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دراسة في الاستخلاص المذيبي للمعقد ثايوسانات الزئبق مع DB18C6

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الخلاصة

تم استخلاص ايون الزئبق كزوج ايوني مع ايونات الثايوسيانات باستخدام المركب الايثري DB18C6 ودرس تاثير العوامل المؤثرة في طبيعة هدا النظام من الاستخلاص . هذه العوامل التي تؤثر بنسب استخلاص الزئبق هي عامل الدالة الحامضية وعامل تركيز ايون الثايوسيانات وعامل طبيعة وتركيز الايون الموجب وتركيز الايون الموجب وتركيز الكاشف العضوي ودرجة الحرارة ونوع المذيب العضوي .بينت النتائج امكانية اجراء الاستخلاص عند تثبيت عوامل مهمه هي العوامل اعلاه.

كذلك تم دراسة امكانية استخلاص الزئبق (II) باستخدام مركبات اخرى مثل 18C6.DCH، 15C5 , BC6 وكربتاند-222 . تم دراسة تكافؤية الاجزاء المستخلصة باستخدام طريقة الميل ومطيافية الاشعة تحت الحمراء والاشعه الفوق البنفسجية والاشعه المرئية . واجراء تحليل CHNباستخدام جهاز تحليل CHN ودرجة الانصهار وجميع التحاليل اكدت وجود الصيغة [k+.CE]2[Hg (SCN)4]

الكلمات المفتاحية :الأستخلاص المذيبي ،الزئبق الأثيرات التاجية ، تحليل الكاربون الهيدروجيني والنتروجيني

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Study on Solvent Extraction of Mercury Complex With DB18C6

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Abstract

Mercury(II) ion is extracted as ion pair with thiocyanate using DCM .The effects of different parameters affecting the ease of extraction are determined . These parameters are pH ,Thiocyanate ion concentration ,type and concentration of the counter cation concentration of the reagent , temperature and type of solvents .Other crown ethers (15C5 DB24C , DCH18C6 and 18C6 and cryptand- 222 are investigated as extracting reagents using slop analysis method UV-visible and IR spectrometry .CHN analysis and melting points determination are perfored for comlex analysis .All these investigations indicated the formula [k+CE]2[Hg (SCN)4]-2.

Key words: solvent extraction ,mercury ,crown ethers CHN analysiss

Introduction

Separation methods are the important step to be taken before determination of any chemical species. The best separation ensure the accurate determination .Various principles are employed in separating the species in the form and physical static suitable for the method of determination. Solvent extraction stands as the best technique for separating trace and large amounts of chemicals since it is fast , Simple , low cost and selective.

Mercury(II) form number of complexes and coordination numbers and stereo structures .It forms linear complexes with coordination number 2 and square planer complexes with coordination number 4. Octahedral complexes of Hg (II) are less common[1].The bonds between Hg (II) and ligands show covalent properties when the coordination number is tow[2]. Hg(II)is classified as soft base and chloride ion as hard base . Hg (II) form stable complexes with ligands coordinating through sulfur ,nitrogen and oxygen[3]. Titanium can not be extracted form nitric acid meditm using oxygenic solvents and TBP[4]. 1.10.phenanthroline iron(II) :2-dipyridyl iron (II)are used for extracting acids [7] and chelate compounds[8],dithiocarbamate [9], Diethyl ammonium diethyl dithiocarbamate [10] and dithiazone [11] are used for extraction of Hg (II) . Crown ethers with their chemical variety are employed for extracting many elements on laboratory[12].

In the present work DB18C6 and other crown ethers are investigated as extractants for Hg(II).and the effect of various related parameters are investigated.

Materials and Methods

Chemicals and reagents:

All chemicals and reagents used are of A.R. grade supplied and employed in the preparation process . M and B Merck and other companies . Mercury standard solution is prepared by dissolving 1.713gm of Hg (NO3)2- H2O in liter of doubly distilled water . The diluted solutions of mercury were freshly prepared due to instability .Doubly distilled water is washed with dithiazone in CC14 before using. All other chemicals are used without further purification.

Instrumentations

1.Single beam UV-visible spectrophotometer 4050-012.

2.Double beam UV-visible spectrophotometer shimadzu-160.

3.Temperature control circulator Churchill chiller.16.00139-40.

4. PW-9418 pH meter .philips.

5. Melting point measuring system(England).

6. Electrical shaker. Scientifically supplies(W.Germany).

7.CHN Elemental Analyzer.EA-1108.

Mercury measurement

Orange yellow complex is formed at pH 2.5 by shaking the aqueous solution with dithizone solution in CCl4.

The organic phase is washed and the measurement is carried out at max=485 nm using UV-visible spectrophotometer.

Results and Discussions

The calibration curve for the determination of Hg(II).using dithiazone method is determined . It gave a linear relation on the concentration range of 4.98 x10-7 - 2.94x10-5M (1-50ug). On evaluating the effect of KSCN concentration on D value of Hg extraction with DB18C6 in DCM form a medium of pH=3. Results indicated increasing of D value till 1.6 MKSCN , after which D value decreases. This attributed to the extraction of the species [K+SCN][SCN]. Fig.(1) the best pH for extracting Hg(II) is found to be 2.5 although D value is constant over pH range 3-7. At lower pH the species [H+CH] [SCN^-] increases. Table (1).

D value is found to be increasing with increasing DB18C6 concentration in DCM. The relation between log D and log [DB18C6] is presented in fig. (2). The slope of the straight line obtained is 1.82 the value which predict the extracted species [K+ CE]2 [Hg (SCN)4]-3 with a little con the extraction system is carried out at acidic medium (HCl) The species centration is of [K+CE] [HG(SCN)3] the dominating species is since [H+CE] 2[Hg(SCN)4]-2 are extracted.

Increasing of Hg (II) concentration gave increasing D value for Hg (II) . Plotting of log D against log [Hg] gave a straight line with a slope of 0.9. This means that the contribution of Hg(II) in the extracted species is constant fig.(3). Ten minutes is found to be the best time of equilibration for the system.

Using of different organic solvents indicate that nitrobenzene is the best .Plotting of log D against log ∑ gave a straight line while of log D versus 1/∑.Gave two linear relations due to the presence of more then two species .fig.(4).Table (2,3) show D values for the extraction of Hg (II) using different crown ethers it can seen that DCH18C6 is the best due to matching between linic raddi and cavitt suize of the crown ether (K+ionic raddi is 2.66A0).

Using different salts of SCN ion gave increasing D values in the order KSCN≥RbSCN≥NaSCN=Cs SCN.

Performing the extraction at different temperatures indicated exothermic extration in the presence of K+ and Cs+ and endothermic reaction Na+ Rb + fig.(5). Slope analysis indicated that Hg:DB18C6 ratio is :2.[K+CE]2[Hg(SCN)4]-2.This ratio is supported by mole ratio method tablel (3). Substoichiometric exraction also supported this ratio fig (7).

Using of chloride ion instead of thiocyanatc ion gave no extraction .UV- visible and IR spectra supported the predicted formula (max DB18C^=250.max [K+CE]2[Hg(scn)4]-2=CHN analysis gave the following results which is also in accordance with theoretical calculations table (4).

KOH was found to be effective in back extracting Hg(II) . It is found that 2.5M of KOH decreases the D value to 0.23. Cryptand 222 in nitrobenzene is used for the extraction of Hg(II) as thiocyanate and chloro complexes . Thiocyanate complex with cryptand -222 was promising while that of chloride is not.

Recent advances in the solvent extraction of mercury(II) with calivareneo and crown ethers [13] , Extraction of mercury(II) with dichloro18 crown 6 and its applications in the treatments of industrial wastes [14], and the complexes of mercury (II) cyndates of crown ethers in dimethyl sulfoxide [15].

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Table(1): Effect of pH on D value of Hg(II).

PH	D value
1	2.72
2	2.78
3	2.84
4	2.88
5	2.86
6	2.84
7	2.80

Table (2): D values of Hg using different crown ethers.

Crown ether	D value(Hg)	Cavity size
15C5	1.72	1.7–2.2
18C6	3.27	2.6–3.2
DCH18C6	4.11	2.6–3.2
DB18C6	2.95	2.6–3.2
DB24C8	1.56	4.5–5.6

Table(3): Mole ratio method.

M:DB18C6	D value
0.668	0.05
1.3336	0.19
2.005	0.46
2.673	0.55
3.341	0.59
4.010	0.62
4.678	0.64
5.346	0.66

Table (4): CHN analysis and melting points determination

	C%	H%	N%	m.p.C
DB18C	65.21 Theo	6.92% Theo	–	195
DB18C	66.68 exp	6.66 exp	–	
[K+CE]2Hg(SCN)4]2–	40.01 Theo	4.72 Theo	3.87 Theo.	182
[K+CE]2Hg(SCN)4]2–	42.91 exp	3.90 exp	4.55 exp.	

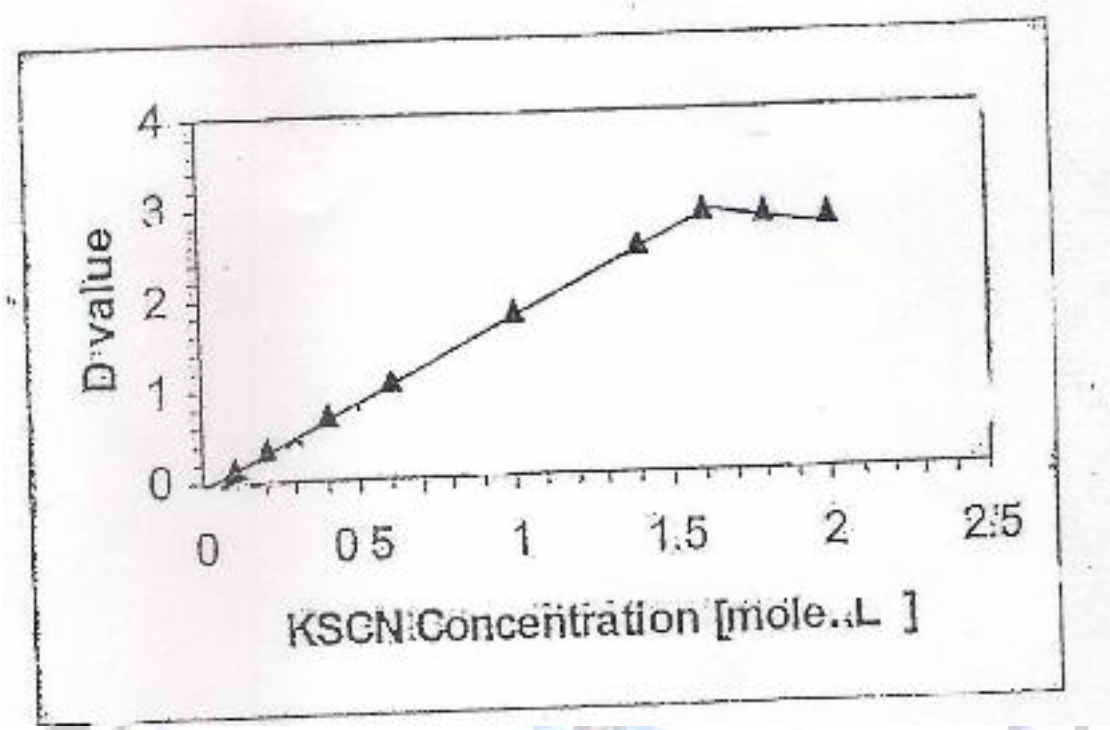

Fig. (1): D Values of Hg (II) extraction as a function of KSCN concentration

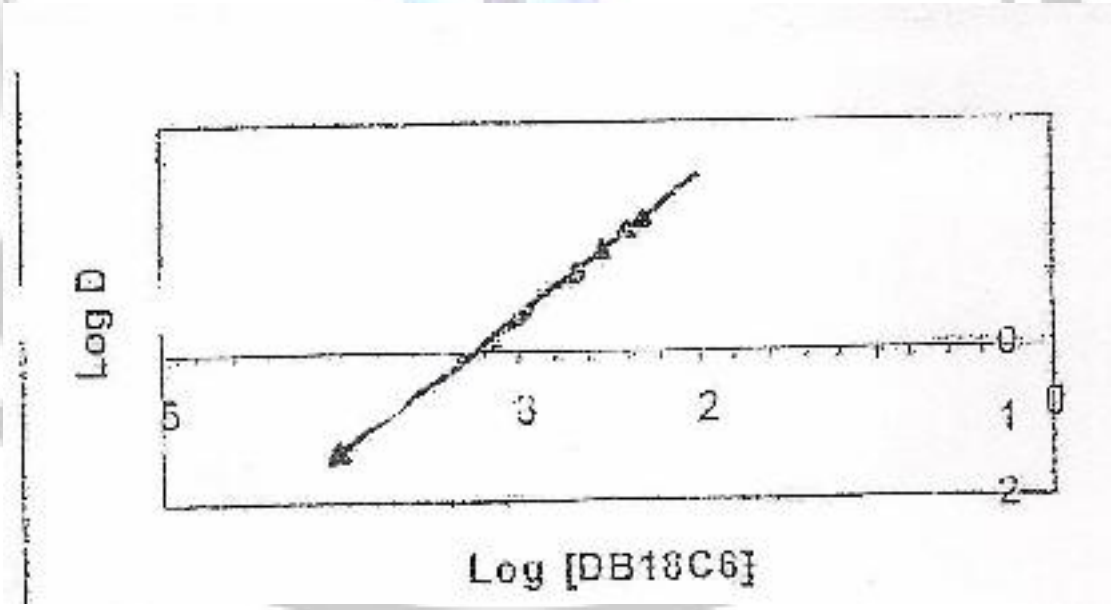

Fig .(2):log D of Hg (II) extraction Vs. log[HDB18C6]

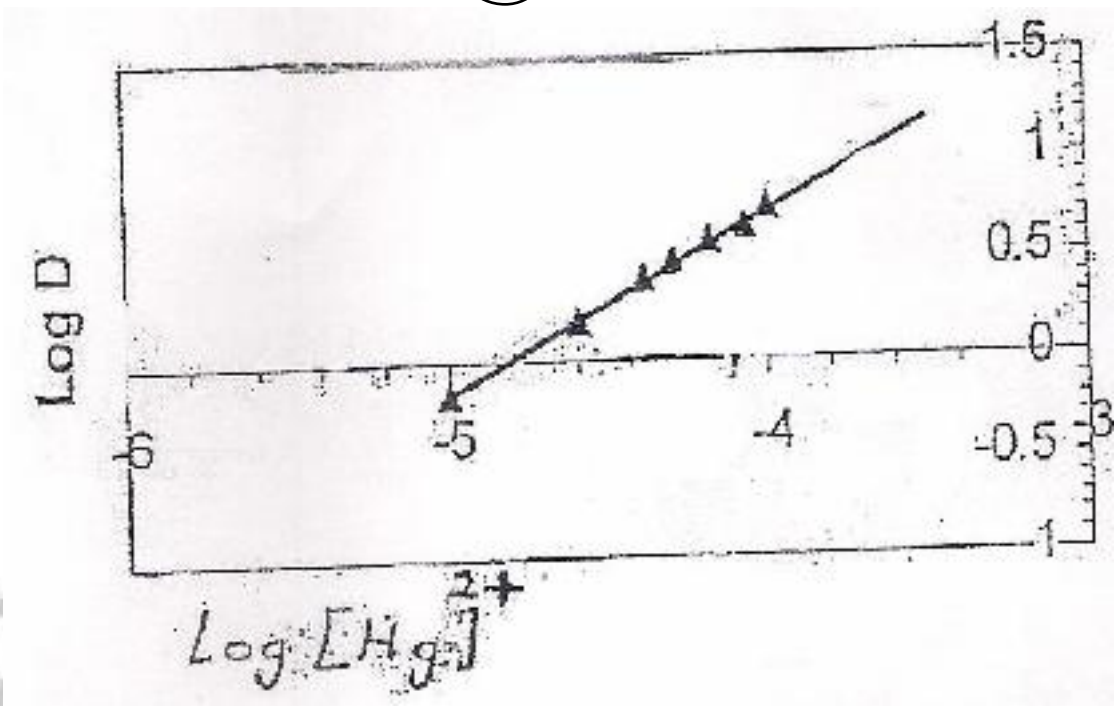

Fig. (3): log D of Hg (II)extraction Vs.log$[Hg]^{2+}$ concentration

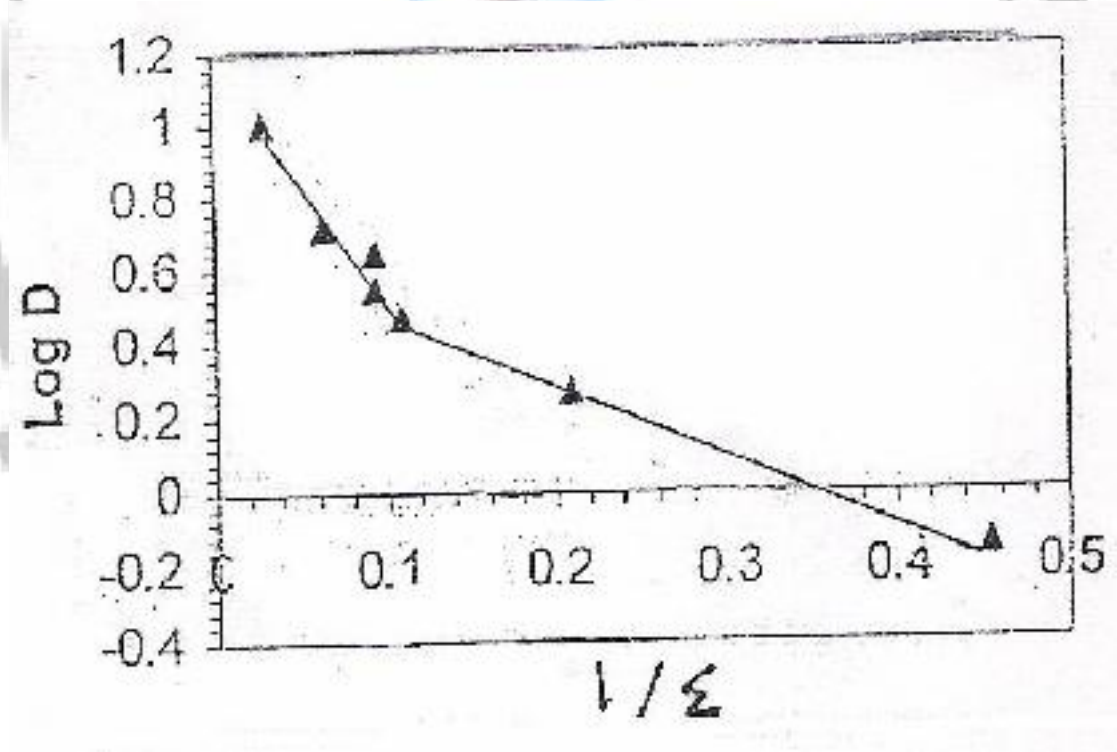

Fig. (4): Log D of Hg (II)extraction as afunction of 1/∑ of the solvent

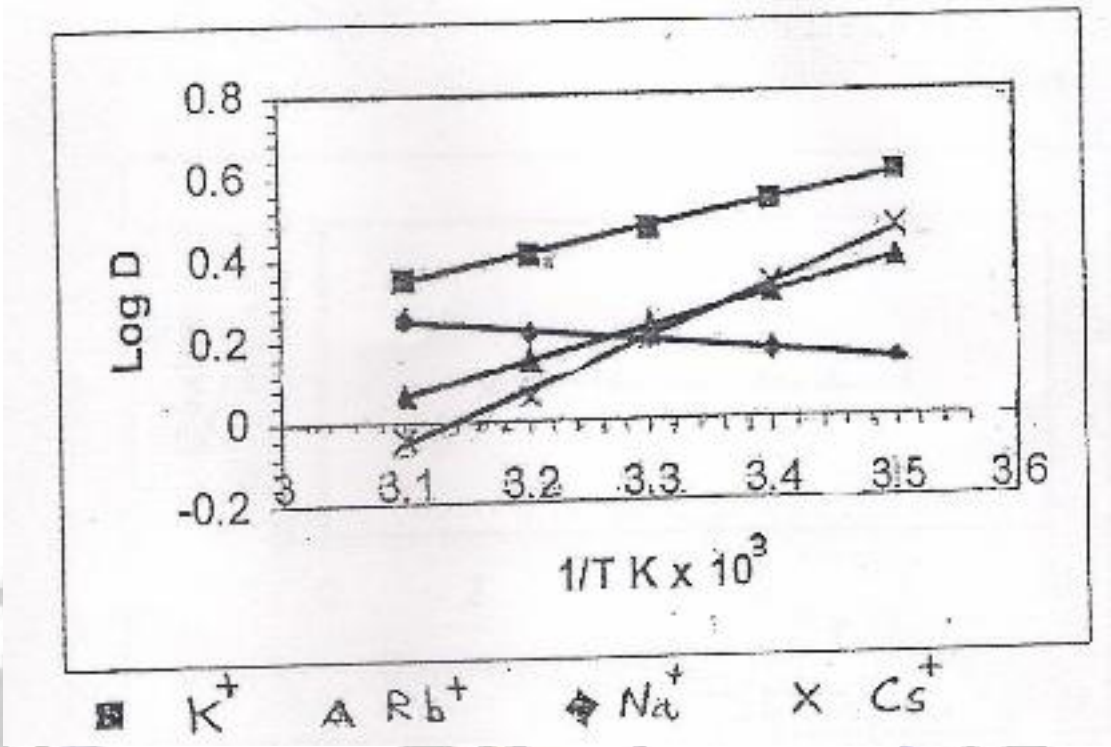

Fig.(5) : Log D as a function of temperature in the presence of different cations

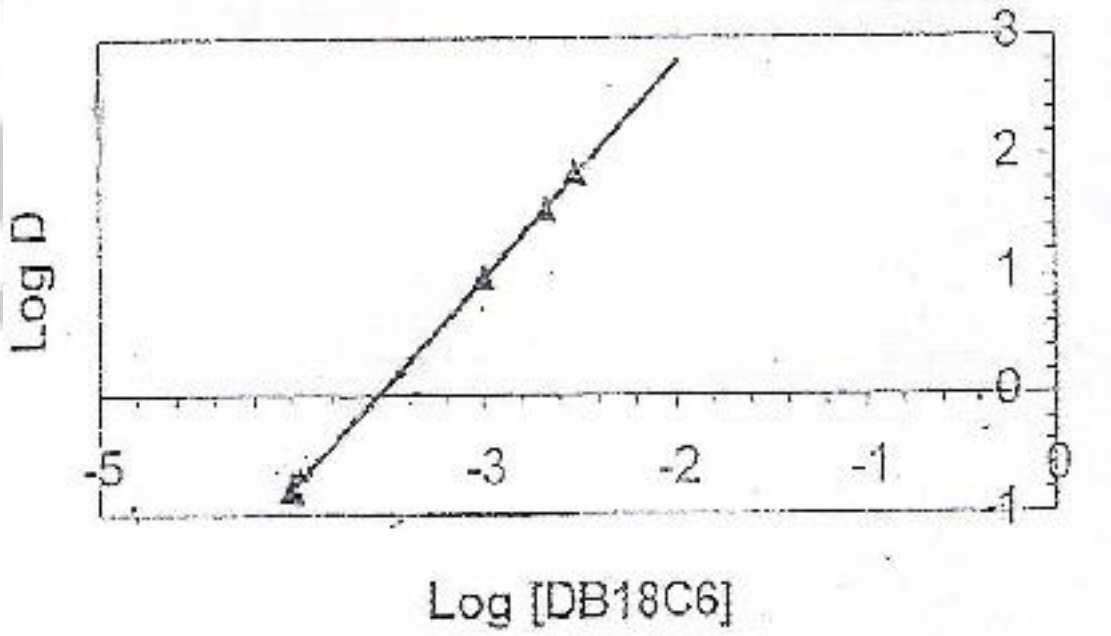

Fig . (6): slope analysis

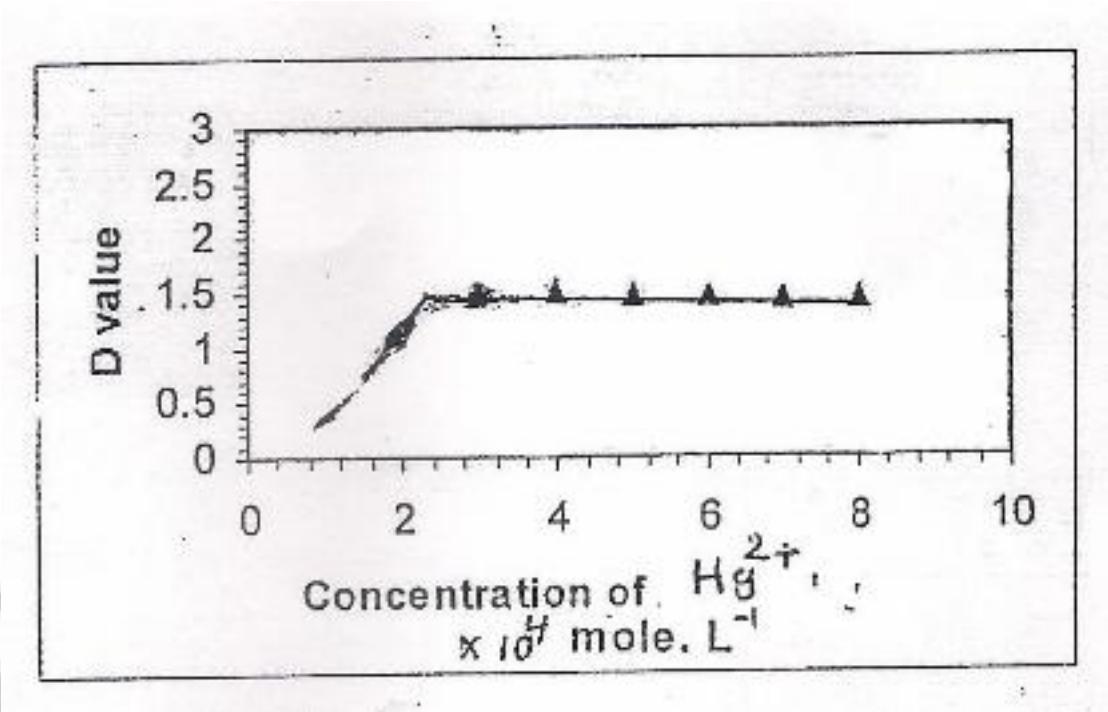

Fig.(7): mole ratio method