

Separation and Spectroscopic Determination of Ge(IV) as an Ion Pair Association Complex Using DB18C6 Ligand

¹Safa Majeed Hameed, ²Sahar Aqeel Hussain, ³Mohammed Alaa Abdulzahra, ⁴Fawzi Yahya Wadday
¹Department of Chemistry, Faculty of Education for Girls, University of Kufa, Al-Najaf-54001, Iraq.
²Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Kufa, Al-Najaf-54001, Iraq.
³Department of Pharmacy, Al-Amal College for specialized medical Sciences, Karbala-56001, Iraq.
⁴Department of Chemistry, Faculty of Science, University of Kufa, Al-Najaf-54001, Iraq.
Safaa.alhassani@uokufa.edu.iq¹, sahar.alaasam@uokufa.edu.iq²
organicmohammed@gmail.com³, fawzialmuwashi@uokufa.edu.iq⁴

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Summary: A solvent extraction was applied using liquid ion exchange as a sensitive method to extract Germanium (IV) as anion complex $K[GeO_2(OH)_2]^-$ from basic media of KOH by used DB18C6 as a ligand dissolved in chloroform to form the ion pair association complex $K-DB18C6^+; K[GeO_2(OH)_2]^-$, the maximum wavelength of the extracted complex was $\lambda_{max}=290nm$, and molar absorptivity $1.269 \times 10^3 L/mol.cm$. the Beer's -lambert law was adhered to within the specified range (1-20)ppm. The limits of detection and quantity were 0.034 and 0.102 ppm, respectively. The research studied optimal conditions of extraction efficiency, such as KOH concentration, shaking time, methanol effect, and electrolyte effect. In addition, a new spectrophotometric method was utilized to determine the remain of Ge(IV) in aqueous solutions and to calculate its distribution ratio (D) using Janus green B. This method was more sensitive when comparing the results with previous studies. DB18C6 as a ligand was used to determine Germanium (IV) in some canned foods widely sold in Iraq.

Keywords: Complex, Solvent extraction, Ion pair association, Spectrophotometric method, Canned foods.

Introduction

Germanium compounds, including both inorganic and organic forms, are readily and almost completely absorbed by mammals when they enter the respiratory and gastrointestinal systems. Nevertheless, the occurrence of systemic toxicity caused by Germanium compounds is rare. The precise target or exact organs affected cannot be determined, however, often reported effects include nephropathy, neuropathy, and hepatotoxicity. Germanium compounds, though do not appear to be carcinogenic [1,2]. There are many methods to determine Germanium, such as atomic absorption spectrometry[3], voltammetry[4], spectrofluorometric[5]and spectrophotometry[6,7]. The level of Germanium ions can also be determined using phenyl fluorine as a complexing agent in different samples[8,9]. Ge(IV) was extracted from a sulfuric acid zinc solution using TOA(trioctylamine) as an extractant, $C_4H_6O_6$ (tartaric acid) as the complexing agent, $C_{12}H_{27}O_4P$ (Triisobutyl phosphate) as the improving reagent, kerosene as diluent and NaOH as the stripping agent[10]. Germanium and some heavy metals were extracted using Alamine336, Aliquat 336 and Cyanex 923. The germanium was exclusively extracted from a solution that included nickel, cadmium, cobalt, and zinc in every extraction system. The efficacy of germanium extraction by the given extractants follows the order:

Aliquat 336 > Alamine 336 > Cyanex 923[11]. The article presents a method for determining the concentration of Ge by sorption-colorimetric analysis[12]. This method involves using ion complexes of $GeMoO_4^-$ with triphenylmethane dyes. This study specifically investigates the absorption of ionic compounds formed by molybdogermanate and a strafloxin on filter paper. These techniques were then used to measure the concentration of germanium (IV) in coked coal, iron ore, and different water samples within the concentration range of 4×10^{-8} to 1×10^{-6} M[13].

Solvent extraction has become a very powerful method of separation, and it is widely used in various fields, such as hydrometallurgical industry, liquid waste treatment, and analytical separations[14,15]. This process involves the transfer of metal ions, cations, and anions from an aqueous phase to an organic phase through reversible chemical reactions[16,17].

The purpose of this study was to spectrophotometrically determine the level of Ge(IV) from aqueous solution to calculate distribution ratio D and the extraction of Ge(IV) as an anion from basic media using DB18C6[18]. This was followed by the separation and determination of Ge(IV) in different samples.

*To whom all correspondence should be addressed.

Experimental

Instruments and Materials

Biochrom Libra S60 spectrophotometer models sourced from the United Kingdom, as well as an electrostatic water bath imported from Germany.

Solutions: The Ge(IV) solution with a concentration of 1mg/mL was obtained by dissolving 0.1444g of GeO₂ (Merck 99.8%) in 100 mL of a 0.1M KOH solution, Dibenzo-18-crown-6 (DB18C6) (Merck) (1×10^{-2} M) prepared by dissolving 0.0360g in 100mL chloroform (Merck 99.98%), and Janus green B (1×10^{-2} M) was synthesized by dissolving 0.0511g (Merck 99.96%) in 100 mL distilled water. Additional viable alternatives were generated via the process of serial dilution using distilled water, resulting in a suitable final volume.

General Procedure [19]

Aqueous solution (5mL) containing 100 μ g of Ge(IV) in 0.8M KOH (pH>11.7).

1. Organic solution (5mL) containing DB18C6 (1×10^{-4} M) in chloroform.
2. Solution (2) was added to (1) and stirred for 10 minutes. The aqueous phase was later separated from the organic phase.
3. 5mL of JGB was later dissolved in water for the aqueous phase separated from step (3), and the solution stirred for 5min. After that, 5mL of chloroform was added to the solution and stirred for another 5min. After the separation had occurred, the absorbance of the organic layer at $\lambda_{\max} = 600\text{nm}$ was measured against chloroform as a blank. The calibration curve in Fig(3) was used to determine the remaining quantity of Ge(IV) ions in the aqueous solution after extraction. The Ge(IV) ions was later subtracted, and the distribution ratio D was calculated as the extraction efficiency parameter according to the formulae below:

$$D = \frac{[\text{Ge(IV)}]_{\text{org.}}}{[\text{Ge(IV)}]_{\text{aq.}}} \quad (1)$$

4. The absorbance of the organic phase separated in step (3) was measured at $\lambda_{\max} = 290\text{nm}$ against chloroform as a blank.

Results and Discussion

Spectroscopic Study

The UV-Vis spectrum for Ge(IV) ion as $\text{K}[\text{GeO}_2(\text{OH})_2]^-$ from KOH media showed

$\lambda_{\max} = 219\text{nm}$ in Fig. 1 for an extracted complex of Ge(IV) ion as $\text{K}[\text{GeO}_2(\text{OH})_2]^-$ complex anion with DB18C6. This is described in Fig. 2 which also shows the wavelength of maximum absorbance was equal to $\lambda_{\max} = 290\text{nm}$.

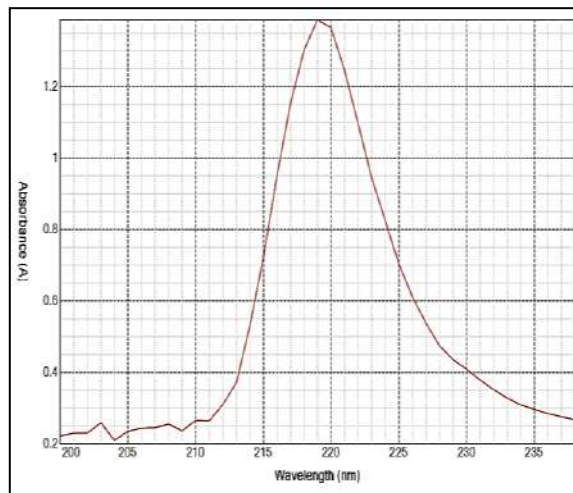


Fig. 1: UV-Vis. Spectrum of $\text{K}[\text{GeO}_2(\text{OH})_2]^-$

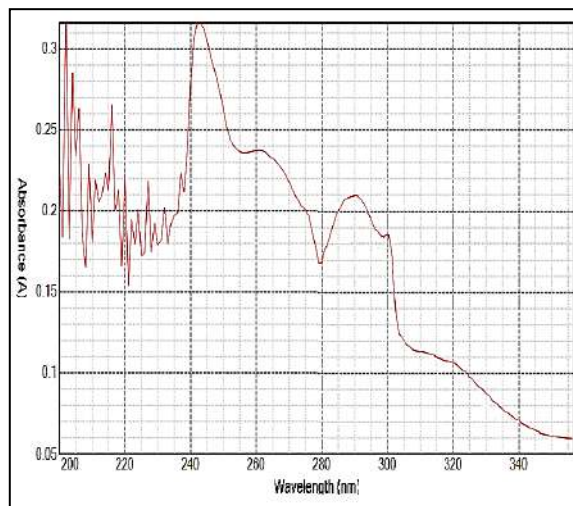


Fig. 2: UV-Vis. Spectrum of the extracted K-DB18C6^+ ; $\text{K}[\text{GeO}_2(\text{OH})_2]^-$ complex.

Preparation of the Calibration Curve for Ge(IV)

A series of 5mL aqueous solutions containing increasing concentrations of Ge(IV) in the range (5-100) μ g was prepared based on the general procedure. Post-separation of the two layers, the absorbance of the organic layer was measured at $\lambda_{\max} = 600\text{nm}$. The calibration curve was constructed by plotting the absorbance against the Ge(IV) concentration, as in Fig. 3.

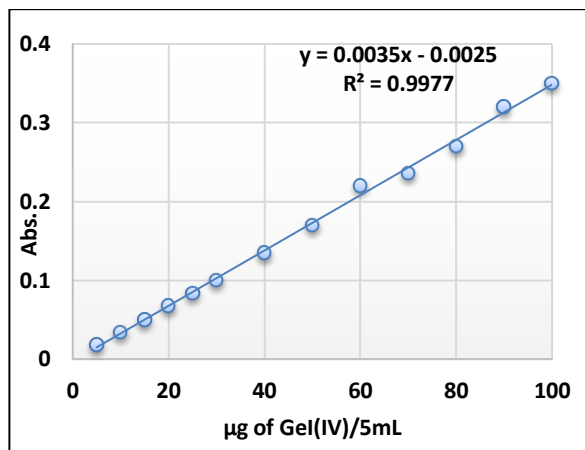


Fig. 3: Calibration curve of Ge(IV) by JGB.

Effect of Potassium Hydroxide

Varying concentrations of KOH from (0.1–1.0)M were used to dissolve GeO_2 to form $\text{K}_2[\text{Ge}(\text{H}_2\text{O})_6]$. The solution was used as an aqueous phase in accordance with the standard procedure. The outcomes are depicted in Figs. 4 and 5.

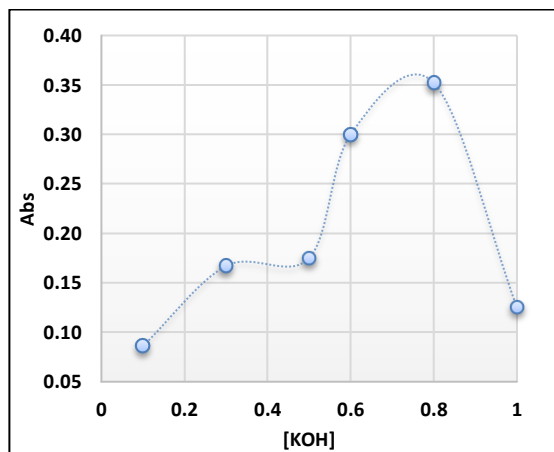


Fig. 4: Effect of [KOH] on complex formation and extraction.

The results showed that the optimum concentration of KOH for dissolving GeO_2 was 0.8M, which gave the highest concentration of $\text{K}[\text{GeO}_2(\text{OH})_2]^-$, the species $\text{GeO}_2(\text{OH})_2^{2-}$ will be predominant only at $\text{pH} > 11.7$ (at 25°C) [20] and the best extraction equilibrium to form an ion pair association complex with DB18C6.

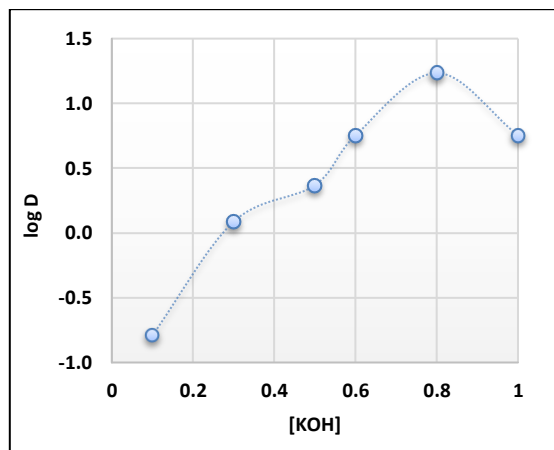


Fig. 5 Effect of [KOH] on the thermodynamic equilibrium for complex formation and extraction.

Effect of Shaking Time

In accordance with the standard procedure, the Ge(IV) extraction process was carried out at various shaking periods (5-30 min). The outcomes are depicted in Figs. 6 and 7.

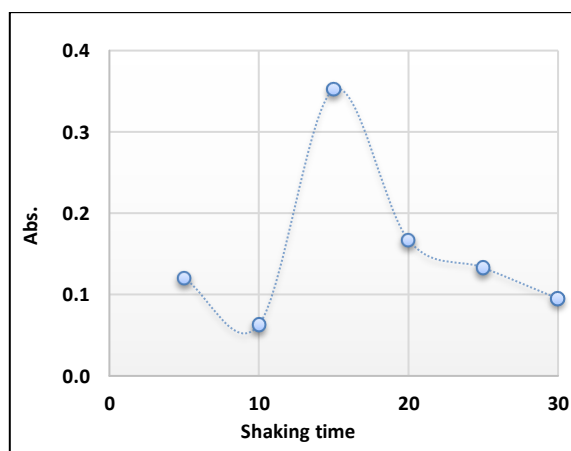


Fig. 6: Shaking time effect on the complex formation and extraction.

Based on the findings, it was determined that 15 minutes was the optimal shaking duration, which results in the best thermodynamic equilibrium for the creation of the ion pair complex and the extraction of high concentrations of the ion pair complex. Shaking time considers the kinetic energy for a transition of the species to the organic phase.

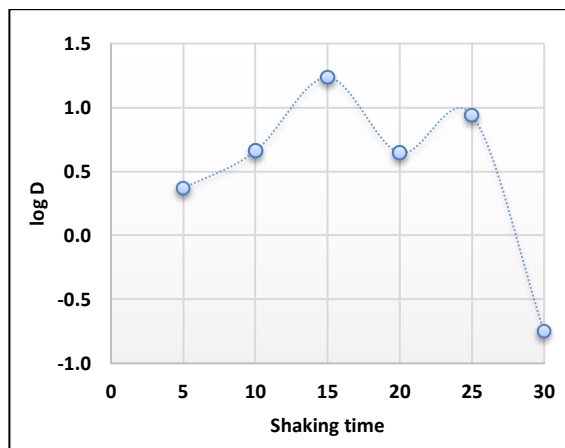


Fig. 7: Shaking time effect on the thermodynamic equilibrium for complex formation and extraction.

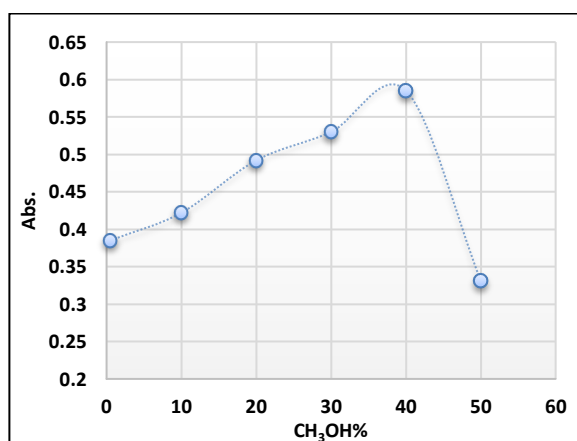


Fig. 8: Effect of methanol on complex formation and extraction.

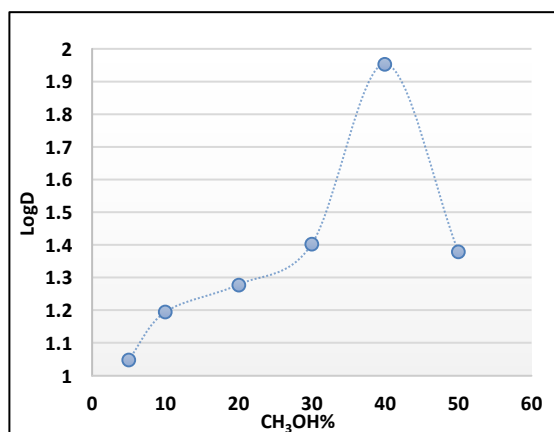


Fig. 9: Effect of methanol on the thermodynamic equilibrium for complex formation and extraction.

Effect of Methanol Presence

Aqueous solutions prepared based on the general procedure contain methanol in varying percentages. The results are shown in Figs. 8 and 9:

The results showed that 40% CH₃OH is the optimum percentage, and its presence increases the extraction efficiency. As a result of CH₃OH presence in aqueous solutions, Ge(IV) ions declined in polarity, which means that it destroys the hydration shell of Ge(IV) ions, which leads to an increase in K⁺-binding and ion pair association complex formation in the organic phase. A lower percentage of CH₃OH causes a decrease in extraction efficiency. Furthermore, if the CH₃OH% percentage is higher than the optimum, the extraction efficiency declines because there is a decrease in the polarity of the aqueous solution, as a result of which some of the DB18C6 is transferred into the aqueous phase, causing the ion pair complex in the organic phase to be less concentrated[21].

Effect of The Ionic Diameter of Cation

To show the importance of the agreement between the cavity size of DB18C6 and the ionic diameter of the cation used, an experiment was carried out by extracting Ge(IV) from 5mL aqueous solution containing 0.8M of alkali or alkaline earth metals as chloride salts and NH₄Cl. This is based on the general procedure. The results are shown in Table-1.

Table-1: The agreement between ionic diameter of cations and cavity size of DB18C6 (2.9 Å).

Cation	ID of cation Å	Abs. at $\lambda_{max}=290nm$	D
Li ⁺	1.20	0.285	6.761
Na ⁺	1.96	0.32	13.183
K ⁺	2.66	0.352	17.179
NH ₄ ⁺	1.40	0.222	5.623
Mg ²⁺	1.32	0.275	5.248
Ca ²⁺	1.98	0.28	6.309

Crown ethers have unfamiliar properties of forming complexes with alkali and alkaline earth cations. The stability of crown ether complexes has been ascribed to the best fitting of the alkali and alkaline earth cations with the cavity size of crown ether. The metal-crown binding was favorable by the best arrangement of (M-O) bonding to reach an optimal arrangement of oxygen donor atoms and electron-withdrawing groups in the crown ether molecule. It is clear from the results that K⁺ gives the highest absorbance and D values because it has the best fitting between the ionic diameter (K⁺=2.66) and cavity size of DB18C6 (2.9Å)[22].

Effect of Crown ether kind

Extraction of Ge(IV) was done using different crown ethers dissolved in chloroform, as detailed in the general procedure. The results are described in Table 2.

Table-2: Effect of crown ether type on extraction efficiency.

Crown ether	cavity size	Abs. at $\lambda_{\text{max}}=290\text{nm}$	D
DCH18C6	2.9Å	0.486	28.183
18C6	2.9Å	0.421	22.387
DB18C6	2.9Å	0.352	17.179
15C5	1.95Å	0.311	13.182
12C4	1.35Å	0.253	7.079

The affinity of the crown for K^+ depends on the cavity size of the crown, hydration of K^+ and thickness of the hydration shell. The stability of crown complexes is dependent on cation diameter and crown ether cavity size, solvent, and the presence or absence of functional groups, which may increase or decrease the binding and interaction effect. Cavity size is not the only influencing factor in which a cation could be complex. However, as a general rule, it provides a good idea of which crown ether can be used to form a complex with the target cation[22].

Thermodynamic study

Extractions of Ge(IV) were performed from aqueous solutions based on the established process and at different temperatures. The outcomes indicated that increasing the temperature to the optimum of 40°C increases both absorbance and D values, as shown in Fig. 10.

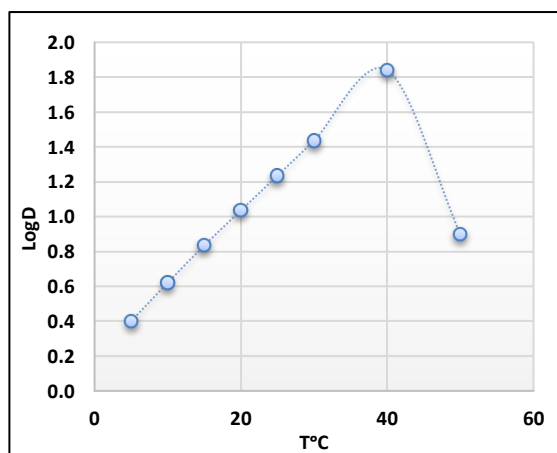


Fig. 10: $D = f(T\ ^\circ\text{C})$.

The extraction constant K_{ex} is calculated based on the following relation[21]:

$$K_{\text{ex}} = \frac{D}{[\text{Ge(IV)}][\text{DB18C6}]} \quad (2)$$

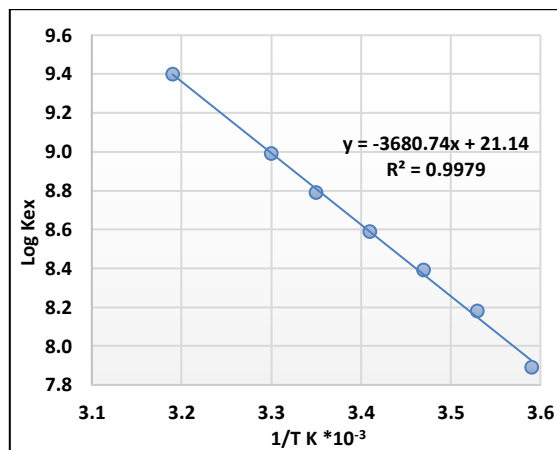


Fig. 11: $K_{\text{ex}} = f(T\ \text{K})$.

Plotting to $\log K_{\text{ex}}$ against $1/T\ \text{K}$ gives a straight line relation, as shown in Fig. 11. The slope of this straight line and thermodynamic relations[23] determined thermodynamics, as shown in Table 3.

Table-3: Thermodynamic data for the extraction Ge(IV).

Slope = $\frac{-\Delta H_{\text{ex}}}{2.303 R}$ (kJmol ⁻¹)	$\Delta G_{\text{ex}} = -RT \ln K_{\text{ex}}$ (kJmol ⁻¹)	$\Delta G_{\text{ex}} = \Delta H_{\text{ex}} - T \Delta S_{\text{ex}}$ (kJmol ⁻¹)
70.48	-56.32	405.11

The results showed a low value of ΔH_{ex} , which reflects the increased ions in the extracted ion pair association complexes as well as high stability in the complexes. It is important to note the large value of ΔS_{ex} , which indicates the dependence of the extraction on entropy to form the ion pair association complex. This also means the method is entropic in the region[24,25].

Organic Solvent Effect

Extraction of Ge(IV) from aqueous solutions was performed as a general procedure using different organic solvents to dissolve the extractant DB18C6. The results are shown in Table (4); organic solvent is significant in calculating the values of free energy for ionic transfer and ion association based on the Born equation[26].

$$\Delta G_t = \frac{Z^2}{2r} \left(\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right) \quad (3)$$

Z = ionic charge of Ge (IV), r = ionic radius of Ge (IV), ϵ_o = Dielectric constant of organic solvent, ϵ_w = Dielectric constant of water.

Association constant values K_A can also be calculated from the equation below[26]:

$$K_A = \frac{[KDB18C6^+; K[GeO_2(OH)]_2^-]_{org.}}{[K[GeO_2(OH)]_2^-]_{org.}[DB18C6]_{org.}} \quad (4)$$

Extraction constant values calculated from equation²⁴:

$$K_{ex} = \frac{K_A \cdot D [K[GeO_2(OH)]_2^-]_{org.}}{[K[GeO_2(OH)]_2^-]_{aq.}[DB18C6]_{org.}} \quad (5)$$

Finally, the free energy of extraction values was calculated from the equation[26]:

$$\Delta G_{ex} = -RT \ln K_{ex} \quad (6)$$

where: $T=25^\circ\text{C}$, $R=8.314 \text{ J/mole.K}$

The free energy values for ionic transfer $-\Delta G_t$ from aqueous to organic phase increases with decreasing dielectric constant. However, the association constant K_A values increase with the rising distribution ratio (D). The results indicated that there is no linear relation between the distribution ratio (D) and dielectric constant values of organic solvents. It also shows organic solvent structure increases extraction efficiency. The extraction constant K_{ex} and free energy for extraction ΔG_{ex} values did not show a linear relationship with rising or decreasing dielectric constant. Therefore, these results pointed to the role of organic solvents in the extraction process, which means the participation of organic solvents in the formation and stability of ion pair association complexes are either tight or loose[27,28].

Composition of the Extracted Complex

Two spectroscopic methods - slope analysis and slope ratio – were used to determine the probable structure of the extracted ion pair complex. This was based on a general procedure.

Slope analysis method

This method involved using different concentrations of DB18C6 and fixed concentrations of

Ge(IV). The results are shown in Fig. 12.

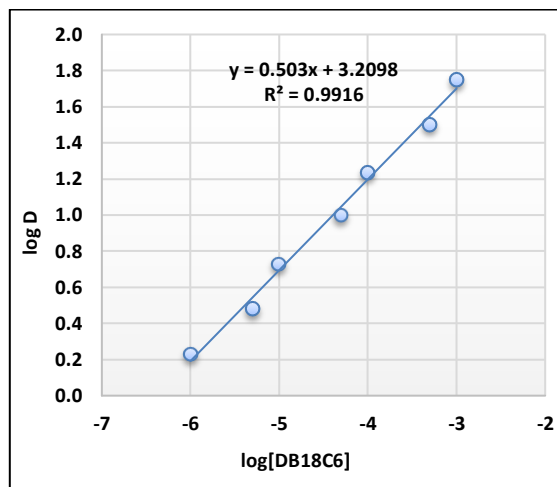


Fig. 12: Slope analysis method.

Slope ratio method

This method included extracting Ge(IV) ions at varying concentrations of DB18C6 and another procedure for extracting different concentrations of Ge(IV) ions with a fixed concentration of DB18C6. The results are shown in Figs 13 and 14.

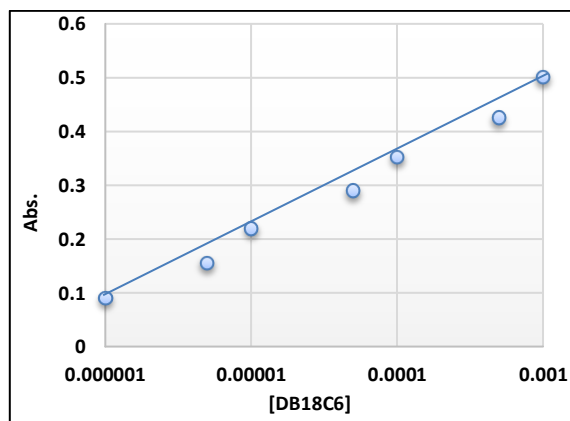


Fig. 13: Effect of DB18C6 concentrations on absorbance.

Table-4: Organic solvent effect on extraction efficiency.

Organic Solvents	ϵ_r	λ_{max}	D	$-\Delta G_t$ kJ.mol ⁻¹	K_A	$K_{ex} \times 10^8$	$-\Delta G_{ex}$ kJ.mol ⁻¹
Nitro benzene	35.74	300	3.42	-0.234	5.70×10^3	6.121	-49.286
1,2-Dichloro ethane	10.65	286	5.56	-1.228	5.73×10^3	16.177	-51.654
Dichloro methane	9.080	283	13.00	-1.473	5.42×10^3	88.435	-55.792
Chloroform	4.806	290	17.179	-2.951	5.21×10^3	154.431	-57.150
Benzene	2.804	247	11.48	-5.193	5.47×10^3	68.964	-55.186
Toluene	2.438	240	10.89	-6.001	5.47×10^4	62.058	-54.929

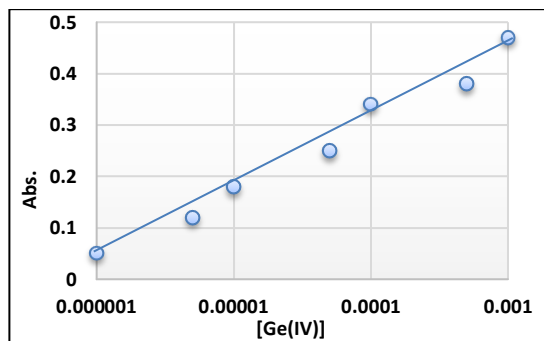


Fig. 14: Effect of Ge(IV) concentrations on absorbance.

$$\text{Slope ratio} = \frac{410.41}{420.420} = 0.976$$

From the values of slope analysis (slope=0.503) and slope ratio method (Slope ratio=0.976), it was shown that the ion pair association complex extracted has a ratio 1:1, $K\text{-DB18C6}^+$; $K[\text{GeO}_2(\text{OH})_2]^-$, Fig. 15.

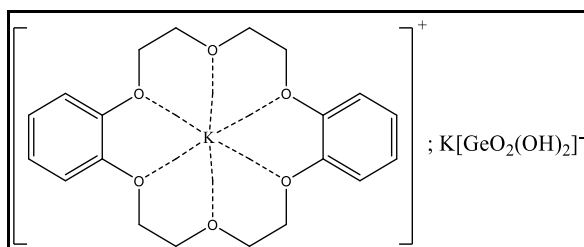


Fig. 15: The probable structure of the extracted complex.

Calibration curve of Ge(IV) using DB18C6

Under optimum extraction conditions, a calibration curve construction for Ge(IV) as per the general procedure using different concentrations of Ge(IV) ranging from (5-100) μg . was carried out. The results are shown in Fig. 16 and Table 5.

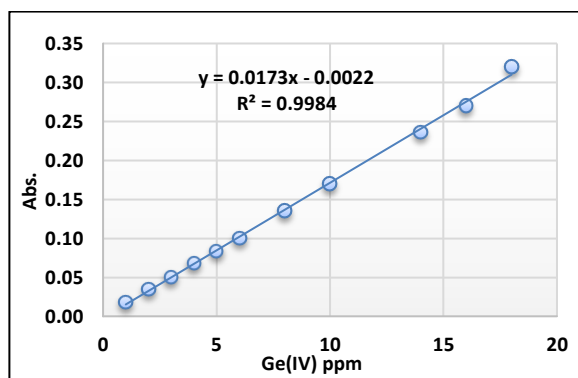


Fig. 16: Calibration curve of Ge(IV) using DB18C6.

Table-5: Statistical parameter of the calibration curve of Ge(IV) and comparison with other studies.

Parameter	Proposed method	Literature method[8]	Literature method[29]
Beer's law	1-20ppm	0.03-2.8 $\mu\text{g}/10\text{mL}$	0-2.4 $\mu\text{g}/10\text{mL}$
Limit of Detection	0.034 ppm	0.1ppm	0.70 ng ml ⁻¹
Limit of Quantity Molar absorptivity (L.mol ⁻¹ .cm ⁻¹)	0.102 ppm	-	0.21 ng.mL ⁻¹
	1.269 $\times 10^3$	2.5 $\times 10^5$	1.7 $\times 10^5$

Spectrophotometric of Ge(IV) in different Samples

The samples of canned food were obtained from the market, and they were treated according to the acid digestion method (nitric-hydrochloric acid digestion 1:3) based on the general procedure[30]. The results are described in Table 6.

Table 6. Germanium determination in some samples.

No.	Sample	Ge ppm	
		Proposed method \pm SD	Reference value[30][31]
1	canned tuna	7.87 \pm 0.01	(2-9)ppm
2	beans	3.45 \pm 0.02	
3	tomato juice	8.76 \pm 0.01	
4	green tea	5.64 \pm 0.02	

The developed method for the separation and spectroscopic determination of Ge(IV) using DB18C6 ligand offers a novel approach to detecting and quantifying germanium ions in complex matrices. This method can be employed in analytical laboratories for the accurate and efficient analysis of Ge(IV) concentrations in environmental samples, industrial processes, and geological samples.

Conclusion

The study used a spectrophotometric method to determine Ge (IV) as anion $K[\text{GeO}_2(\text{OH})_2]^-$ using KOH media and DB18C6 as ligand; the maximum wavelength of the extracted complex was $\lambda_{\text{max}}=290\text{nm}$. Beer's law was adhered to in the range (1-20)ppm. The optimum concentration of KOH was 0.8M, the optimum shaking time was 15 minutes, and the optimum percentage of CH_3OH was 40%. K^+ ions showed the highest absorbance and D values because it has the best fitting based on the ionic diameter ($\text{K}^+=2.66$) and cavity size of DB18C6(2.9 \AA). Cavity size is not the only influencing factor in which a cation could be complex. However, as a general rule, crown ether can be used to form a complex with the target cation. The results showed participation of organic solvents in the formation and stability of ion pair association complexes is either tight or loose. The structure of the ion pair association complex extracted was 1:1, $K\text{-DB18C6}^+$; $K[\text{GeO}_2(\text{OH})_2]^-$.

The future work includes the optimization of experimental conditions to enhance sensitivity and

selectivity, Validation of the method using certified reference materials and real samples, Investigation of interference effects and strategies for mitigation and useful other metals and different ligands

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