

Effect of Temperature on The Solvent Extraction of Cobalt(II), Nickel(II), and Copper(II) Metal Ions by o-diphenylamino Benzoic Acid

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Abstract:

The solvent extraction of cobalt, nickel, and copper ions by the ligand o-diphenylamino benzoic acid in chloroform at 273, 293, and 318 K has been investigated. The values of $pH_{1/2}$ and k_{ex} as well as the values for the thermodynamic parameters ΔG , ΔH , and ΔS have been calculated.

الخلاصة

تم دراسة الاستخلاص المذيبي لأيونات الكوبالت، النيكل، والنحاس بواسطة الليكاند أورثو ثنائي فنيل أمين حامض البنزويك المذاب في الكلوروفورم بدرجات حرارة 273، 293، و 318 كلفن. قيم الدالة الحامضية $pH_{1/2}$ وثابت الاستخلاص k_{ex} وكذلك الدوال الترموديناميكية (ΔS , ΔH , ΔG) تم احتسابها.

Keywords: Solvent extraction, o-diphenylamino benzoic acid (HN), cobalt(II), Nickel(II), and copper(II) metal ions.

Introduction:

Organometallic chemistry, compounds in which an organic molecule (sometimes with a net negative charge) is bonded to a metal atom through an oxygen or nitrogen atom, is one of the most rapidly growing areas of chemical research⁽¹⁾. In recent years much work has been carried out on the systematic examination of the various factors affecting the solvent extraction of metal chelates, but only a few studies have been reported concerning the effect of temperature. A change in temperature is accompanied by changes in all the parameters affecting the extraction process, and these changes may be highly variable.

The extraction of a chelate compound at different temperatures was probably studied for the first time by Dyre and Schweitzer⁽²⁾ who

followed the extraction of silver dithizonate. It was found that the extraction constant decreases with increasing temperature. Schweitzer and Bramlitt⁽³⁾ studied the chloroform extraction of silver hydroxyquinolate at 273, 293, and 318 K. Here too, the solvent extraction constant decreases with the increase in temperature. On the other hand, the extraction constant of indium hydroxyquinoline with a three molar solution of hydroxyquinoline in chloroform⁽⁴⁾ remained unchanged between 273 K and 293 K ($k_{ex} = 3.98$). The extraction of tellurium(IV) dithizonate was studied at different temperatures⁽⁵⁾. It was found that the distribution ratios decrease with increasing temperature. Bankovskii et al⁽⁶⁾, showed that the distribution ratio of 8-mercaptoquinoline between iso-octane

and water ($\text{pH}_{1/2} = 5.2$) increases with increasing temperature. The thermodynamics of extracting In(III) with diethylhexyl mono thiophosphoric acid as an extractant in a H_2SO_4 system was studied and the thermodynamic quantities for the extraction process were calculated⁽⁷⁾. The influence of temperature on the extraction of the thorium(IV) and europium(III) ions from 1M sodium nitrate medium into 1,2-dichloroethane by diphenyl-*N,N*-dimethyl carbamoylmethylphosphine oxide was studied as a function of temperature in the range 20–40 °C. It was found that the distribution ratios of europium ions decrease when raising the temperature, while with thorium ions the opposite phenomenon was observed⁽⁸⁾. From the distribution measurements, thermodynamic parameters such as the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes associated with the extraction processes was evaluated.

Experimental:

Instrumentation:

A. Flame Atomic Absorption Spectrophotometer type Shimadzu AA – 680 G., Japan used for the determination of Co^{2+} , Ni^{2+} , and Cu^{2+} concentrations.

B. pH meter type Titro-Processor 686 Metrohm Swiss made.

C. Balance: Type Sartorius Analytic GMBH Gottingen Germany, range between 0 – 200 mg.

D. Mechanical shaker, Gallenkamp SGL - 700

The ligand *o*-diphenylamino benzoic acid (HN) was prepared by the method reported by Goldberg and Nimerovsky⁽⁹⁾. All the metal ion solutions were prepared by dissolving an analar grade metal in an appropriate acid⁽¹⁰⁾. The ionic strength of the aqueous phase was maintained at 0.1

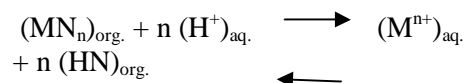
M with NaClO_4 . The pH of the aqueous phase was measured with an accuracy of 0.01 pH unit. The initial concentrations of the metal ions were 1×10^{-4} M and the initial concentration of the ligand was 1×10^{-3} M in all the extraction experiments. The metal ions extraction was studied at 273, 293, and 318 K. The temperature was measured with an accuracy of 0.1 K.

Shake – Out test:

Twenty milliliters of aqueous solution which contains the metal ion in certain acidity and 20 ml of the chloroform solution of the ligand were added to clean and dry 100 ml quick fit cylindrical tubes. The tubes were then stoppered and the shaking started immediately inside the bath by the use of a mechanical shaker. After an appropriate time of shaking for each metal ion, the two phases were allowed to separate in the bath. Some volume of the top layer (aqueous) was carefully drawn off for pH and concentration measurements.

Results and Discussions:

The mechanism for the extraction of the metal ions by the ligand (HN) can be represented by:



Where: M = Co, Ni, Cu; aq. and org. are aqueous and organic phases respectively.

Copper (II) extractions at 273, 293, and 318 K:

No change in the amount of extracted Cu (II) ions was observed in the extraction experiments carried out at 273, 293, and 318 K, suggesting that the Cu (II) / HN extraction system is temperature independent in the range covered.

Because the concentration of the ligand is always greater than that of the metal ion, and polymerization in the organic phase as well as hydrolysis and complexation in the aqueous phase are neglected, plots of $\log D$ (the distribution ratio) Vs pH are straight lines with slopes ≈ 2 . From the plots of $\log D$ Vs pH, for the three experiments, the equation is:

$$\log D = 2.05 \text{ pH} - 12.69 \quad \dots (1)$$

D = conc. of metal ion in the org. phase/ conc. of metal ion in the aqueous phase

The value of $\text{pH}_{1/2}$ (the pH at which 50% of the metal ion is extracted) is found to be (6.19 ± 0.01) .

The value for the extraction constant (k_{ex}) can be calculated from the following equation:

$$\begin{aligned} -\log k_{\text{ex}} &= n [\text{pH}_{1/2} + \log [\text{HN}]_{\text{org.}}] \quad \dots(2) \\ -\log k_{\text{ex}} &= 2.05 [6.19 + \log (10^{-3} \text{ mol / l})] \\ \log k_{\text{ex}} &= -6.54 \\ k_{\text{ex}} &= 2.88 \times 10^{-7} \end{aligned}$$

The free energy change (ΔG) can then be calculated from Vant hoff's equation:

$$\begin{aligned} \Delta G &= -2.303 RT \log k_{\text{ex}} \quad \dots(3) \\ &= 36.69 \text{ KJ / mol at } 293 \text{ K} \end{aligned}$$

Because the system is temperature – independent, the value of the enthalpy change is almost zero, indicating that the heat of solvation of chloroform is compensated by the heat absorbed during the process of the release of solvated water molecules.

The entropy change (ΔS) can be calculated using the equation:

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S \quad \dots(4) \\ 36.69 &= 0 - 293 \Delta S \\ \Delta S &= -125.23 \text{ J / mol. K} \end{aligned}$$

The entropy change represents the degree of disorder of the system in the reaction. In the extraction process, the coordinated water molecules are converted to free water molecules and the total number of particles in this system increases, and cause the increase in the entropy change. However, the lower value for the entropy changes when the extraction reaction involves the acid (HN), may be attributed to the increased solvent structuring in the aqueous phase as the hydrogen ions replace the metal cations.

Nickel (II) extractions at 273, 293, and 318 K:

It is found that the percentage of extraction of nickel ions is the same at 293 K and 318 K, i.e. increasing the temperature from 293 K to 318 K has no effect on the extraction. The equation for the extraction is:

$$\log D = 1.98 \text{ pH} - 14.77 \quad \dots(5)$$

from which the value of $\text{pH}_{1/2}$ is determined to be (7.46 ± 0.04) .

The value for k_{ex} can be calculated according to equation (2):

$$\begin{aligned} -\log k_{\text{ex}} &= 1.98 [7.46 + \log (10^{-3} \text{ mol / l})] \\ \log k_{\text{ex}} &= -8.83 \\ k_{\text{ex}} &= 1.48 \times 10^{-9} \end{aligned}$$

At 273 K, the equation is:

$$\log D = 1.98 \text{ pH} - 13.89$$

and $\text{pH}_{1/2}$ is (7.02 ± 0.03) . This means that nickel (II) can be extracted from slightly more acidic solutions when the temperature decreased from the room temperature value (293 K).

The value for ($k_{\text{ex}} = 1.09 \times 10^{-8}$) which is higher than that at 293 K ($k_{\text{ex}} = 1.48 \times 10^{-9}$), an indication of its better extraction at lower temperature.

From 293 to 318 K, the enthalpy change ΔH is zero, and from equation (3):

$$\begin{aligned} \Delta G &= 49.54 \text{ KJ / mole at } 293 \text{ K,} \\ \Delta G &= 53.76 \text{ KJ / mole at } 318 \text{ K} \end{aligned}$$

The entropy change, ΔS can be calculated from equation (4):

$$\Delta S = -169.08 \text{ J / mol. K}$$

From equations (3) and (4) we can derive the following:

$$-RT \ln k_{ex} = \Delta H - T \Delta S \quad \dots(6)$$

$$\ln k_{ex1} = \Delta S / R - \Delta H / RT_1 \text{ and}$$

$$\ln k_{ex2} = \Delta S / R - \Delta H / RT_2 \quad \dots (7)$$

$$\ln (k_{ex1} / k_{ex2}) = (\Delta H / R) \times (1 / T_2 - 1 / T_1) \quad \dots(8)$$

From equation (8), the enthalpy change can be calculated:

$$2.303 \log (k_{ex1} / k_{ex2}) = (\Delta H / R) \times (1 / T_2 - 1 / T_1)$$

$$2.303 (-7.96) - 2.303 (-8.83) = [\Delta H / (8.314 \times 10^{-3})] \times [(1 / 293) - (1 / 273)]$$

$$\Delta H = -66.6 \text{ KJ / mole.}$$

Now the value of ΔH can be substituted in equation (7) to get ΔS :

$$2.303 (-7.96) = [\Delta S / (8.314 \times 10^{-3})] - [(-66.6) / \{(8.314 \times 10^{-3}) (273)\}]$$

$$\Delta S = -396.45 \text{ J / mole. K}$$

The negative values of ΔH and ΔS would indicate that the ligand (HN) does not disrupt the hydration layer about the nickel ion to a greater extent⁽¹¹⁾. Also the negative values of ΔS can be attributed to the strong bonds, in the formed complex, would result in a large decrease in configurational entropy of the chelating ligand. It is also suggested that, the retention of a water molecule in the chelate ring make the ΔH more exothermic and the ΔS more negative than might be expected, which is in agreement with the experimental data.

Cobalt (II) extractions at 273, 293, and 318 K:

The cobalt extraction system behaves in a manner similar to the nickel extraction system explained above. At 293 K and 318 K, the equation is:

$$\log D = 1.97 \text{ pH} - 14.42 \quad \dots (9)$$

From equation (9),

$$\text{pH}_{1/2} = 7.32 \pm 0.02, \text{ and}$$

$$-\log k_{ex} = 1.97 [7.32 + \log (10^{-3} \text{ mol / l})]$$

$$\log k_{ex} = -8.51$$

$$k_{ex} = 3.09 \times 10^{-9}$$

At 273 K, the equation is:

$$\log D = 1.97 \text{ pH} - 14.0$$

$$\text{pH}_{1/2} = 7.11 \pm 0.03$$

$$\log k_{ex} = -8.097$$

$$k_{ex} = 7.99 \times 10^{-9}$$

Here, too, the value for the extraction constant at 273 K is higher than that at 293 K, an indication of better extraction at low temperatures.

Between 293 K and 318 K;

$$\Delta H = 0$$

$$\Delta G = 47.47 \text{ KJ / mole at 293 K,}$$

$$\Delta G = 51.82 \text{ KJ / mole at 318 K}$$

The entropy change, ΔS can be calculated from equation (4):

$$\Delta S = -162.94 \text{ J / mole. K}$$

Between 273 K and 293 K the enthalpy change can be calculated according to equation (8):

$$\Delta H = -31.63 \text{ KJ / mole}$$

Substituting the value of ΔH in equation (7) gives:

$$\Delta S = -270.89 \text{ J / mole. K}$$

The similar explanation for Ni (II) is offered for the above results of Co (II).

Conclusions:

The copper extraction system is temperature – independent, i.e. there is no change in the values of the extraction constants upon decreasing or increasing the temperature from the room temperature value until 318 K.

It was found that it is advantageous to extract cobalt and a nickel ion from the aqueous phase at lower temperature than at room temperature as the values of the extraction constant is higher. Accordingly, they can be extracted from more acidic solutions at low

temperature (273 K), away from their hydrolysis region.

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