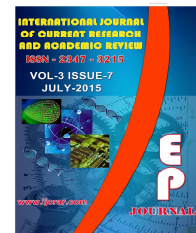




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A new method for determination of potassium ion (II) using the organic reagent bidentate ligand of 1,4-bis(9-O-dihydroquininyl) anthraquinone

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KEYWORDS

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A B S T R A C T

The study includes the determination of K(I) using azo reagent bidentate ligand of 1,4-bis(9-O-dihydroquininyl)anthraquinone [(DHQ)2AQN] spectrophotometric at (λ_{max} 548m) wave length. The effect of different parameters on determination is evaluated. The study shows that best PH=(7±0.1). The study includes obey concentration of Beer-Lambert law to determination of the calibration graph of K (I) by azo reagent. From this graph we note obey the concentration of law was between (5 – 60) µg of K (I) after this values the absorbance increased. The stoichiometry of complex Potassium ion is determined by molar ratio method. Result indicated reagent to metal ratio was (1:2) the stability constant of the complex determination through mole ratio method and its value indicated good stability. The UV-Vis spectra and the IR spectra of the complex and reagent were measured. From all mentioned studies proposed structural formula of K(I) complex.

Introduction

Potassium is a chemical element with the symbol K (derived from Neo-Latin *kalium*) and atomic number 19. Elemental potassium is a soft silvery-white alkali metal that oxidizes rapidly in air and is very reactive with water, generating sufficient heat to ignite hydrogen emitted in the reaction and burning with a lilac flame. Naturally occurring potassium is composed of three isotopes, one of which, ⁴⁰K, is radioactive. Traces (0.012%) of this isotope are found in all potassium, making ⁴⁰K the most common radioisotope in the human

body and in many biological materials, as well as in common building substances such as concrete.

Because potassium and sodium are chemically very similar, their salts were not at first differentiated. The existence of multiple elements in their salts was suspected in 1702 (Andreas Siegmund, 1761), and this was proven in 1807 when potassium and sodium were individually isolated from different salts by electrolysis. Potassium in nature occurs only in ionic

salts. As such, it is found dissolved in seawater (which is 0.04% potassium by weight (Webb, 1939; Anthoni, 2006), and is part of many minerals.

Most industrial chemical applications of potassium employ the relatively high solubility in water of potassium compounds, such as potassium soaps. Potassium metal has only a few special applications, being replaced in most chemical reactions with sodium metal.

Potassium ions are necessary for the function of all living cells. Potassium ion diffusion is a key mechanism in nerve transmission, and potassium depletion in animals, including humans, results in various cardiac dysfunctions.

Potassium accumulates in plant cells, and thus fresh fruits and vegetables are a good dietary source of it. This resulted in potassium first being isolated from potash, the ashes of plants, giving the element its name. For the same reason, heavy crop production rapidly depletes soils of potassium, and agricultural fertilizers consume 95% of global potassium chemical production (Jungwirth *et al.*, 2006).

Conversely, plants are intolerant of sodium ions and thus sodium is present in only low concentrations, except specialist halophytes (WHO, 1977; Fernandes-Lerans and Oalla-Herrero, 2003; IPCS, 1995). The present study was conducted to estimate the ion potassium(I) spectrally using a reagent (bidentate ligand of 1,4-bis(9-O-dihydroquininyl) anthraquinone [(DHQ)₂AQN]) at λ_{\max} 548 nm wavelength which contains inhomogeneous loop in its structure different atoms is nitrogen (Kda *et al.*, 1998), which owns electronic pairs nonbonding qualifies them to link with the different elements especially metallic ones to form complexes (Fig. 1).

Practical part

Prepared solutions

1 - Ion potassium (I) solution (1×10^{-3}) molar: attended by dissolving 0.332 grams of potassium salt in 100 ml of distilled water and from which attended diluted concentrations using volumetric flask 10 ml.

2 - Organic reagent solution (1×10^{-3}) molar Chiral ligand of hydroquinine anthraquinone-1,4-diyl diether of (DHQ)₂AQN (Fig. 1) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Chloroform was from (Beijing, China).

3 - Buffer solutions with different PH functions between (4-10) as tablets form, which equipped directly from the MZN / India Company and have been calibrated with a pH meter.

2-2 The used devices:-

1 - PH measurement device (PH meter Hanna/ Italy).

2 - (UV-Vis) Spectroscopy measuring device (PG/ USA 990).

3 - Spectroscopy FTIR measuring device (Shimadzu 66x).

4 - Melting point measuring device (Thermo/ Germany).

Procedure:

The optimal conditions was studied for estimating Potassium ion (I) spectrometry using the organic detector (hydroquinine anthraquinone-1,4-diyl diether) the best acidic function for complexity has been appointed, by preparing several solutions of different acidic functions ranged between 4 and 10 using buffer solutions of ammonium acetate, and use equal sizes for both of the metal ion and organic reagent, in an equal

concentrations. also the extent of concentrations compliance of Beer-Lambert law was studied by mixing 2 ml of the metal ion solution which containing 10–100 micrograms of the mentioned ion with the equivalent volume of the of the organic reagent with concentration (0.001%). Also the complex equivalence was study by the molar ratios method which included the preparation of different concentrations of the organic reagent ranged (0.5×10^{-4} - 1.5×10^{-4}) Molar certifying the metal ion concentration and by which the stability constant for the potassium complex (I) has been calculated, and to find out the effect of the presence of concentrations of some negative and positive ions on the complexity process these ions added to the metal ion solution and the organic detector. The melting point was measured for each of the metal ion and the organic reagent that used.

Results and Discussion

The effect of different factors was studied to determine the optimum conditions for the process of complexity of Potassium ion (I) and reagent (bidentate ligand of 1,4-bis(9-O-dihydroquininyl) anthraquinone [(DHQ)₂AQN]), these factors are:

Acidic function

Buffer solutions of metal ion were prepared in a concentration of (1×10^{-5}) Molar with acidic function ranged between 4–10, then the same volume of the organic reagent added to them, of an equivalent concentration to the metal ion, it observed variation the complexity of the process with variation of the acidic function as shown in figure 2, the complex showed higher absorption when the acidic function (7) so it is the best function of the consistency process between all of the mentioned ion and the reagent, this results are consistent

with previous studies to set the potassium ion (I) (Galls-Gouher, 1991; Sillep M. Janrson, 1992) because it is the best acidic function in which the reagent can give non covalent electronic couples to participate in the consistency process on the one hand and on the other hand the aggregates viable consistency become more freedom to contribute in the complexity process at this point. While the acidic function (9) showed high absorption value but the color of the reagent has change, the reason may be attributed to aggregates arrangement change and ties in the structure of the organic reagent along the lines of the principle of chemical indicators.

Metallic ion concentration

Different concentrations of Potassium ion(I) were prepared to determine the obey concentrations of Beer's- Lambert law ranged between 5-60 µg/ ml, then the same volume of organic reagent of the concentration (0.001%) was added for each solution, then measured at the optimum acidic function and the results were as set out in figure 3, we note that obey of the mentioned law is located between the concentrations 10–40 µg/ml equivalent the concentrations 1.5×10^{-4} – 15×10^{-4} molar after these concentrations absorbance values deviate a positive deviation, the reason may be due to increasing of the mentioned ion concentration comparing to the organic reagent concentration which upset the balance process and distort the reaction to back according to Le Chatelier principle and in figure 3 we note that the value of the molar absorption constant is (1.5×10^4), where this value indicates the good stability of the formative complex.

Table 1 shows that this method using organic reagent (bidentate ligand of 1,4-bis(9-O-dihydroquininyl) anthraquinone

[(DHQ)₂AQN]) fall within the most accurate, sensitive and selective for the appointment of potassium ion (I).

The formative complex valence

Molar ratio adopted for the study of valence of Potassium complex(I), where different concentrations of organic reagent were prepared in the range between (0.25×10^{-4} - 2.5×10^{-4}) molar and constant concentration of the metal ion, the results are shown in figure 4, and the proportion of the organic reagent to the metal ion was found equal to 1:2 and by which the stability constant of the complex was calculated (Lester, 2006), which amounted (0.904×10^4), this value refers to the good stability of this complex.

The effect of positive and negative ions

A concentration of 50 mg/liter of a group of positive and negative ions separately added to the mentioned ion solution and reagent to find out the effect of the presence of a number of positive and negative ions on the spectral estimation process of potassium ion (I).

The results displayed in table 2. Those results showed influence of negative ions on the complexity process and the reason has been attributed to the fact that negative Potassium ion (I) produces stable complexes with both tartrates sulfates ion and less stable complexes with chloride ion (IPCS, 1995) on the one hand and on the other hand the presence of positive ions affects the consistency process, especially Cadmium ion (II) and Nickel (II) with the organic reagent (www.unep.org/resourcepanel/Portals/24102/PDFs/Metalstocksinsociety.pdf), which affects negatively on the basic consistency process.

Also the melting point of the Potassium ion complex(I) and the reagent (bidentate ligand of 1,4-bis(9-O-dihydroquininyl)

anthraquinone [(DHQ)₂AQN]) were measured, the melting point of a metalloproteinase ion complex was (490 °C) while for the detector one was (180 °C), referring to an increase in the molecular weight of the complex, resulting from the complexity process face increasing in the melting point. Table 3 shows some chemical characteristics for each of the organic reagent and complex.

A spectral study was conducted such as of UV-visible spectroscopy (UV-Vis) and infrared spectroscopy FT-IR for both of the organic reagent and complex, the spectroscopy study of the ultraviolet-visible (UV-UV-Vis) During experiments, we measured the emission spectra for the mixtures of (DHQ)₂ANQ and KNO₃ at the molar ratios from 1:0 to 1:10 in the methanol solution. As shown in figures 5, the emission at approximately 360 nm did not show a significant difference with the increase of the relative molar fractions of KNO₃. However, the emission at 525 nm gradually weakened when the KNO₃ solution was added. When the molar ratios of KNO₃ relative to the ligand increased to 10, a weak emission peak was observed at approximately 470 nm, which was in agreement with that observed in the K-(DHQ)₂AQN complex nanocrystals. These results suggested that the blue shift and quenching of the second emission peak may be attributed to the formation of metal-ligand complexes.

The complex have been diagnosed using spectroscopy Infrared IR (Figure 6), and when comparing its spectrum with the organic detector spectrum (Figure 7) we note clear changes, that appeared new packages were not already present before in the spectrum of the detector sometimes or disappearance of some packages or change its shape at other times as indicated in table

4 where we note the frequencies of the most important peaks and the changes that have obtained shows that the frequencies of the hydroxyl group (OH) move away from its position toward the higher frequency at consistency, and the reason of this attributed to break the implicit hydrogen bonds in the detector particle and involve the group in the

overall episode of the complex after losing its proton by the effect of metalloproteinase ion and the acidic function of the solution (<http://www.aspera-eu.org/index.php?option=com-content&task=view&id=418&Itemid=98>; <http://www.nature.com/news/2010/100415/full/news.2010.186.html>).

Table.1 The values of the molar absorption coefficient to set the Potassium ion (I) using different reagents

The ion	Molar absorption	Reagents
K (I)	6.86×10^4	Dithzone
	4×10^4	4-(2-Pyridylazo)resorcinol
	1×10^4	6-MBTABP
	4.9×10^4	5-(5-BrmoPyridylazo)-5-diethylamino phenol
	1.04×10^4	Xylenol orang
	1.5×10^4	1-Hydroxy-7-azabenzotriazole

Table.2 The effect of the presence of some ions on the process of complexity through the values of the relative deviation (E) *

Positive ion	relative deviation (E)	Negative ion	Relative deviation (E)
Na ⁺	0.043	SO ₄ ⁻²	0.213
Mn ⁺²	0.207	Tartrate	0.152
Mg ⁺²	0.291	IO ⁻³	0.043
Ni ⁺²	0.324	Br ⁻	0.248
Zn ⁺²	0.231	MnO ⁻⁴	0.027
Ba ⁺²	0.126	CrO ₄ ⁻²	0.329
Cd ⁺²	0.364	-	-

* The concentration of the metal ion 1×10^{-4} molar

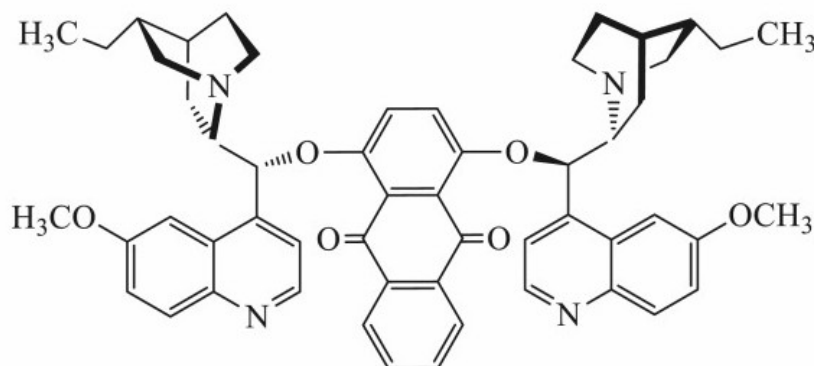
Table.3 Some qualities of each of the complex and the organic detector

The Substance	Color	Melting point °C	Wave length λ_{max} 548 nm	Molecular weight g mol ⁻¹
The reagent	Green	180	330	136.11
The complex	Red brown	206	548	490

Table.4 The values of the infrared spectra frequencies FTIR (cm-1) for both the organic and the complex detectors

Compound	ν O-H str.	C-N str	ν C-H alp.str	ν C-H arm.str	ν C=O
The reagent	-	1531.37(s)	2921.96(m) 2904.6 (m)	3056.95(w)	1739.67(s)
The complex	3259.47(s)	1591.16(s)	2927.74(m) 2856.38(m)	3095(w)	1743.53(s)

Figure 1



(DHQ)₂ANQ

Fig.2 The relationship of the acidic function with the absorption for potassium ion complex(I)

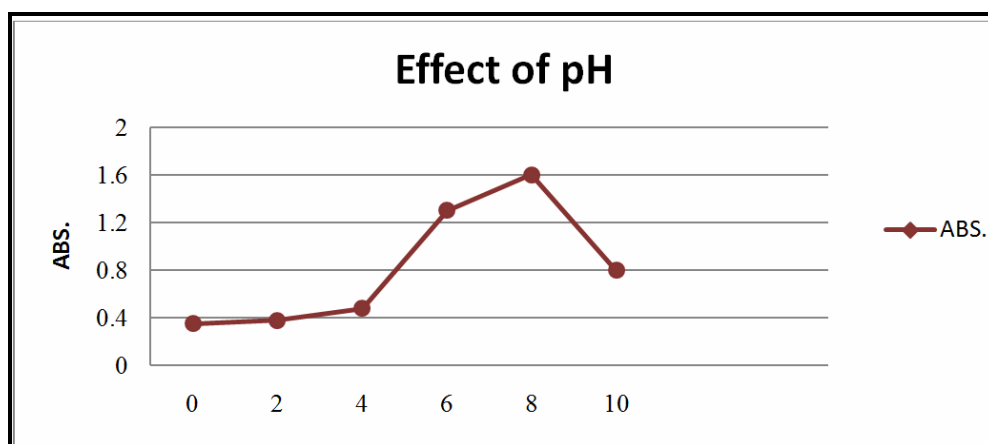


Fig.3 The standard calibration curve for duo ion potassium using the new organic reagent

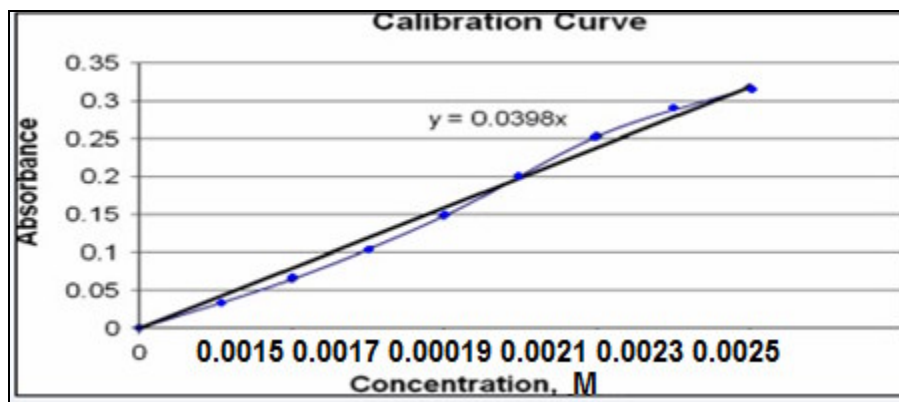


Fig.4 The relationship between the molar ratio M:L and the absorption of Potassium complex (II) at the greatest wavelength

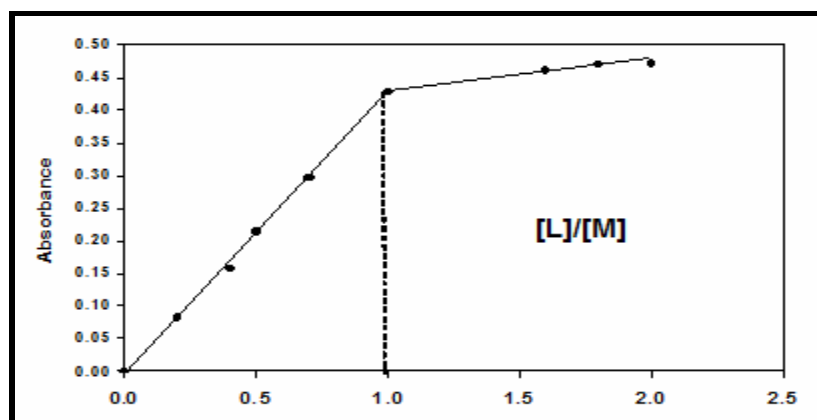


Fig.5a UV-visible spectrum of metallic ion; **b** UV-visible spectrum of reagent; **c** UV-visible spectrum of complex

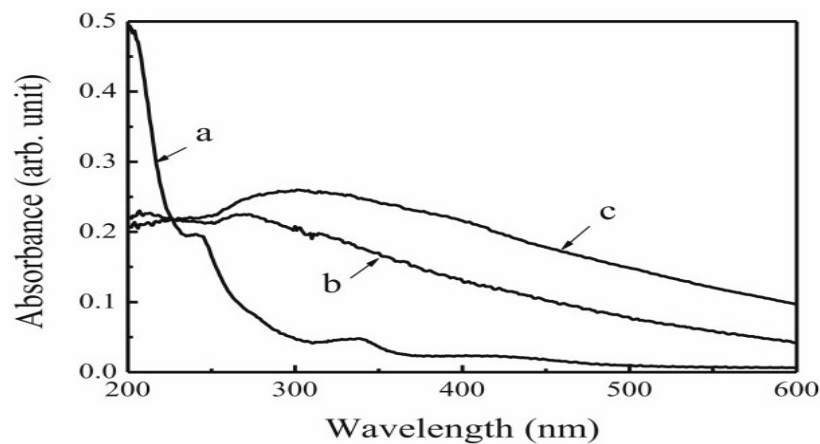


Fig.6 Infrared image of the detector (bidentate ligand of 1,4-bis(9-O-dihydroquininyl)anthraquinone [(DHQ)2AQN])

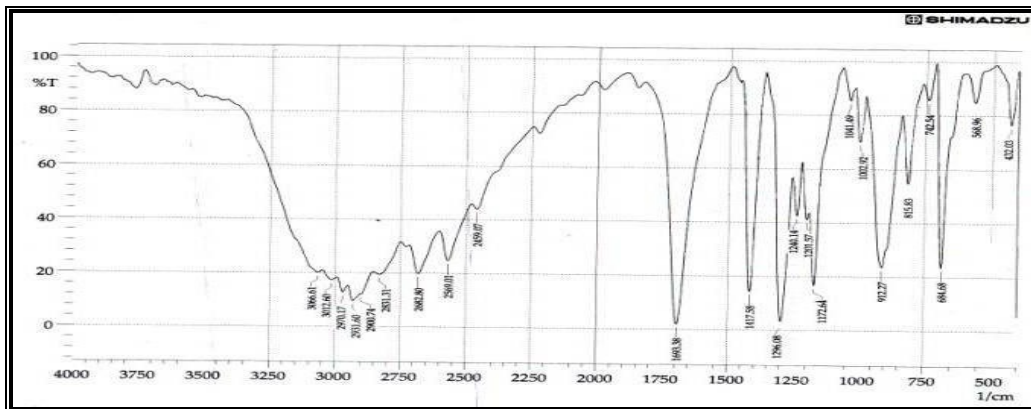


Fig.7 Infrared image of the complex

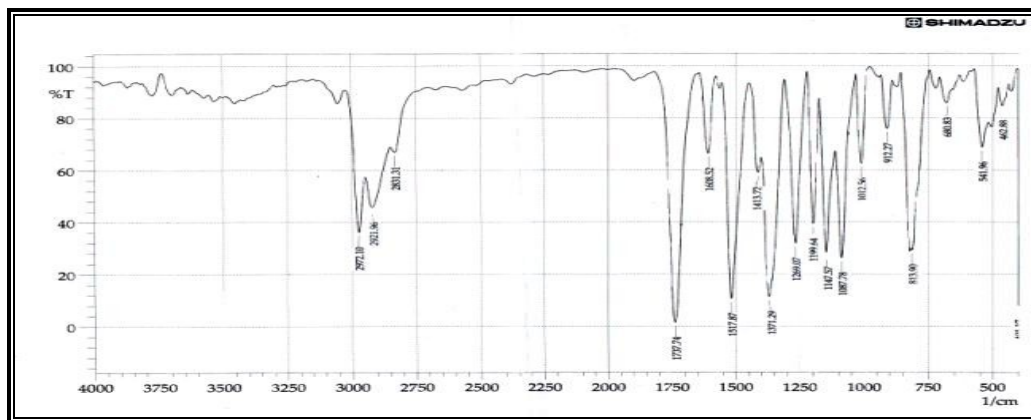
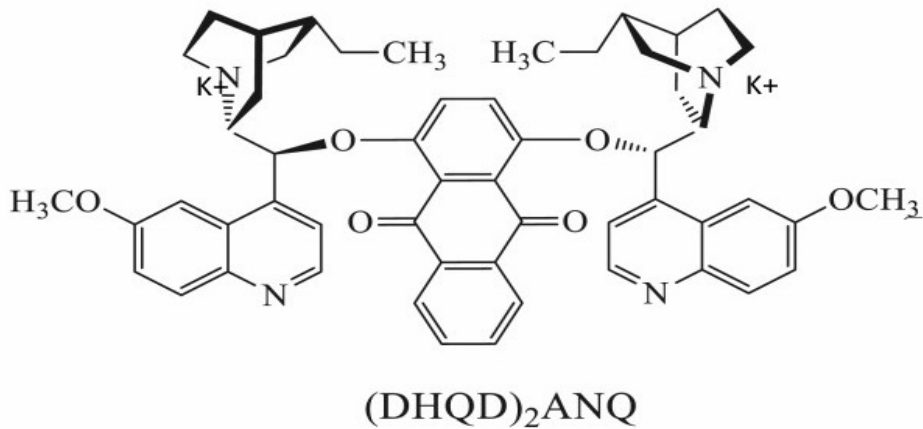


Fig.8 The proposed vacuum figure of potassium ion complex(I).



Also the (C = N) pack suffer from change in its shape, that refer to force it in the consistency process (www.pencils.com). Changes got to vibrations of other groups such as (N = N), which are affected by the consistency process as well as the emergence of new packages such as (M-O). In the complex spectrum, we note the presence of a broad package at 3550cm^{-1} is attributed to the presence of water molecule within the complex structure and which confirms this conclusion is the weight difference of amount of the complex before and after the heating process to the degree of 105°C . Figure 6 and 7 confirm the results we have obtained.

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