

Ability of some Schiff base ligands to specific cation – transport through three phase system.

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Abstract

This paper reports the specific and uphill transport of Cu (II) ions across a liquid membrane [CH₂ Cl₂ – C₂H₄Cl₂] mediated by a tetradentate Schiff base ligands as carriers .The transport is driven by pH gradient between two aqueous phase (source and receiving phase) and the cation transfer has been coupled by a counter flow of protons .The concentration of metal ions in SP(source phase) , and RP(receiving phase) monitored by spectrophotometric method and was found to decrease progressively in SP, whereas Cu (II) ions appeared in RP and their concentration increased with time .

Key words: - Selective liquid membrane; Schiff - base; copper (II).

1 – INTRODUCTION

Liquid membrane is a water- immiscible organic layer (bulk or supported on a microporous film) that separates two aqueous layers [1] . This organic layer contains a molecular system (carrier) able to extract a substrate from one of the aqueous layers (the source phase) , and to release it to the other one (the receiving phase) . The carrier works in a cyclic way , shutting back and forth between the two membrane / aqueous phase interfaces [2].The liquid membrane may be heavier than water (e.g. CH₂ Cl₂ ,CHCl₃ ...ect) [1],or lighter than water such as toluene[3] . Liquid membranes containing mobile complexing agents have been widely studied in recent, years.The earliest examples of this process were in carrier – facilitated gas transport for example the transport of oxygen using the hemoglobin – oxyhemoglobin reaction , or carbon dioxide using the carbonate – bicarbonate reaction .More recently ,the use of liquid membrane containing carrier has been extended to the transport of ions from aqueous solutions [4]. Among the natural carrier the macrocyclic antibiotics (enniantin, valinomycin ,monactinetc) ,were successfully utilized in membrane processes , however their high prices imposed the substitution with synthetic crown ethers as carriers [5 ,6].

The separation based on a selective filtration substrates through the membrane and substrates are moved from a higher – concentration to a lower –concentration side through the membrane in terms of a diffusion control . However, the metabolism in living bodies is in many cases carried out in a system of an antidiffusion control through cell membranes , namely by active transport [7] .

Carrier –mediated transport has long been recognized by biological scientists , and in recent years the subject has also attracted the attention of those interested in nonbiological application , particularly selective separation and concentration of species [5,8-10] In the biological context it is axiomatic that chemical carriers or cataphores , especially ionophores , play a crucial role not only in accelerating membrane and intracellular transport but also in the energy transduction or coupling between chemical reactions and transport processes [8] . Incorporation of ligands in to hydrophobic membrane to serve as carriers offers a method to exploit the high selectivity [9-11] .

Liquid membranes have been suggested as a clean technology due to characteristic such as high specificity intensity results from the concentration driving force , and productivity as well as low emissions and low energy utilization [12] . Liquid membrane seems to be a prospective separation technique for the ions and molecules because of its relatively low cost

and energy saving in comparison to solvent extraction processes [12–16]. The effectiveness of membrane separation process is determined by the flux of species through the membrane and by the selectivity of the membrane [16]. Other advantages of liquid membrane technologies are low capital and operating costs [15], and removal of undesirable chemical species from the environment or from biological system [9, 16–18], separating toxic pollutant ions [4,9,11] such as cyanide anions [16], phenols [18], radio active ions, rare earth elements [19–21], organic acids [6,11,12], bioactive products, gases [11], chiral products, [11,12] drug [11,22,23] and fructose [24], and liquid membrane play attractive role in concentration and recovery valuable species and metals [4–6,12,17–21,25], and treatment of water such as removal of heavy metals [14], and nitrogen compounds from waste water [16,26–30]. The application of supported liquid membrane for recovery and concentration [17] of organic acids and chiral product [7,12] and metals ions such as gold(I) were reported [25]. So separated of phenylalanine enantiomers from model solution and the extraction of phenylalanine and lactic acid from real industrial solution using emulsion liquid membrane [12].

Specific transport of metal ions across a membrane plays an essential role in many biochemical processes [5,9,19,31–34]. Although cationic transport is known to be mediated by several antibiotics and synthetic carrier, in marked contrast, little attention directed toward selective membrane transport of anionic species and very few carrier models have been reported [33–36], and only a few synthesis carrier for selective transport of transition and heavy metal ions which are also important from biochemical and medical points of view have been reported [31–33,37–39].

Much research into transport phenomena has been carried out, both in chemistry and biology [34], and many kinds of synthetic and naturally derived carriers such as crown ethers and cryptands and macrocyclic compounds have been shown to mimic the function of natural carrier in transporting alkali metal ions [5,17,37,40] and organic ammonium cations and organic substrates [5,34–36]. Double armed crowns, azacrown ethers and a number of cyclic carriers have been found to be efficient for the specific transport of alkali and alkaline earth cations and some transition metal cations [37]. And use synthetic linear oligomer carrier for highly selective copper (II) ions [31] and use the metal complexes as carrier to transport of amino acid and simple organic anions [34,36].

A type of synthetic the metal complexes are using as carrier to transport of amino acid and simple organic anions [34,36], and imide-containing nucleosides and nucleotides [41]. In other hand lipophilic metal complexes like ferrocene [42] and nickel complexes [1] or organic substrates like quinones [1,5] are used as electrons carriers.

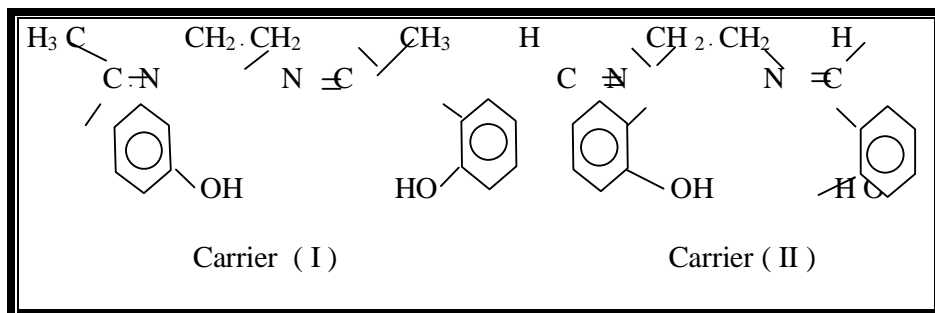
2 – EXPERIMENTAL SECTION:

2.1. Chemicals :-

Carriers (I) and (II):

They were prepared in alcohol by condensation of ethylenediamine (0.1 mol.) with :-

2-hydroxyacetophenone (0.2 mol.) to form carrier I and with Salicylaldehyde (0.2 mol.) to form carrier II, they were prepared by using reflux and recrystallized of the yellow crystals from alcohol [43], and cyclohexane respectively, the melting points were 191–193 °C and 124–125 °C respectively and C.H.N. analysis (found C=72.89, H=7.13, N=9.54; cal., C=72.99, H=6.81, N=9.46) for I and (found C=71.64, H=5.97, N=10.45; cal., C=71.69, H=6.25, N=10.40) for II.



Membranes : a mixture of dichloromethane and dichloroethane (50 –50 %) containing ligands (Schiff bases I or II) .

Metals salts : $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 9\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Reagents for spectrophotometric determination of metal ions, for Cu ions was : 1-[Pyridyl –2-azo]- naphthol -2 (PAN), and for Zn and Ni ions was : 1,5-Diphenylthiocarbazon (Dithizone) , and for Mg ions was (8 - hydroxyquinoline) .

2.2 - Apparatus :

Liquid membrane experimentals were performed by using U-tube shaped glass cells as described in Fig. 1 [1] . It of 2 cm diameter , 14 cm height and the base width (distance between the two legs) was 3 cm .

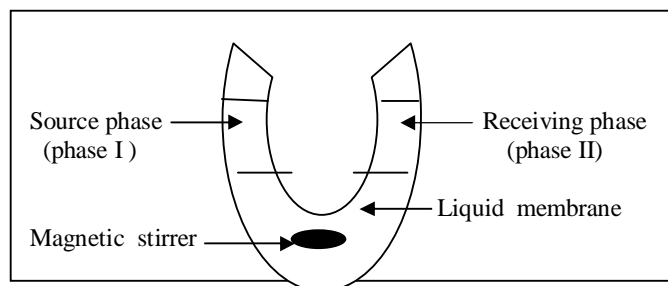


Fig. (1) U – shaped glass tube cell for transport experiment . A liquid heavier than water interface two aqueous layeres, phase I and phase II , the liquid membrane is magnetically stirred ,Spectrophotometer:

The concentration of metal ions in both aqueous phase was monitored by spectrophotometry method by using CECIL CE1011 INSTRUMENTS No.124 392 made in France , and in membrane study using thermospectronic (helios Alpha No.UVA 102024 made in England) .

2.3 - Procedure :

The liquid membrane technology involves two processes in one single stage,extraction of metal ion from the aqueous donor solution to the organic phase containing the carriers molecules (membrane)and re-extraction of this metal ion from the membrane to the aqueous acceptor phase [10,39] .

The transport experiments were carried out at $25 - 27^\circ \text{C}$ by using U-tube consisted of 25 ml of membrane phase containing 0.001 M or 0.01 M carrier (in mixture of CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$) stirred at 200 rpm by magnetic stirrer .The membrane phase was loaded in the bottom of the cell and interfaced to both a 8 ml [source phase (aq. I) aqueous solutions of metals sulfate, given 1×10^{-3} M of metal ions] and 8 ml of [receiving phase(aq .II) acidic solutions of 1 M HCl, and after a period of 24 ,48, and 72 hours a 2 ml sample of aqueous phases (source and receiving) was withdrawn and the concentration for each cation was determined by spectrophotometric methods (after making calibration curves for Cu ions by PAN reagent at 575 nm , at 550 nm , 545 nm for Zn ions and Ni ions respectively by dithizone and at 390 nm for Mg ions by 8- hydroxyquinoline) .

2.4 - Extraction experiment: -

10 ml of (1×10^{-3} M) metal ion in distilled water and 15 ml from membrane(1×10^{-3} M of carrier) were placed in round flask and stirred at 200 rpm for 3 hours and drawn 2 ml from donor phase (each 1 hour) after that separate the phases and filter a membrane phase and mix it with 10 ml of HCl and stir them at 200 rpm for 3 hours and drawn 2 ml from receiving phase (each 1 hour) and determine the concentration for each cation in two phases .

3- RESULTS AND DISCUSSION:

Selective transport of transition metal ions through liquid membrane has become increasingly noteworthy, a number of carriers for heavy metal ions and in particular Cu (II), which is both vital and toxic to many biological systems, have been reported [45-50].

Schiff base ligands showed excellent transport ability for Cu (II) cations [38], this may return to presence nitrogen and oxygen atoms in the structure of ligands which contain them on cavity to incorporate a metal ion. The Cu (II) ions transfer process can be interpreted according to the scheme depicted in Fig. 2, after a few hours from beginning of the experiment the liquid membrane color change from yellow to Brown - pale colorless this confirms the presence of the Cu (II) in the membrane. The complexing ability of the closely related ligands and the complexes are shown to be essentially at higher carrier concentration – complexes formed in the membrane phase, the metal moves from the source phase to membrane which contains Schiff base carrier forming a stable neutral complex 2:1 or 1:1 (M : L) composition in comparison with a Schiff bases which are study in transport Cu (II) ions which appear to be 1:2 (M:L) [38]. This neutral complex moves towards the interface of membrane and receiving phase and availability of protons in the receiving phase effects the release of free metal ion into the receiving phase by protonation of the Schiff base carrier. As a consequence the proton abundance in source aqueous phase (I) increases and that in receiving phase (II) decreases. The net result is the transport of metal ions from the aq. (I) to aq. (II) across the bulk membrane. Fig. 2 wherein the concentration of Cu (II) in aq. (II) increased proportionally with time. Transport was complete after 72 hours maximum transport attained being 54 % for Cu (II) ions, low transport rate Cal. 0% for Ni (II), Zn (II), after 72 hours. That shows the complexes of Ni, Zn are more stable than the corresponding Cu (II), Mg (II) complex, this may return to suit the size of ligands cavity and metal ion size. Thereby not decomplexed into the receiving phase. Moreover low stability of Cu –complex helps the decomplex at inter phase of membrane and (aq. II). It is noted that in the absence of HCl in the receiving phase no transport was observed, when the aq. HCl in phase II was replaced. So transport by the present set of carriers is pH driven and occurs when a pH gradient is applied between two aqueous phases as noted in Table 1 and 2. Extraction experiment was carried out to observed the ability of these ligands to form complexes with metal ions and the strength of these complexes, the data in Table 3. shown the extraction ratio to Cu ion was more than to other ions.

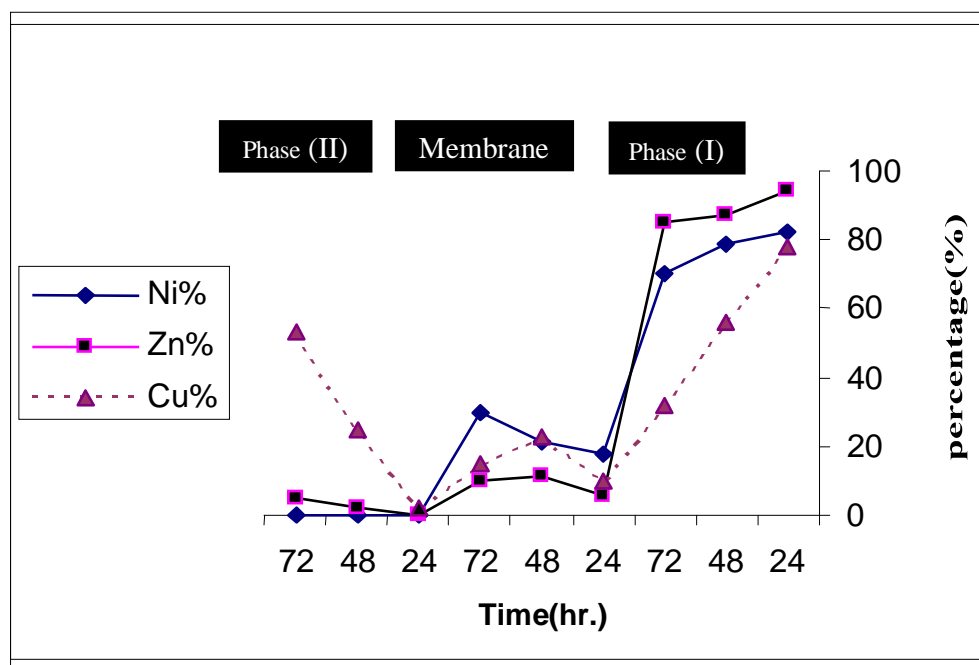


Fig 2 . Time evolution of reduced concentration of M²⁺ by (1x10⁻³ M) Schiff base (I), phase (I) 0.5 M ammonia solution .

Table: 1: Initial conditions : Aq .(I) 8 ml of 1×10^{-3} M to ions in 0.5 M ammonia solution and aq. (II) 8 ml solution of HCl (1M) ; 25 ml organic phase of dichloromethane : dichloroethane (50:50 %) containing 1×10^{-3} M of Schiff base ligands .

Ligand	Metal ions	Time (hours)	% of transport membrane		
			aq .I	aq. II	
(I)	Cu (II)	24 ,48 ,72	78 ,52 ,32	10 ,23 ,15	12 ,25 ,53
	Zn (II)	24 ,48 ,72	94 ,87 ,85	6 , 11, 10	0 , 2 , 5
	Ni (II)	24 ,48 ,72	82 ,79 ,70	18 , 21 , 30	0 , 0 , 0
(II)	Cu (II)	24 ,48 ,72	75 ,49 ,27	11 ,22 ,17	14 ,29 ,56
	Zn (II)	24 ,48 ,72	93 ,90 ,90	7 , 9 , 5	0 , 1 , 5
	Ni (II)	24 ,48 ,72	80 ,75 ,69	20 ,25 ,28	0 , 0 , 3

Tabel: 2: Initial conditions : Aq .(I) 8 ml of 1×10^{-3} M to ions in distilled water and aq. (II) 8 ml solution of HCl (1M) ; 25 ml organic phase of dichloromethane : dichloroethane (50:50 %) containing 1×10^{-3} M of Schiff base ligands .

Ligand	Metal ions	Time (hours)	% of transport membrane		
			aq .I	aq. II	
(I)	Cu (II)	24 ,48 ,72	89 , 63 , 49	3 , 16 , 12	8 , 21 , 39
	Mg (II)	24 ,48 ,72	91 , 73 , 52	6 ,20 ,18	3 , 7 , 30
	Zn (II)	24 ,48 ,72	95 , 89 , 89	5 , 11 , 11	0 , 0 , 0
	Ni (II)	24 ,48 ,72	90 , 83 , 80	10 , 17 , 20	0 , 0 , 0
(II)	Cu (II)	24 ,48 ,72	83 ,59 , 46	6 , 18 , 14	11 , 23 , 40
	Mg (II)	24 ,48 ,72	88 ,70 , 53	7 ,21 ,18	5 , 9 , 29
	Zn (II)	24 ,48 ,72	82 ,79 , 76	18 ,21 ,24	0 , 0 , 0
	Ni (II)	24 ,48 ,72	84 , 77 , 75	16 ,23 , 25	0 , 0 , 0

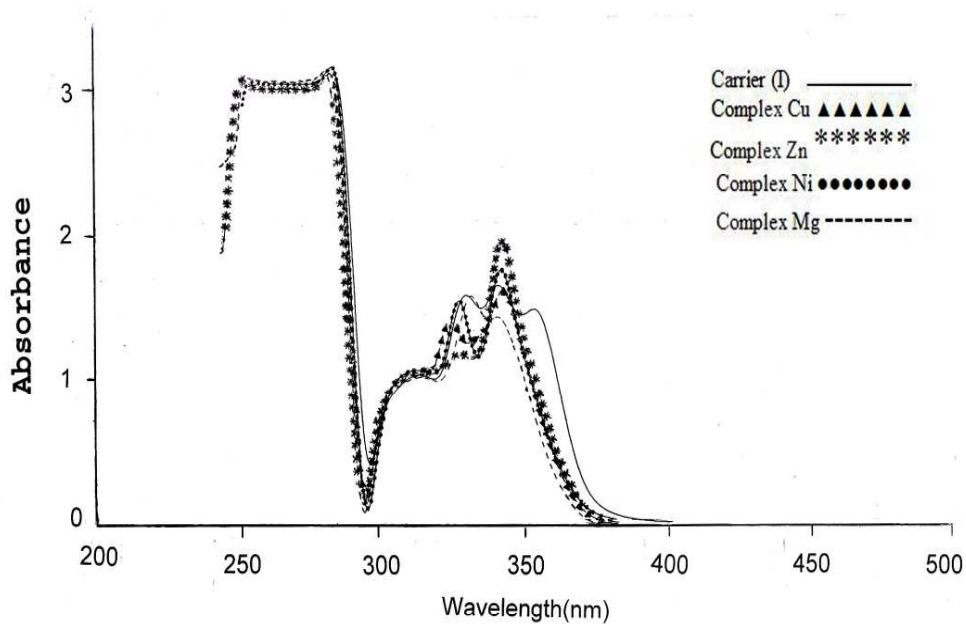
Table: 3: 1×10^{-3} M metal ions in 10ml of distilled water (aq. I) extracted with 15 ml of 1×10^{-3} M from carrier (I) in organic layer, and aq .II 10 ml of 1 M HCl .

Metal ions	Extraction %		
	after 1 hour	after 2 hours	after 3 hours
Cu (II)	78	80	80
Zn (II)	2	4	5
Ni (II)	0	0	2
Mg (II)	10	28	40

Spectra study to membrane :-

It can be seen that in both cases (membrane before transport ,and after transport) the absorption bands are very intense therefore quite appropriate for the detection of even trace amounts of carrier or metal – carrier complex in the aqueous phases [10]

The ultra –violet absorption spectra of Schiff base in dichloromethane and dichloroethane has three maxims at 355 nm and 340 nm and 327 nm and shoulder from 315 to 300 nm while , Cu(II) ,Zn(II) ,Ni(II) ,Mg(II) , complexes generally show two absorption bands at the shorter wave -length and shoulder (Fig . 3 and 4) .



Fig(3) In dichloromethane and dichloromethane(50:50):quartz cell,length 1cm;35-37c ;
 concn.Of schiff base 5×10^{-4} M

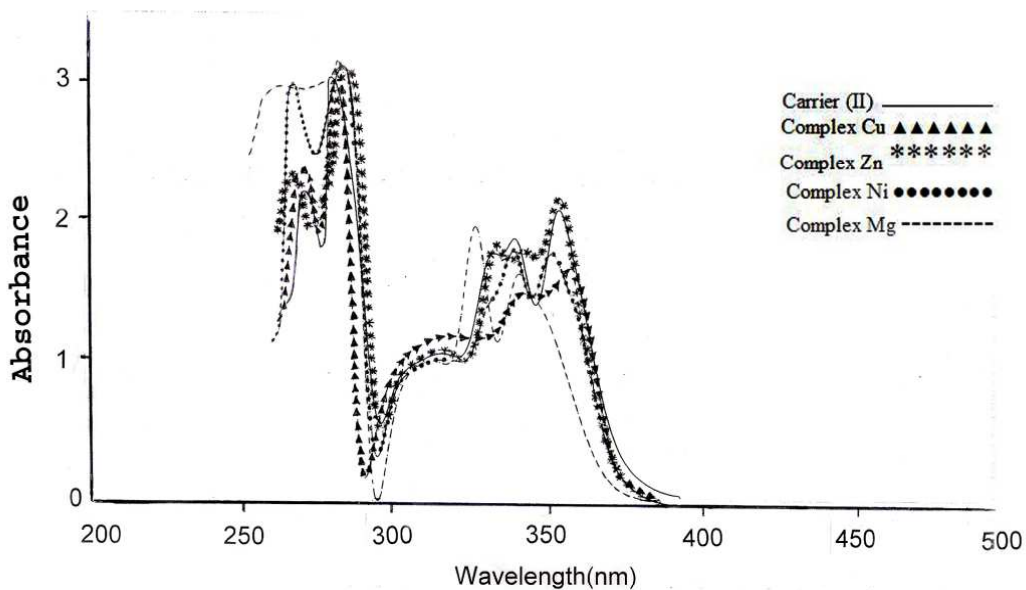


Fig. (4) In dichloromethane and dichloromethane(50:50):quartz cell,length 1cm;35-37c ;
 concn.Of schiff base 5×10^{-4} M

The curves for the Cu, Zn, Ni with a similar ligands were studied by Sone [45]. And in each case the position of the two maxims is shifted from the original position of the ligands and the curves of Cu(II), Zn(II), Ni(II), and salicylaldehyde chelates between 265–450 nm were quite similar in shape to that of the free ligand [45].

Carrier concentration :-

The influence of the carrier concentration in the transport of ions was investigated by using 1×10^{-2} M and 1×10^{-3} M and noted an amount of Cu(II) ions which are transported by 1×10^{-2} M (of carrier) (81%) larger than when using 1×10^{-3} M. And blank experiment (without present carrier in membrane) were carried out for each aq. phases for Cu and Zn ions to determine the cations leakage and it demonstrate no transport was happened.

String power effect :-

Using 50 and 200 rpm to membrane and found in 50 rpm the transport percent was very less than 200 rpm (% of transport for Cu(II) at 50 rpm was (after 24 hour = 2%, 48 h. = 7%, 72 h. = 11.4% & for Zn (II) was 0 after 24 h., 0 after 48 h., 1% after 72).

Conclusion :-

These results demonstrate that the present tetradentate Schiff base ligands which are lipophilic in nature and good carriers for selective transport of Cu (II) ions are more selective than the transport of Zn (II), Ni (II), Mg (II) through liquid membrane.

Acknowledgment

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الخلاصة:

سجل هذا البحث نقل عالي لأيونات النحاس الثنائي عبر غشاء سائل من ثنائي كلوروميثان:ثنائي كلورو ايثان
توسطه ليكنادات عبارة عن قواعد شف رباعية العطاء كناقلات للأيونات. وكان النقل مسير بوساطة انحدار الأس
الهيدروجيني pH بين الطبقتين (الواهبة والمستقبلة) وكان الكاتيون ينتقل بوساطة سيل معاكس من البروتونات من
الطبقة المستقبلة للكاتيون . وقد تركيز أيونات الفلز في كلا الطبقتين الواهبة والمستقبلة بوساطة الطريقة الطيفية
ووجد بأنه يقل في الطبقة الواهبة ويزداد في الطبقة المستقبلة مع مرور الزمن .