

Partition of Chlorides and Nitrates of Nickel(II) and Cobalt(II) between Aqueous Solutions and N-butyl Alcohol

An Absorptiometric Study

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With 2 Figures

Abstract

Partition co-efficient of the chlorides and Nitrates of Nickel and Cobalt were studied and the average partition co-efficients have been determined. Effect of temperature, acids and ketones have also been investigated. The partition co-efficient increases with the increase in temperature in case of Nitrates while a reverse influence is seen in the case of the Chlorides. Acids have analogous effect to that of common ion and depress solubilities of Chlorides and Nitrates in water. Lower ketones like acetone, methyl ethyl ketone and acetyl acetone appreciably decrease the partition co-efficient. The other Ketones did not show any appreciable partitioning effect.

The partition of inorganic materials between organic and inorganic phases have been reported earlier but in recent years it has aroused much interest and the techniques of extraction for removal, has acquired considerable importance. A great deal of work based upon this has already appeared in scientific literature and several of the methods have been successfully utilised for the separation of various elements and their salts by solvent extraction techniques, such as counter current and paper partition chromatography. A well documented summary of the subject has been given by IRVING¹). GARWIN and HIXSON²) have described the separation of the chlorides of nickel and cobalt, particularly with an intention of achieving separation of these salts. These workers have reported separation of nickel chloride from cobalt chloride through the selective extraction of the latter by capryl alcohol from solutions containing HCl or CaCl₂ at high concentration. Extraction of these salts from aqueous solutions by 2-Octanol and effect of electrolytes has been

¹) H. IRVING, Qtr. Rev. **5**, 200 (1951).

²) L. GARWIN and A. N. HIXSON, Ind. Eng. Chem. **41**, 2295 (1949).

reported by MOORE et al.³⁾⁴⁾. Several other workers like IVAN et al.⁵⁾, MORRIS et al.⁶⁾, IRVING et al.⁷⁾, HEALY et al.⁸⁾, KENNEDY⁹⁾, SOLOVKIN et al.¹⁰⁾, GERHARD WERDMANN¹¹⁾, and KULIKOV¹²⁾, have reported the extraction from aqueous solution; from pure aqueous solutions as well as in presence of other ions.

WŁODZIMIEZZ et al.¹³⁾ have studied the extraction of bivalent metal nitrates and perchlorates including that of nickel and cobalt and have reported their extraction curves with alcohols. Distribution of various nitrates including that of cobalt and nickel between water and diethyl ether has been reported by NIKITIN et al.¹⁴⁾. GINDIN et al.¹⁵⁾ have also studied distribution coefficients and separation co-efficients of Cobalt chloride and nickel chloride with a series of solvents.

The authors have investigated in particular the distribution of chlorides and nitrates of nickel and cobalt between water and N-butyl alcohol and effect of common ions as well as of Ketones upon the partition co-efficients of the same.

Experimental

Materials

Chlorides and nitrates of cobalt and nickel (C. P.) E. Merck; N-butyl alcohol B. P. 117.7°C (B. D. H.) reagent grade (free from Ketones) were used. B. D. H. C. P. grade Ketones and E. Merck C. P. grade acids were used. Double distilled water was used for all purposes.

Standard solution (5% W/V) of nickel chloride, nickel nitrate, cobalt chloride and cobalt nitrate respectively were prepared in double distilled water. Of each solution 2.5, 5.0, 7.5 and 10 ml. respectively were taken. The final volume in all cases was made upto 10.0 ml. by distilled water. These were then shaken with 20.0 ml. of N-butanol previously saturated with distilled water, for 30 minutes and allowed to stand at room temperature ($21 \pm 1^\circ\text{C}$) for another two hours to achieve equilibrium. The two layers were then separated and the amounts of the respective salts determined colorimetrically using a photo electric colorimeter. A number of such experiments were performed. The results obtained have been tabulated in Table I.

3) T. E. MOORE et al., J. Phys. Chem. **59**, 90 (1955).

4) T. E. MOORE, et al., J. Phys. Chem. **60**, 564 (1956).

5) J. G. IVAN, et al., Bull. Inst. Nuclear Sci. "Boriskidrich" Belgrade **8**, 67 (1958).

6) D. F. C. MORRIS, et al., J. Inorg. Nucl. Chem. **10**, 337 (1959).

7) H. IRVING, et al., J. Inorg. Nucl. Chem. **10**, 30618 (1959).

8) T. V. HEALY, et al., J. Inorg. Nucl. Chem. **10**, 137 (1959).

9) J. KENNEDY, J. Appl. Chem. London **9**, 26 (1959).

10) A. S. SOLOVKIN, et al., Zhur. Neorg Khim **4**, 1454 (1959).

11) G. WERDMANN, Can. J. Chem. **38**, 459 (1960).

12) F. S. KULIKOV, Mezhouz Konf Moscow of C. A. 55 7770h, 283—95 (1957).

13) WŁODZIMIEZZ, Roozniki Chem. **31**, 1293 (1957).

14) B. A. NIKITIN, et al., Trudy-Radievogo Inst. im V. G. Khlopina **8**, 3 (1958).

15) L. M. GINDIN, et al., Zhur. Neorg Khim **5**, 149 (1960).

Table I

Salts	Conc. in gms/L		Average partition co-efficient
	Conc. in Aqueous phase	Conc. in n-butanol	
Nickel nitrate	29.7090	1.5410	19.28
Nickel chloride	30.1120	1.1380	26.46
Cobalt nitrate	29.1750	2.0750	14.06
Cobalt chloride	29.6100	1.6400	18.05

Study of temperature effect

Partition co-efficients were also determined at different temperatures following similar procedure. A constant temperature was obtained by employing TOWSON and MERCERS precision thermostat. The results obtained have been detailed in Table II.

Table II

Salts	Average partition co-efficient at temperature		
	45 °C	65 °C	99 °C
Nickel nitrate	21.37	23.30	26.50
Nickel chloride	21.08	18.45	14.80
Cobalt nitrate	16.40	18.50	22.40
Cobalt chloride	16.55	15.20	12.90

Study of effect of Nitric and hydrochloric acid on nitrates and chlorides respectively

To see the effect of nitric acid and hydrochloric acid on the partitioning of the nitrates and chlorides respectively, the salt solutions were taken in

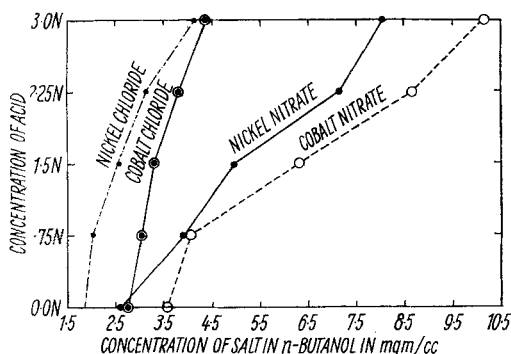


Fig. 1

different concentrations of the acids and the concentration in the n-butanol layer was determined in the same manner as in the previous experiments.

The results are tabulated in Table III and IV, and graphically represented in Fig. 1.

Concentrations of the acids were chosen between 0.75 N to 3.0 N. When the concentration was increased further it was observed that the miscibility of the two phases increased considerably at 5.0 concentration of the acids, phase separation could not be achieved.

Table III

Salts	Concentration mgm/cc in presence of HNO ₃				
	0.0 N	0.75 N	1.50 N	2.25 N	3.0 N
Nickel Nitrate	2.59	3.90	4.95	7.12	8.04
Cobalt Nitrate	3.55	4.06	6.30	8.64	10.16

Table IV

Salts	Concentration mgm/cc in presence of HCl				
	0.0 N	0.75 N	1.50 N	2.25 N	3.0 N
Nickel chloride	1.89	2.09	2.55	3.16	4.16
Cobalt chloride	2.77	3.02	3.29	3.80	4.37

Study of effect of Ketones

Experiments were carried out in the same manner as with acids. Six different concentrations of Ketone in water were taken. As many as ten diffe-

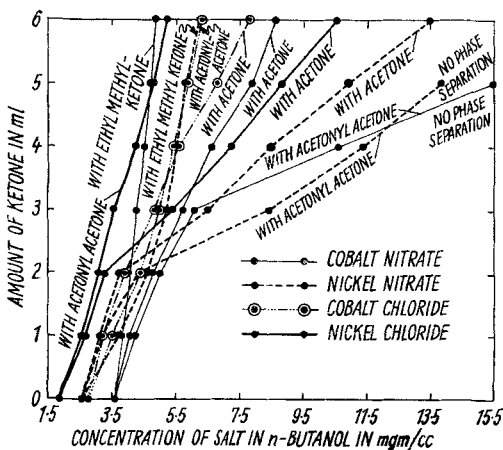


Fig. 2

rent Ketones were studied (Ethyl methyl Ketone, Acetonyl acetone, Cyclohexanone, Acetone, Methylisopropyl Ketone, Acetyl Acetone, Acetophenone

Benzophenone, Mesityl oxide, Benzoyl acetone). Only in three cases appreciable change in partitioning was observed. The results obtained with these are given in table V, and graphically represented in Fig. 2.

Table V

Ketone	Conc. in mgm/cc of N-butanol phase in presence of different amounts of Ketones added to 10.0 ml. of aqueous solution						
	0.0	1.0	2.0	3.0	4.0	5.0	6.0
Amount of Ketone in ml.	0.0	1.0	2.0	3.0	4.0	5.0	6.0
With Ethyl methyl Ketone							
1. Amount of cobalt nitrate	3.55	3.86	4.16	4.28	4.50	4.68	4.86
2. Amount of nickel nitrate	2.59	3.77	4.61	5.20	5.52	5.80	6.29
With Acetonyl acetone							
1. Amount of cobalt nitrate	3.55	4.25	5.02	6.15	10.66	15.46	No phase separation
2. Amount of nickel nitrate	2.59	3.23	4.25	8.45	11.36	13.84	No phase separation
3. Amount of cobalt chloride	2.77	3.46	4.28	5.04	5.44	5.86	6.38
4. Amount of nickel chloride	1.89	2.50	3.10	3.58	4.20	4.72	5.26
With Acetone							
1. Amount of cobalt nitrate	3.55	4.04	4.78	5.70	6.68	7.94	8.64
2. Amount of nickel nitrate	2.59	3.18	3.77	6.54	8.42	10.91	13.41
3. Amount of cobalt chloride	2.77	3.24	3.92	4.80	5.68	6.86	7.80
4. Amount of nickel chloride	1.89	2.62	3.28	5.40	7.22	8.84	10.56

Discussion

The partition co-efficient of the salts between water and n-butanol when determined utilising pure solvents indicate that all of these are retained mainly in water. Temperature has a considerable effect both on chlorides as

well as on nitrates. In the case of nitrates the partition co-efficients show a rise with increase in temperature. However, in the case of chlorides a reverse effect was observed (refer Table II). Addition of HCl and HNO₃ to phase mixtures containing chlorides and nitrates respectively depress the solubilities in water resulting in increased concentration of these in the n-butanol phase. This is in analogy with common ion or salting out effect and as the concentration of the acids is increased more and more of the salt pass in the organic phase. However acid concentrations of 5 N and above brings about increased miscibility of the solvents and phase separation does not take place. Out of a variety of Ketones added to the phase mixtures only a few have been found to have any appreciable influence on partition co-efficients. In general all these suppress solubility in water and brings about an increase in the concentration of the salts in the n-butanol phase (refer Table V). It was particularly noticed during study of the effect of Ketones that only those possessing lower molecular weights show appreciable effect on the partitioning of these salts. However in no case a depression in solubility in n-butanol was observed. Such an effect of the Ketones could be because of greater miscibility with water in comparison with n-butanol where-by they selectively suppress solubility in water.

Further work on the separation of metals by solvent extraction in ores and minerals and estimation by spectrophotometric methods is in progress.

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