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RESEARCH ARTICLE

Kinetics of liquid-liquid membrane extraction of transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) using series of Sudan Azo Dyestuffs

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Abstract

Kinetics of extraction is an important parameter to determine rate of extraction of metal ions through ligands/ ionophores, in which the corresponding change in the concentration of metal ions in the membrane phase was determined with time. Kinetics of liquid-liquid membrane extraction studies of transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) using series of Sudan Azo Dyestuffs (Sudan-I, Sudan-III and Sudan-III) have been carried out at room temperature and rate of extraction were determined spectrophotometrically. Chloroform is used as Organic liquid membrane. From the results, it has been observed that during the process of extraction the performance of extraction increases as the time of extraction is increases and maximum extraction reached at particular time for particular metal ion and then decreases due to the back extraction process.

Introduction

The kinetics of solvent extraction[1] is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species those are responsible for the extraction process.

The dependence of the kinetics on the chemical reactions is easily understood by considering that the final products of any extraction process are usually in a chemical state is different from the initial unreacted species. This is true even for the simple partition of neutral molecules between two immiscible liquid phases, where the chemical change is in the solvation environment of the extracted species. More drastic chemical changes take place in the extraction of a metal cation from an aqueous solution by a chelating extractant dissolved in an organic diluent. In the extraction some of the solvation water molecules can be removed from the metal ion, and a new coordination compound, soluble in the organic phase, is formed with the chelating group of the extractant. In addition, the extracting reagent can undergo a dissociation reaction together with the extractant-metal complex, can undergo changes in aggregation in the organic phase. Consequently, whenever at least one of the chemical steps of the overall reaction mechanism is slow enough, compared with the diffusion rate, the kinetics of extraction would depend on the rate of the slow chemical reactions [2].

For solvent extraction systems, there are two additional complications. First, the chemical reactions can take place, at least in principle, in two bulk phases, since these is dealing with two immiscible liquid layers. Second, the chemical reactions can occur in the two-dimensional region called the liquid– liquid interface, that separates the two immiscible liquids, or in a thin volume region very close to it. When interfacial chemical reactions are important, the situation is analogous to that describing the kinetics of the chemical reactions encountered in heterogeneous catalysis and in some electrode processes. Although a relatively large number of sophisticated techniques are available for studying chemical reactions at solid–fluid interfaces. Very few tools have been developed to investigate chemical changes occurring at liquid–liquid interfaces. Information about such interfacial reactions, therefore, is still limited and is based largely on indirect evidence and speculations[3].

In the present investigation extraction kinetics of metal chelates - azo (for instance, nickel, copper, cobalt, zinc), complexes with S-I, S-III and S-IV have been carried out. In most cases experimental data have been obtained for the kinetic region. The systems were investigated at a definite temperature. The phases were mixed by means of an apparatus for intensive shaking.

Experimental

Materials

All chemicals, throughout the course of experimental work, used were of AnalaR or GR grade and were used as supplied.

Ionophores/ ligands 1-(phenylazo)-2-naphthol (Sudan-I), 1-[4-(Phenylazo)phenylazo]-2-naphthol (Sudan-III) and 1-[2-Methyl-4-(2-methylphenylazo) phenylazo]-2-naphthol (Sudan-IV) were obtained from Fluka. Chloroform from Merck was used as solvent systems. Solutions of Metal Salts i.e. $Co(NO_3)_2$, $NiSO_4$, $Cu(NO_3)_2$, $ZnSO_4$ were prepared in doubly distilled water.

Instruments used:

Absorbance measurements were carried out on 104-Systronics UV/VIS spectrophotometer. Both phases of liquid membrane were stirrered well using 1MLH magnetic stirrer Remi Equipments.

Kinetics of extraction studies:

It is evident from the discussion and careful survey of the existing literature that complexation studies of azo dyestuffs with transition metal cations has received but very little attention. There is however, no information available regarding the complexation study of sudan azo dyes with transition metal cations by extraction with their kinetics behavior.

Hence, the present investigation was therefore, undertaken which deals with the complexation studies of selected Sudan azo dyestuffs (I-IV) with transition metal cations (i.e. Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) in organic solvent.

This investigations have been performed to study the kinetics of extraction. For these work aqueous metal salt solution was vigorously stirred with ionophore solution in Chloroform in different sets of beakers keeping the amount of salt solution, ionophore solution and solvent volume as constant[4,5]. The time of this process was varied up to half an hour to 4 hours for different sets. The depleted aqueous phase was removed from beaker at some assigned time from beaker to each to measure the change in the absorbance of ionophore after complexation with metal ions and the analysis of metal content. The absorbance was measured at the λ_{max} of ionophores. These were observed at 480nm for S-I, at 515nm for S-III and at 525nm for S-IV. The metal content in aqueous phase was analyzed by volumetric method. To study the kinetics of extraction the graphs were obtained between the time and extracted amount of metal ions by ionophore.

Results of kinetics of extraction reported in the tables i.e. from 1 to 3 and Graph from 1 to 10 has also been plotted between log x and time in minute for kinetic investigation on extraction.

Results and Discussion

Kinetics of extraction is an important parameter to determine rate of extraction of metal ions through ligands/ ionophores, in which the corresponding change in the concentration of metal ions in the membrane phase was determined with time.

In the present work kinetics of extraction of transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) with ionophores (S-I, S-III and S-IV) containing liquid membrane have been determined.

Kinetic studies were carried out at optimum concentration of metal ions (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and ionophores (S-I, S-III and S-IV). All experiments were performed at constant temperature and rate of extraction were determined spectrophotometrically. The experiments were performed in a glass vessel. The reactor was sunk in a water bath and temperature was maintained constant. The mixture was continuously stirred to ensure limiting internal diffusion.

From the results it has been observed that during the process of extraction the performance of extraction increases as the time of extraction increases and maximum extraction reached at particular time for particular metal ion (Tables-1 to 3).

Kinetics of extraction of metal ions with ionophore S-I:

Figure (1) shows the nature of extraction of the Co^{2+} metal ions using the S-I ligand. The results showed that the graph is parabola in nature and the extraction of Co^{2+} is rapid in first 210 minutes and then remained constant. Here the saturation of membrane phase is assumed.

Extraction of Ni^{2+} ions with ionophore S-I with time is represented in figure (2). It is observed that the rate of extraction is increase with increase in time in linear manner. Temperature was maintained at 27 ^{0}C.

In case of extraction of Cu^{2+} and Zn^{2+} ions with ionophore S-I, from (figure 3 and 4 respectively) it is observed that during the process of extraction the rate of extraction is increase with increase in time up to 180 minute and then decreases. It is attributed to the back extraction process[6,7]. Which is arises due to the instability of emulsion liquid membrane over longer extraction time.

Kinetics of extraction of metal ions with ionophore S-III:

From the results of kinetics of extraction of metal ions (Co^{2+}, Ni^{2+} and Zn^{2+}) with ionophore S-III it is observed that in case of Co^{2+} and Zn^{2+} ions the graph obtained is parabolic in nature. The rate of extraction is increases rapidly and reached at equilibrium in first 180 minutes in case of Co^{2+} and 210 minutes in case of Zn^{2+} and then the rate of extraction is decreases due to back extraction (table- 2).

While in case of Ni^{2+} cation with ionophore S-III, the rate of extraction is increases with time and a straight line in graph is obtained (Figure-6).

Kinetics of extraction of metal ions with ionophore S-IV:

A very different trend of extraction is observed in the results of kinetics of extraction of metal ions (Co^{2+}, Cu^{2+} and Zn^{2+}) with ionophore S-IV. In case of extraction of Co^{2+} and Zn^{2+} ions by ionophore S-IV, a rapid increase in the rate of extraction is observed within the first 180 minutes and 210 minutes respectively, after that it attends the equilibrium position. After approximately 30 minutes time interval a decreases in the rate of extraction is observed (Figure- 8 and 10). The decrease in the rate is assumed due to the back extraction process. Because the complex formed in the liquid membrane is quite unstable in nature. This nature is similar to the nature of biological membrane process[8].

In case of kinetics of extraction of Cu^{2+} ions with S-IV a rapid increase in rate of extraction is observed upto 240 minute at room temperature (27 ^{0}C) (Figure-9).

Thus, the time of attending maximum rate is different for different cations. From the results, it is clear that it is important to investigate the rate at which the solute is transferred between two phases. It is also observed that by an alteration of contact time it is possible to alter the selectivity of the extraction.

The rate of extraction of Co^{2+} and Ni^{2+} ions are much greater than the rate of extraction of Cu^{2+} ions with ionophore S-I. This selectivity is depends upon the rate of ligand exchange at these metal centers.

The rate of extraction of Zn^{2+} is greater than Co^{2+} and Ni^{2+} ions with ionophores S-III and S-IV.

The study demonstrates that the extraction efficiency of an ionophore to extract a specific cation across a liquid membrane depends on rate of uptake. A lipophilic envelope is formed around a cation through ionophore by using donor sites to extract in to organic membrane. The study demonstrate that S-I has shown to be suitable carrier ability

for extraction of Co^{2+} and Ni^{2+} over Cu^{2+} and Zn^{2+}. Ionophores S-III and S-IV have shown to be suitable carrier ability for extraction of Zn^{2+} over Co^{2+} and Ni^{2+}.

Table – 1 Kinetics of extraction of Metal cation by Ionophore S-I at (480nm)

Metal Salt concentration = 1.0×10^{-1} M
Concentration of Ionophore (S-I)= 1.0×10^{-4}M, and for $ZnSO_4$ Concentration of Ionophore=1.0×10^{-6}M

Times in min	Abs	log x	Abs	log x	Abs	log x	Abs	log x
	$Co(NO_2)_3$+ S-I		$NiSO_4$+S-I		$Cu(NO_2)_3$+S-I		$ZnSO_4$+S-I	
0	2.333	0.3679	2.333	0.3679	2.333	0.3679	1.47	0.1673
30	2.376	0.3758	2.339	0.3690	2.359	0.3727	1.54	0.1875
60	2.429	0.3854	2.343	0.3697	2.462	0.3912	1.90	0.2787
90	2.431	0.3857	2.345	0.3701	2.467	0.3921	2.00	0.3010
120	2.476	0.3937	2.348	0.3706	2.468	0.3923	1.99	0.2988
150	2.487	0.3956	2.352	0.3714	2.468	0.3923	2.20	0.3424
180	2.489	0.3960	2.358	0.3725	2.470	0.3926	2.34	0.3692
210	2.501	0.3981	2.367	0.3741	2.410	0.3820	2.02	0.3053
240	2.501	0.3981	2.391	0.3785	-	-	1.73	0.2380

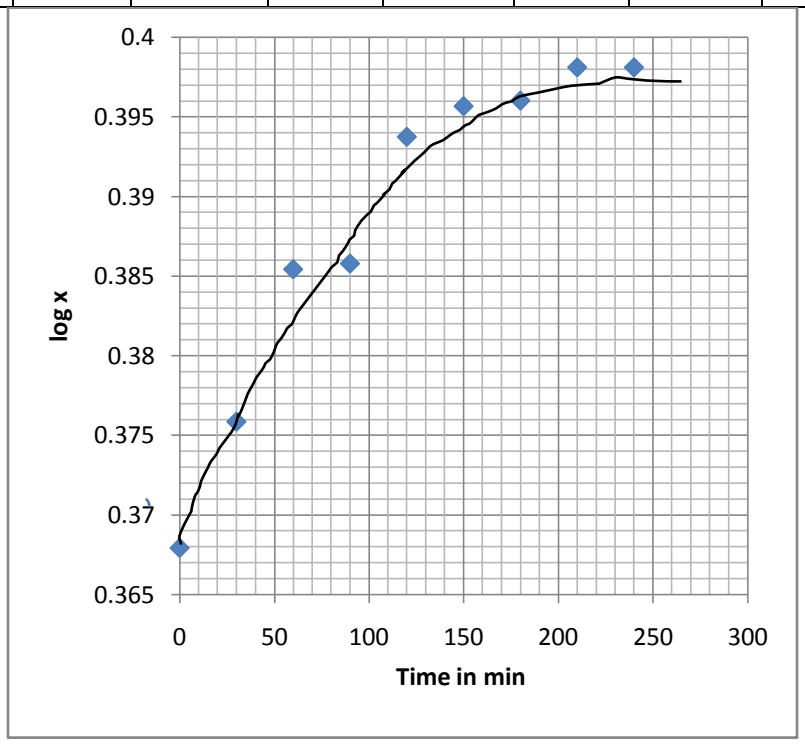

Figure – 1: log x vs. Time in min ($Co(NO_2)_3$+ S-I)

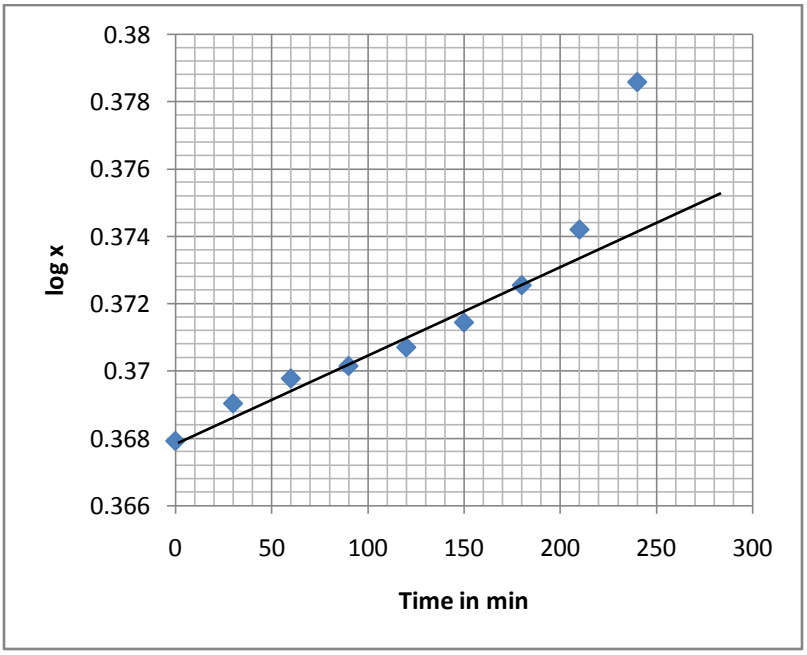

Figure – 2: log x vs. Time in min ($NiSO_4$+S-I)

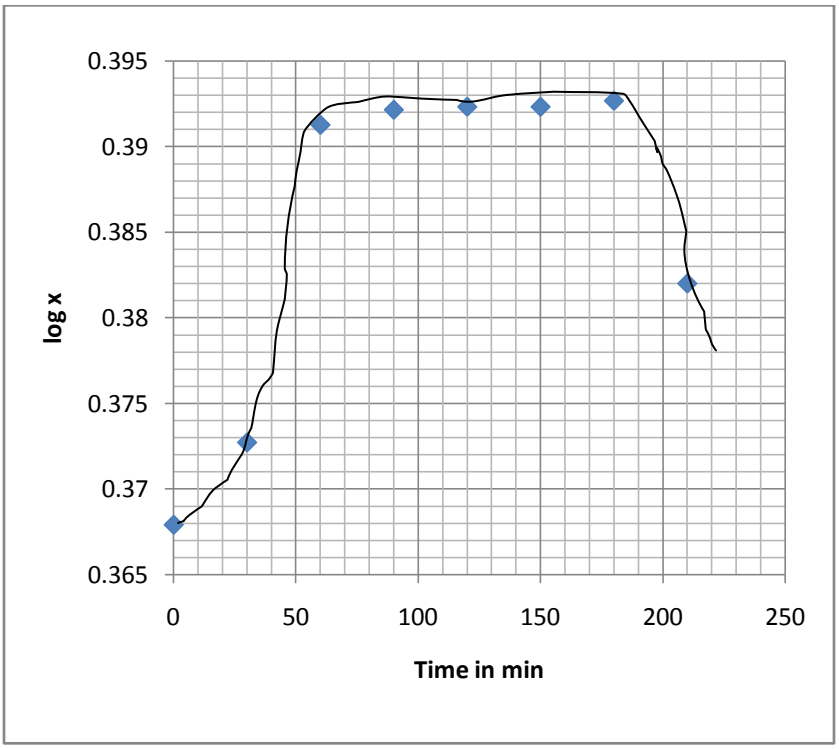

Figure – 3: log x vs. Time in min ($Cu(NO_2)_3$+S-I)

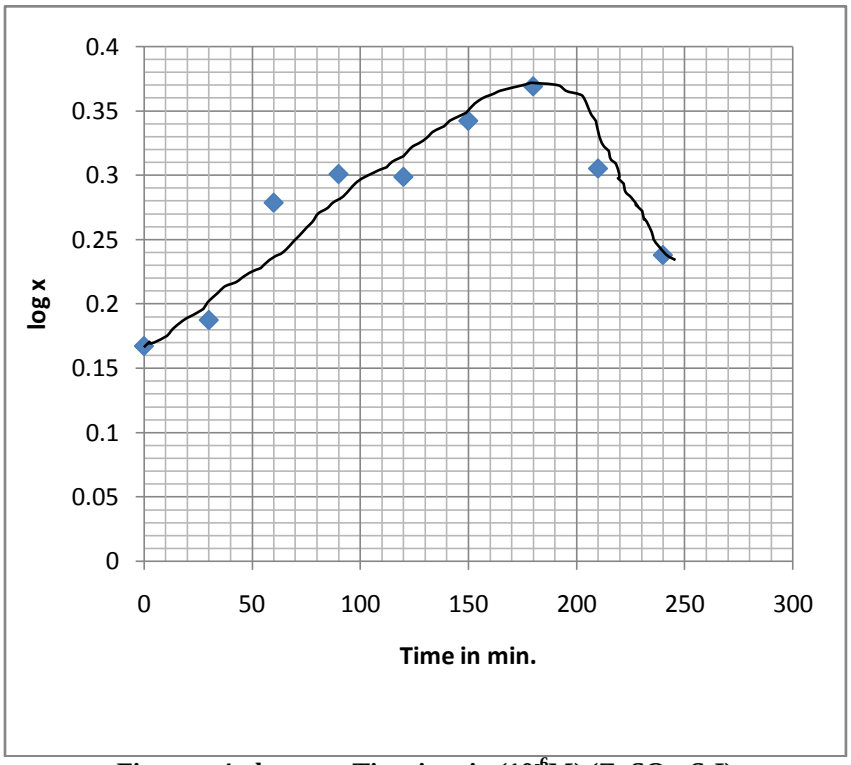

Figure – 4: log x vs. Time in min (10^{-6}M) ($ZnSO_4$+S-I)

Table: 2 Kinetics of Extraction of Metal cation by ionophore S-III (515nm)

Metal salts concentration ($NiSO_4$), $ZnSO_4$= 1.0×10^{-1}M, and $Co(NO_2)_3$= 1.0×10^{-2}M
Ionophore concentration (S-III) = 1.0×10^{-5} M

Times in min	Abs	logx×10^{-1}	Abs	logx×10^{-1}	Abs	logx×10^{-1}
	$Co(NO_2)_3$ + S-III		$NiSO_4$+S-III		$ZnSO_4$+ S-III	
0	5.35	0.7283	5.30	0.7242	5.35	0.7283
30	5.86	0.7678	5.35	0.7283	5.39	0.7315
60	5.99	0.7774	5.40	0.7323	5.45	0.7363
90	6.23	0.7944	5.42	0.7339	5.48	0.7387
120	6.29	0.7986	5.48	0.7387	5.53	0.7427
150	6.30	0.7993	5.50	0.7403	5.55	0.7442
180	6.32	0.8007	5.52	0.7419	5.56	0.7450
210	5.96	0.7752	5.55	0.7442	5.60	0.7481
240	5.41	0.7331	5.62	0.7497	5.55	0.7442

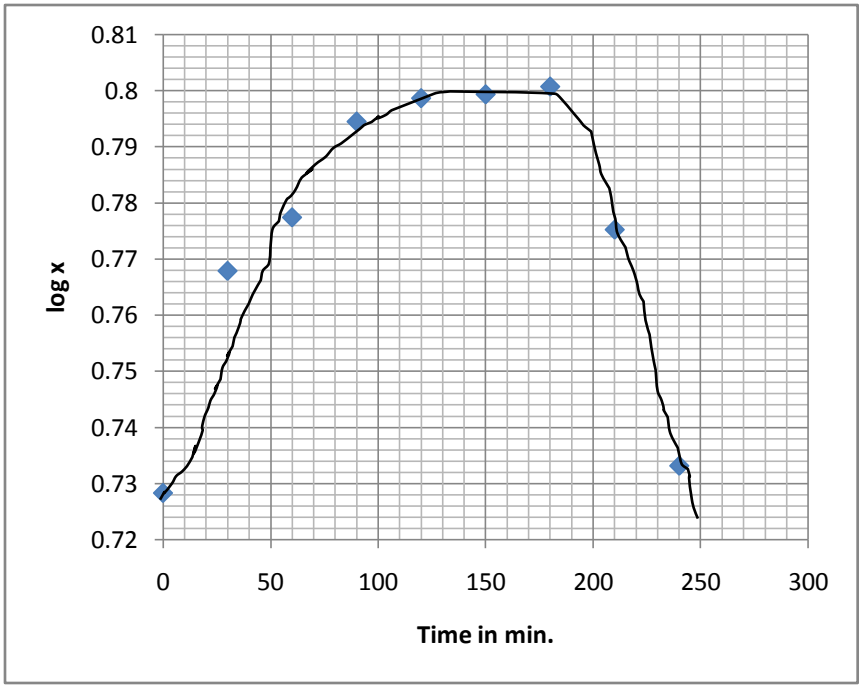

Figure – 5: log x vs. Time in min ($Co(NO_2)_3$ + S-III)

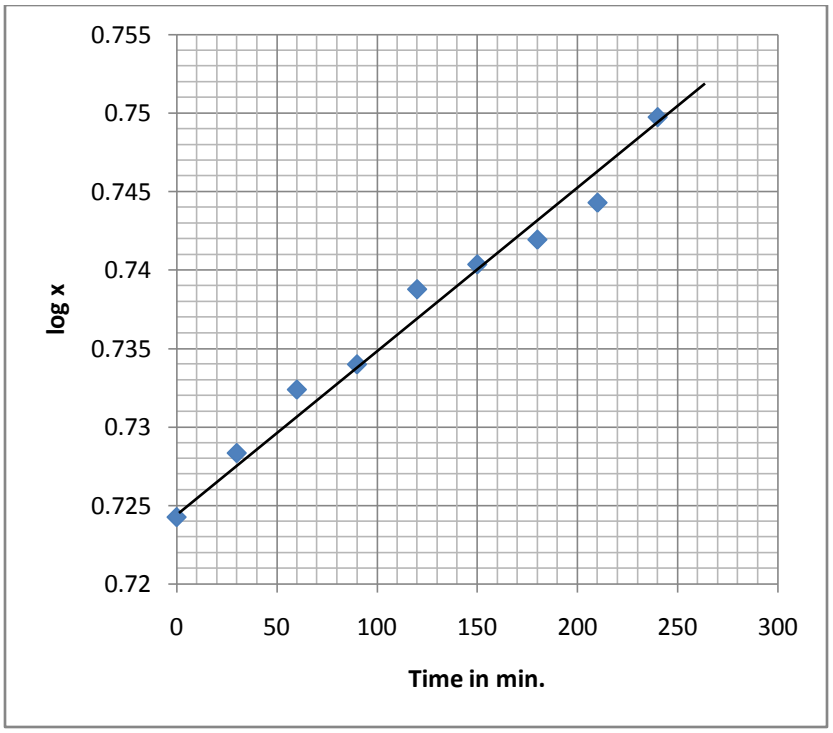

Figure – 6: log x vs. Time in min ($NiSO_4$+S-III)

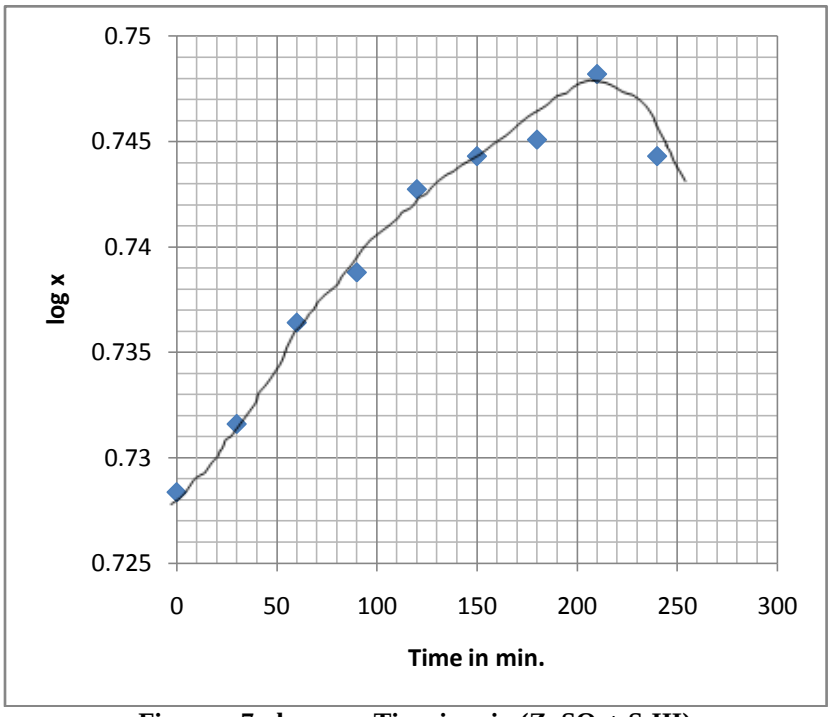

Figure – 7: log x vs. Time in min ($ZnSO_4$+ S-III)

Table: 3 Kinetics of Extraction of Metal cation by ionophore S-IV (525nm)

Metal salts concentration $Co(NO_3)_2$, $Cu(NO_2)_3$ = 1.0×10^{-1}M and for $ZnSO_4$= 1.0×10^{-2}M

Ionophore concentration (S-IV) = 1.0×10^{-5} M

Times in min	**Abs**	**log x×10^{-1}**	**Abs**	**log x×10^{-1}**	**Abs**	**log x×10^{-1}**
	$Co(NO_2)_3$+ S-IV		**$Cu(NO_2)_3$+ S-IV**		**$ZnSO_4$+S-IV**	
0	4.35	0.6384	4.35	0.6384	4.35	0.6384
30	4.35	0.6384	4.39	0.6424	4.37	0.6404
60	4.37	0.6404	4.4	0.6434	4.41	0.6444
90	4.39	0.6424	4.41	0.6444	4.44	0.6473
120	4.40	0.6434	4.45	0.6483	4.50	0.6532
150	4.40	0.6434	4.48	0.6512	4.55	0.6580
180	4.41	0.6444	4.5	0.6532	4.61	0.6637
210	4.40	0.6434	4.55	0.6580	4.66	0.6683
240	4.39	0.6424	4.62	0.6646	4.63	0.6655

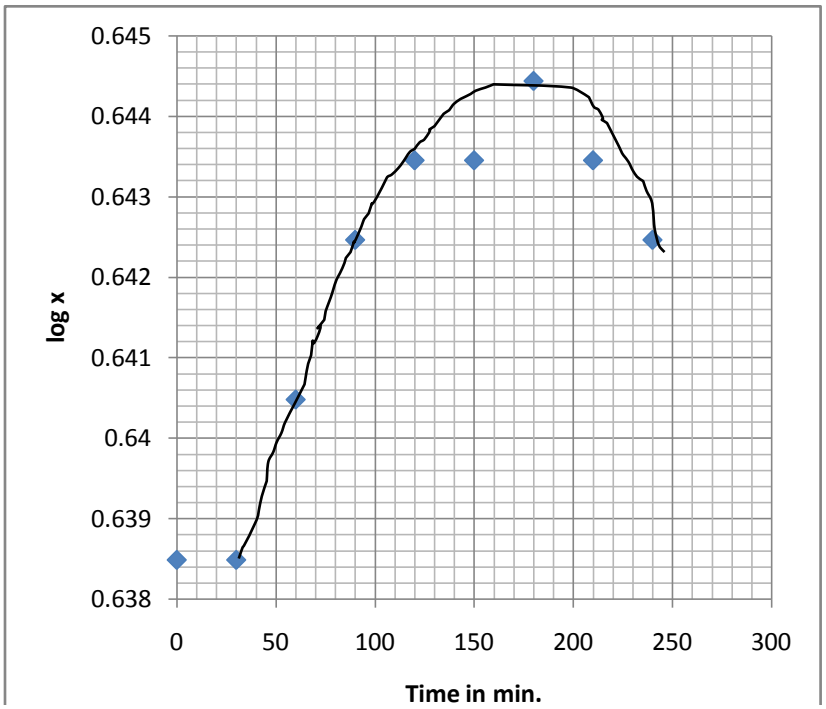

Figure – 8: log x vs. Time in min ($Co(NO_2)_3$+ S-IV)

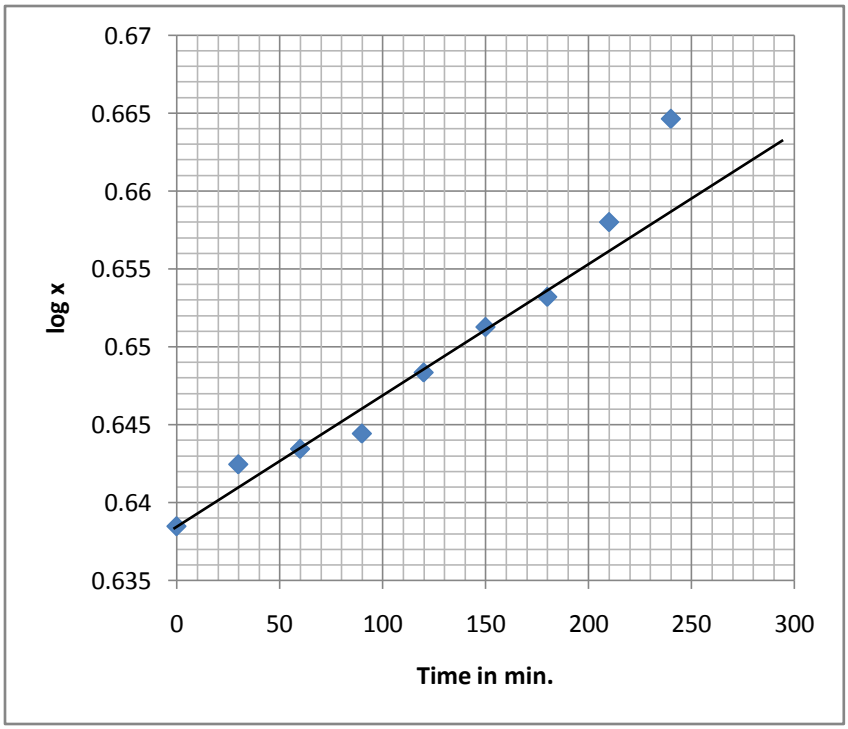

Figure – 9: log x vs. Time in min ($Cu(NO_2)_3$+ S-IV)

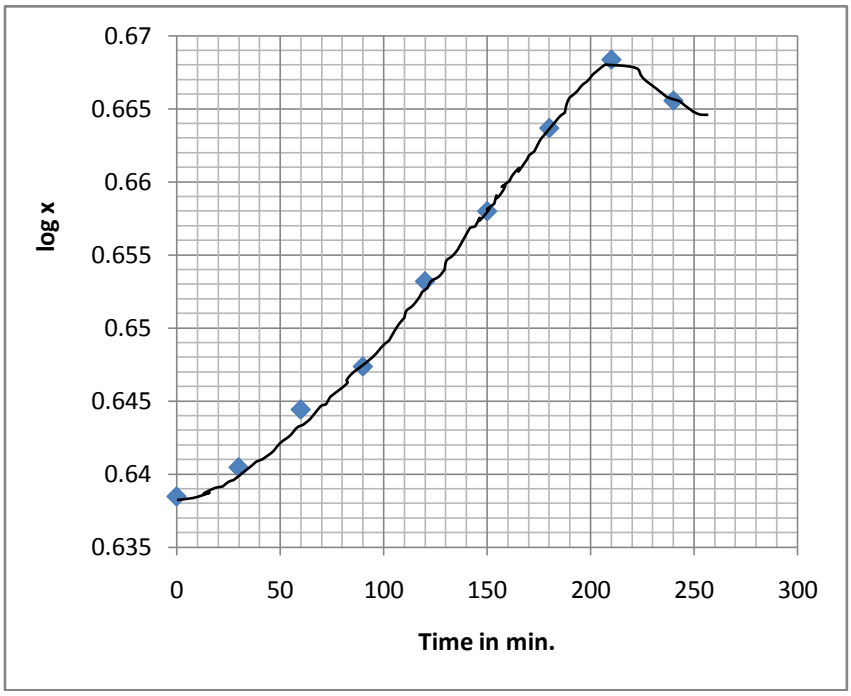

Figure – 10: log x vs. Time in min ($ZnSO_4$+S-IV)

Conclusion

From the results of experiment performed on the kinetics of extraction, it has been observed that during the process of extraction the performance of extraction increases with the time of extraction and maximum extraction reached at particular time for particular metal ion and then decreases due to the back extraction process. The results reported are in good agreement with the similar type of work performed by the other workers[6,7,8].

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References

1. Y. Yulizar, A. Ohashi, H. Nagatani and H. Watarai, *Analytica Chimica Acta*, 2000, 491, 107.
2. P. R. Chiarizia, *The Kinetics of Metal Solvent Extraction*, *Crit. Rev. Anal. Chem*., 1980, 10:1.
3. K. Kundo, K. Kita, F. Nakashio, *Journal of Chemical Engineering of Japan,* 1981**,** 14(1), 20.
4. M. Bhatnagar and U. Sharma, *J. Sci. I. R. Iran*, 13, 2002, 2.
5. M. Mimrot, J.Tomar and U. Sharma, *Main Group Metal Chemistry*, 31(6), 2011, 289.
6. C. Basualtoa, J. Marchese, F. Valenzuelaa and A. Acosta, *Talanta*, 59, 2003, 999.
7. P. Raizada, V. Vyas and U. Sharma, *Indian J. Chem. Technol*., 17, 2010, 267.
8. C. H. Nielsen, *Anal. Bioanal. Chem*., 395(3), 2009, 697.