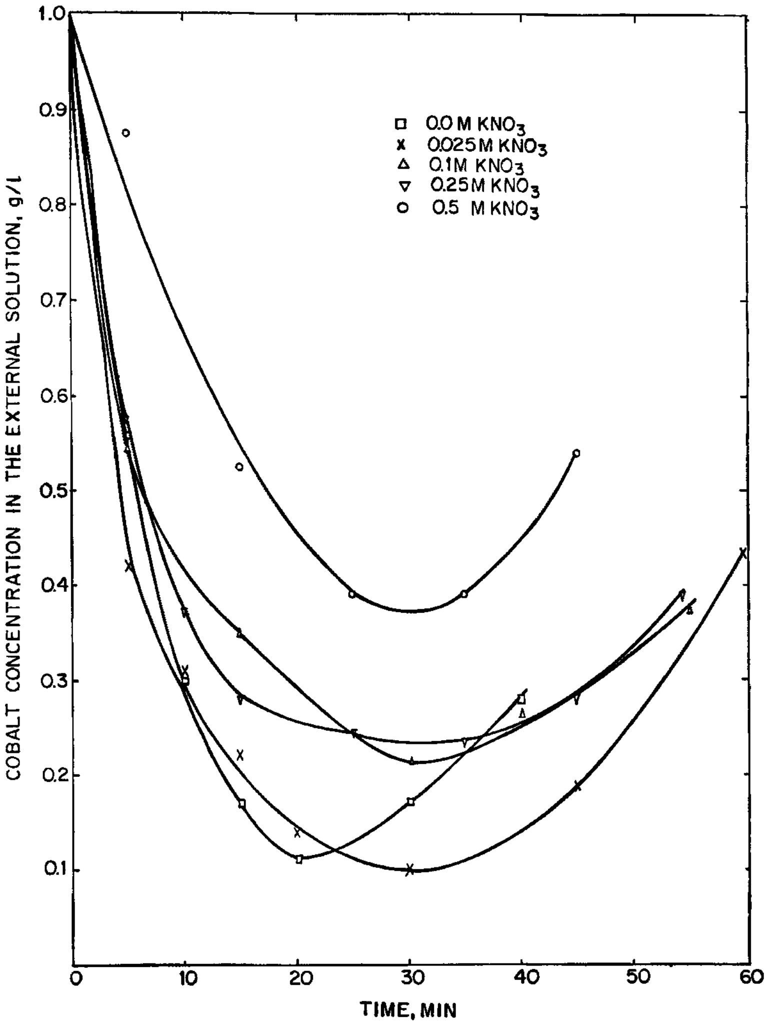

FIG. 6. Kinetics of cobalt separation at various KNO_3 concentrations in the external solution. Membrane and stirring as for Fig. 5. The pH of the external solution is equal to 3.1.

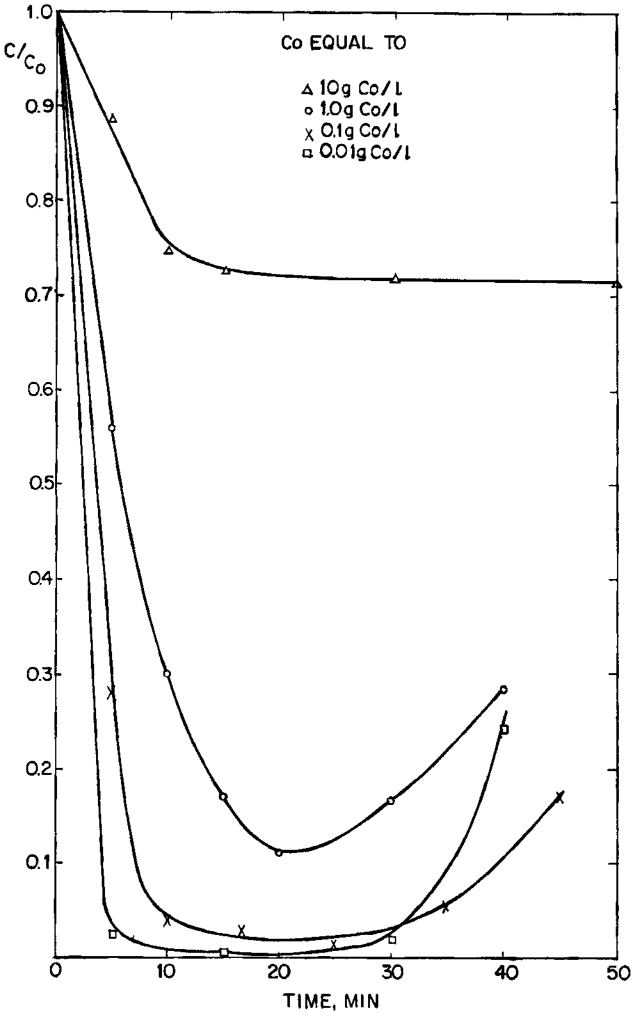

FIG. 7. Kinetics of cobalt separation at various initial cobalt concentrations. c_0 is the initial cobalt concentration, and c is the actual cobalt concentration. Membrane and stirring as for Fig. 5. No KNO_3 in the external solution. The pH of the external solution is equal to 3.1.

with the ionic strength of the external solution (KNO_3 concentration) (Fig. 6).

Besides the lowering of cobalt ion-exchange reaction rate, the presence of an electrolyte at a reasonable concentration can lead to a competitive cation–hydrogen exchange at the membrane interface.

The cobalt concentration in the external solution influences the liquid membrane separation process (Fig. 7). For initial Co(II) concentrations equal to 0.01, 0.1, and 1.0 g/l, its recovery was equal to 99.9, 99, and 90%, respectively, at a maximum recovery time from 10 to 25 min. The cobalt recovery for an initial concentration at 10 g/l was only about 21%.

Over a stirring range of 410 to 900 rpm, the cobalt recovery changes slightly (Fig. 8) with the optimum at 750 rpm with the emulsion stability highest at 650 rpm (Fig. 9). From previous studies (*4*) it appears that there is a significant difference in emulsion stability for copper and cobalt liquid membranes systems. This reinforces the assumption that the nature of metal–D2EHPA complexes, namely, their surface activity, differs. Generally the liquid membrane separation of copper seems to be slower, but, taking into account the molar Me/D2EHPA ratio for the hypothetical single-stage complexation process (i.e., 55% Co and 59% Cu recovery from the initial metal concentration in the external solution of 1.0 g/l), adequate recovery times are similar. Thus retardation of the copper separation rate must occur when the Cu–D2EHPA complex is formed at the emulsion interface because the complex surface concentration governs the observed separation rate as well as the emulsion stability. The differences in the spatial structures of Co–D2EHPA and Cu–D2EHPA complexes, where the former is tetrahedral and the latter is square planar (*7*) according to the results of studies on the surface activity as well as on the structure of adsorption layers of these complexes (*8*), indicate lower surface activity for Cu–D2EHPA compared to Co–D2EHPA.

CONCLUSIONS

The results presented show the effectiveness of a liquid surfactant membrane separation process for cobalt recovery from aqueous solution. They indicate an analogy to the process for cobalt and copper (*4*). The model of multiple Me–D2EHPA diffusion through the liquid membrane was experimentally proved, and over 55% recovery of cobalt (the stoichiometric maximum recovery under experimental conditions) was achieved. The amount of cobalt transferred to the internal solution based on its

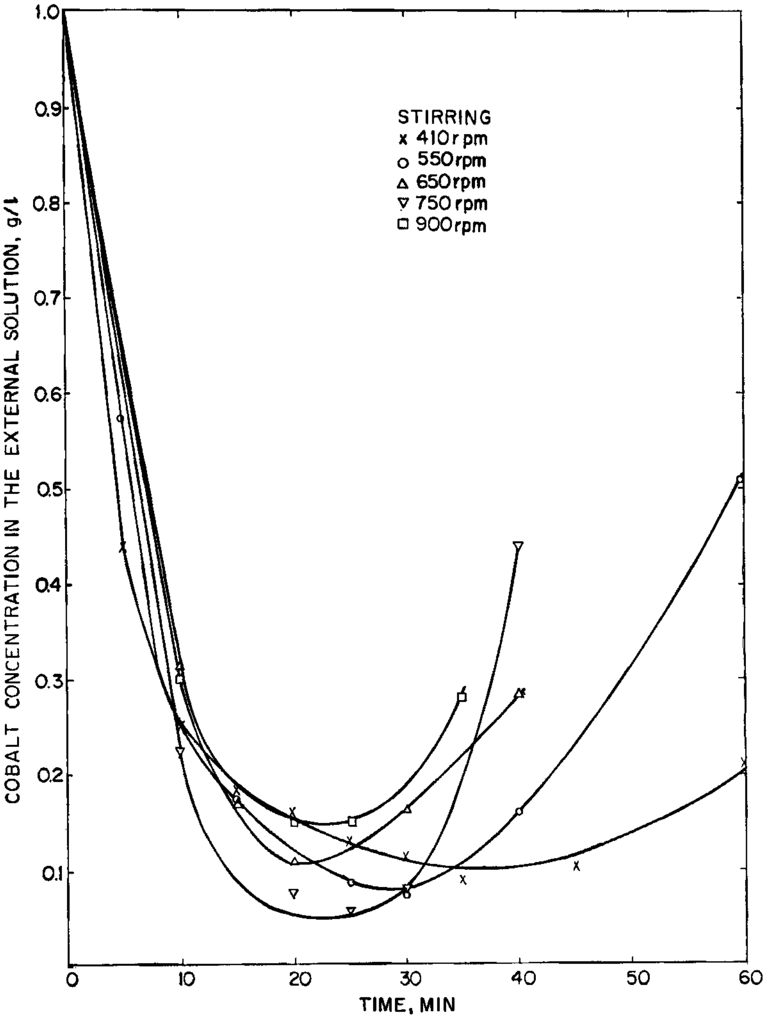

FIG. 8. Kinetics of cobalt separation at various rates of stirring. Membrane and external solution as for Fig. 7.

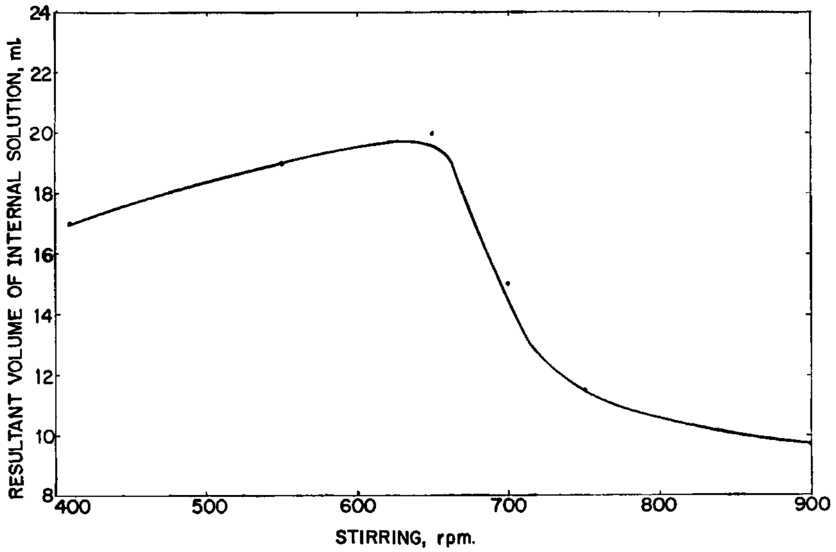

FIG. 9. The resultant volume of internal solution at various rates of stirring. Membrane and external solution as for Fig. 7.

initial concentration of 10 g/l is fourfold greater than expected stoichiometrically (Fig. 7).

From the experimental results it appears there are some important differences between the liquid surfactant membrane separation courses for copper and cobalt.

In particular, the dependence of the process on the pH of the external solution and on the recovery time differs for these cations and allows for their effective separation.

The subsequent experimental results on the liquid surfactant membrane separation of copper, cobalt, and nickel will be published (*9*).

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