

Conductivity measurement of barbituric acid (BA) Drug and it's complexes with alkaline-earth metal chloride

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Abstract

This work includes a conductivity study of Barbituric acid (BA) in water at temperatures (288.16-318.16). The data were analyzed by applying Lee-Wheaton equation for symmetrical electrolyte. It is found that the equivalent conductivity at infinite dilution (Λ^0) and the ion association constants K_A increase with increasing temperature. The distance parameter between ions (R) indicates the formation of solvent separated ion pairs.

The association of (BA) and its complexes with alkaline-earth metals Mg, Ca and Ba as chlorides have been carried out at temperatures (288.16-318.16°K). Analysis of the results indicate that the ionic conductivity $\lambda^0 M^{2+}$ increase with increasing temperature with the formation of ion-pair $(MX)^+$. The (R) values for the three complexes found to be (7.0-9.0A°). The Walden -product ($\Lambda^0 \mu$) is also determined and discussed.

	(Barbituric acid)		(318.16-288.16)
	-	:	(1:1)
	(Λ_0)		(K_A)
	$\sigma_s(\Lambda)$	(R)	(K_A) (Λ_0)
	(R=5)		
	(Barbituric acid)		($\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$)
UV-	Ba(II) Ca(II) Mg(II)		IR Visible
	(318.16-288.16)		
	(1:2)		
A ⁰)	($\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$)		
			(R=9-7

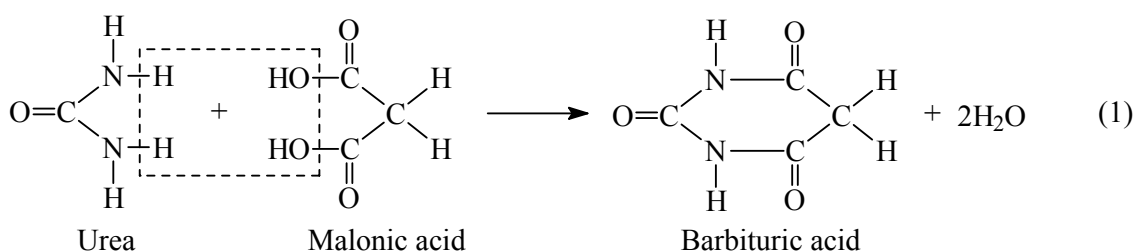
(Walden-product)

Introduction

was determined. The Barbituric acid was discovered in the 4th of December, 1863 by the Belgia researchers Adolf Von Baeyer. His

discovery came on the day of Saint Barbara's Feast Day.

It was prepared from urea and malonic acid¹.



Previously anti-tumor, anti-infection, immunosystem modulators and anti-depressive properties of a family of barbituric acid derivatives were unknown. Recently new barbituric acid derivatives are prepared and these compounds are effective for killing tumor cells, especially carcinoma, lymphoma and leukemia cells; for killing pathogenic organisms, especially viruses, for stimulating T cell formation and for alleviating symptoms of depression are readily tolerated by the animal being treated².

Pelkonen and Karki in 1973 studied the effect of physiochemical and pharmacokinetic properties of eleven barbiturates on the induction of drug metabolism. The results suggest that the ability of a given compound to induce drug metabolism is related to the nature of chemical groups present in the molecule³.

The electrical conductivities of 5-(p-substituted phenylazo) barbituric acid compounds and their complexes were measured. The results illustrate faint semi-conducting behaviour for

these systems. The metal ion forms a bridge between the ligands to facilitate the transfer of current carriers with some degree of delocalization in the excited state⁴.

The complexation process of Ni(II) and Fe(III) ions with (BA) in the solution and on the surface of their oxides was examined by methods of conductometry and spectrophotometry. It was determined that nickel (II) and ferric (III) ions form complexes with BA both in solution and on the surface of their oxides⁵.

A cyclic polyether Schiff base has been designed and prepared to investigate the strong binding capability to barbituric acid via noncovalent intermolecular interaction such as hydrogen bonding⁶. The 1:1 complex formation reaction between the cyclic polyether Schiff base and a BA has been confirmed in detail by ¹HNMR spectroscopic titration. Kondo *et al.*⁷, synthesized 5-anthryl-5-butylbarbituric acid as a probe for spectral determination (UV-Vis and fluorescence) of association constants

for a barbiturate receptor via six hydrogen bonds in organic solvents.

Synthesis and characterization of [o-carboxy phenylazo] moiety of barbituric acid, thiobarbituric acid, and their complexes derived from cobalt (II), nickel (II) and copper (II) salts were done. The stereochemistry and the mode of bonding of the complexes were achieved based on elemental analysis, NMR, UV-Vis, IR and ESR. The dissociation constants of the free azo ligands are evaluated by spectrophotometric methods⁸.

In this work the electrical conductivities of barbituric acid have been measured then with its complexes in deionized water at different temperatures. The applicability of (LW) equation have been tested for the first time to the barbituric acid which is of the type (1:1) electrolyte, and for barbituric acid complexes of the type (2:1) electrolytes^{9,10}. The thermodynamic parameters, ΔG° , ΔH° and ΔS° for ion-pair formation were then calculated and discussed. Also the Walden-product

Experimental

Instruments Used for the

Analysis of the Complexes:

Magnetic Measurements:

Magnetic susceptibility was measured through applying (Faraday Method). The instrument used is of the type BRUKER B.M. 6.

Electronic Spectral

Measurements:

A SHIMADZU UV-Visible spectrophotometer (Computerized UV-1650 PC) is used. All measurements were carried out at room temperature by using quartz cell with 1 cm diameter. The spectrum and data were printed by Epson Stylus-Printer.

Infrared Spectral

Measurements:

The infrared absorption spectra were recorded on two instruments:

1. Perkin-Elmer 590B infrared spectrophotometer (200-4000 cm^{-1}).
2. Thermo Nicolet, Fourier-Transform infrared (FT-IR) spectrophotometer 2002 (500-4000 cm^{-1}) with CsI or KBr disc technique were used

The conductivity

measurements:

Were made using (WTW) conductivity meter (model LBR) with a frequency range of 50Hz-3KHz and sensitivity between 10^{-1} and 10^{-9} Siemens.

Through the conductivity measurements the whole system was completely isolated from the outside atmosphere and the isolation was maintained during the addition of the solute.

Syringe

Plastic syringes (1 ml) were used for injecting the stock solution into the conductivity cell. It was found by Akrawi⁽¹¹⁾ that the plastic syringe was more efficient due to losses of weight (by evaporation) which were much smaller than that of the glass syringe, because the plastic syringe has a much closer fitting plunger.

Water Thermostat:

A thermostat of type Grant was used for controlling the temperature of the conductance cell, its sensitivity was within ± 0.1 °C.

Two kinds of balance were used for weighing:

- a. A balance type Sartorius 2004 MP6 electronic semi-micro balance with five digits was used for weighing the syringes, with sensitivity within $\pm 0.00001\%$.
- b. A balance type Gallenkamp with maximum weight of 800 grams was used for weighing

the cell before and after the conductivity measurements.

Chemicals and Reagents:

Barbituric acid & KCl (Fluka analar grade) and the transition metal chlorides were reagent grade (BDH) products and were used without any further purification.

Preparation of Conductivity water:

Conductivity water was prepared by redistilling distilled water three times with addition of a little amount of potassium permanganate and small pilletes of KOH. The specific conductance of this water was less than 1.2×10^{-6} Siemens cm^{-1} .

Preparation of complexes:

These complexes were prepared by mixing 2 mmole of barbituric acid dissolved in 50 ml of 50% ethanol-water with vigorous stirring and 1 mmole of metal chloride dissolved in ethanol and refluxed for about 3 hrs. The crystals of the complex appeared by evaporating the excess of the solvent and cooling the solution and the crystals then recrystallised in 50% ethanol, suctioned and filtered. The yield was 74-77%.

Conductivity Measurements:

The conductivity measurements in water, methanol and ethanol are highly sensitive to atmospheric carbon dioxide, the whole system is completely isolated from the outside atmosphere and isolation was maintained during the addition of solute.

The design of the conductance cell and the nitrogen line was the same as that previously used in literature¹².

The cell constant for the conductivity cell was measured using the method of Johnes and Bradshaw¹³. Solutions of 0.001M and 0.01M KCl

were prepared from KCl. The cell constant was checked regularly and found to be $0.05887 \text{cm}^{-1} \pm 0.001$. The electrodes used were of platinum type (WTW). Plastic syringes (1ml) with a fitting plunger were used for injection the stock solution into the conductivity cell. This syringe was found to be more efficient due to the very small losses of weight (by evaporation) due to closer-fitting plunger.

Nitrogen Line:

Nitrogen gas line was used which passed through several traps: a trap of lime water for carbon dioxide absorption, a trap of pyrogallol in KOH for oxygen absorption, another two traps one for concentrated sulphuric acid and the other for calcium chloride for water absorption.

General Procedure:

A general method has been used for measuring the conductance of the electrolytes. The conductivity cell was dried, weighed empty and kept at a constant temperature ($25^\circ \pm 0.01^\circ\text{C}$). purified nitrogen was passed through the cell then 100ml of solvent¹⁴ was added to the cell and the nitrogen gas was passes again for 10-15min. until the conductance of the solvent was constant, then the cell plus contents where weighed ascertain amount of the concentrated complex solution was injected into the conductivity cell from a plastic syringe (which was weighed before and after each addition).

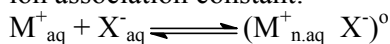
Nitrogen gas was passed for several minutes and the conductivity of the solution was measured. This procedure was repeated for about 10-14 times for each run. After all additions where completed, the cell was dried, reweighed to find the weight change which had taken place through the run. This loss was found to be not more than 0.02%.

Conductivity Measurements for Barbituric Acid:

According to (LW) equation for the specific case of solution containing only a single symmetrical electrolyte:

$$\Lambda_{\text{equiv.}} = f(\Lambda_0, R, K_A)$$

where Λ_0 is the equivalent conductance at infinite dilution. K_A the pair wise ion association constant:



where n is the number of solvent molecule and may be zero, and R is the distance parameter between anion and cation.

The input data to the computer program {(LW) equation for (1:1) symmetrical electrolytes} ⁹ are: solvent data (Temp. T, Dielectric constant D, Viscosity η); K_A ; Λ_0 ; and R in the

form of $R_{\text{min.}}$, $R_{\text{max.}}$ (the minimum and maximum distance between ions), ΔR , together with the solution molarities (mol.L^{-1}) and the corresponding equivalent conductance (Siemens $\text{equiv.}^{-1}.\text{cm}^2$).

This program calculates those values of Λ_0 , K_A and R (the characteristic ion-pair distance parameter) which gives the "best fit" of the experimental conductance.

Table (1) shows the conductivity-concentration data for the studied drug in water at different temperatures. The plot of $\Lambda_{\text{equiv.}}$ against the square root of the molar concentration ($C^{1/2}$) is shown in Figure (1).

Table (1): Variation of equivalent conductivity ($\Lambda_{\text{equiv.}}$ Siemens $\text{cm}^2.\text{equiv.}^{-1}$) and molar concentration (M) of Barbituric acid in water at different temperatures

288.16 K		298.16 K		305.16 K		310.16 K		318.16 K	
M $\times 10^4$	$\Lambda_{\text{equiv.}}$	M $\times 10^4$	$\Lambda_{\text{equiv.}}$	M $\times 10^4$	$\Lambda_{\text{equiv.}}$	M $\times 10^4$	$\Lambda_{\text{equiv.}}$	M $\times 10^4$	$\Lambda_{\text{equiv.}}$
1.163	170.187	1.405	178.655	1.231	210.914	1.466	228.887	1.348	244.264
2.313	159.097	2.756	165.817	2.455	187.718	2.793	192.614	2.579	212.092
4.981	126.508	5.486	133.097	5.234	142.618	5.631	147.913	5.428	164.141
7.516	112.828	8.345	113.612	7.920	122.483	8.479	128.092	8.170	142.907
12.244	93.295	13.659	92.679	13.199	100.261	13.798	104.313	13.492	116.211
17.023	75.059	18.832	82.541	18.353	86.860	19.015	91.175	18.653	102.672
21.657	64.161	23.954	73.986	23.455	79.763	24.076	84.233	23.673	91.595
26.334	60.144	28.913	68.217	28.444	72.809	28.988	75.442	28.378	83.471
30.651	58.779	33.769	62.244	33.349	67.397	33.856	71.028	33.223	78.025
35.078	55.389	38.553	59.558	38.133	62.800	38.614	66.699	37.960	74.344
39.274	53.069	43.187	55.895	42.817	60.056	43.284	63.991	42.611	72.163
42.729	50.569	47.783	53.475	47.419	58.820	47.869	62.165	47.172	69.679
46.346	50.434	52.266	51.929	51.940	55.401	52.389	58.601	51.600	65.524
50.341	48.068	56.515	50.212	55.646	54.673	56.786	56.551	55.989	62.596
54.235	46.679	60.806	49.186	59.866	53.769	61.339	54.176	60.247	60.127

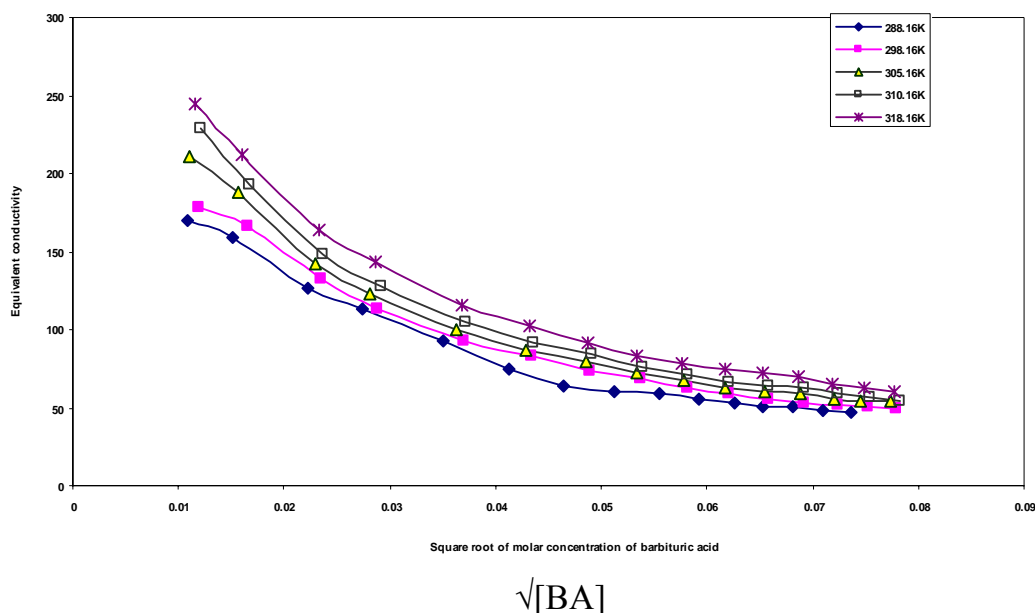


Figure (1): Plot of equivalent conductivity against square root of concentration for Barbituric acid at different temperatures in water

It is clear from the plot that the compound behave as a weak electrolyte at different temperatures.

Table (2) shows the best fit parameters of analysis of conductance data using (LW) equation. This

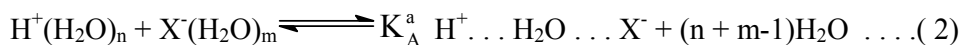
analysis shows that both of (Λ_0) and (K_A) increase with the increasing of temperature. The same behavior was obtained by Doe *et al.*¹⁵

Table (2): Best fit parameters of analysis of conductance data for barbituric acid in water at different temperatures

Temp. (K)	K_A	Λ_0	R ($^\circ$)	$\sigma_s(\Lambda)$
288.16	2642	234.032	5.0	0.038
298.16	3468	251.885	5.0	0.027
305.16	4738	304.059	5.0	0.020
310.16	6478	366.393	5.0	0.085
318.16	7928	369.563	5.0	0.014

Here the effect of viscosity plays an important role and has an effect on the mobility of ions more than the effect of dielectric constant

When solvent-separated ion pairs are formed, ion-association takes place in a number of stages for example:



Hence the magnitude of (K_A) as determined from equ. $\Lambda_{\text{equiv.}} = f(\Lambda_o, R, K_A)$ will depend upon the stability of both $\text{H}^+ \dots \text{H}_2\text{O} \dots \text{X}^-$ and $\text{H}^+ \dots \text{X}^-$.

The distance between the ions (R) is almost 5 \AA and the small values of $\sigma_s(\Lambda)$ give an indication of good agreement between the experimental and the theoretical values.

The plot of $\ln K_A$ against $1/T$ is shown in Figure (2).

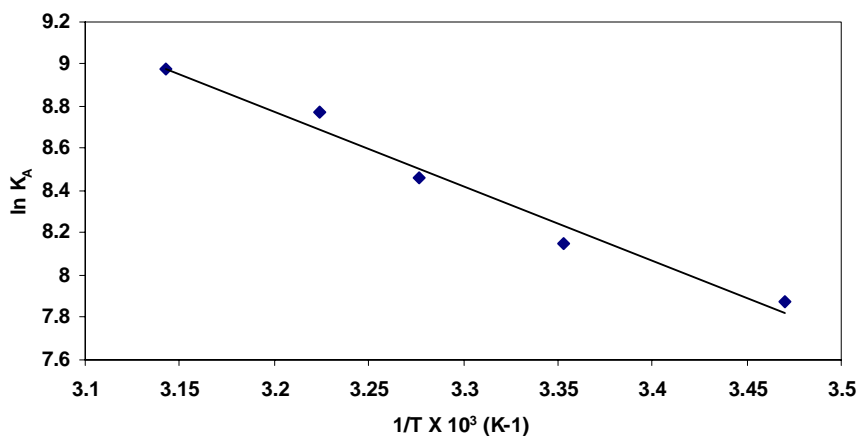


Figure (2): Plot of $\ln K_A$ against $1/T$ for Barbituric acid

The standard enthalpy calculated from the above graph and according to this equation:

$$\ln K_A = -\Delta H^\circ / RT + C \dots (4)$$

The standard entropy of ion-pair formation is a linear combination of two variables $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \dots (5)$

and the standard Gibb's energy calculated from the relationship:

$$\Delta G^\circ = -R T \ln K_A \dots (6)$$

where the results are shown in Table (3):

Table (3): Thermodynamic parameters from the ion association constant of barbituric acid in water at different temperatures

Temp. K	$-\Delta G^\circ$ kJ.mol ⁻¹	ΔH° kJ.mol ⁻¹	ΔS° J.K ⁻¹ .mol ⁻¹
288.16	18.876	29.382	167.469
298.16	20.208		166.319
305.16	21.472		166.646
310.16	22.630		167.693
318.16	23.749		166.992

The value of (ΔH°) is positive and in agreement with the theoretical (ΔH°) values¹⁵, since the theoretical equation for (ΔH°) contains the $(1 + d\ln D/d\ln T)$ terms. Thus the experimental value of $d\ln D/d\ln T$ makes the theoretical (ΔH°) value positive ($d\ln D/d\ln T < -1$). This agreement of the experimental and theoretical value of (ΔH°) may mean that the temperature dependence of D , $d\ln D/d\ln T$ represents how much the ion-solvation is weakened by ion-association. The positive value of (ΔS°) has been considered¹⁶ as due to the decreased orientation of solvent molecules when the ion-pair forms. The values of (ΔG°) of the ion-association are negative and should depend on the kind of the ion¹⁶. There are several theories regarding ion association¹⁶, the theories, however, give positive ΔH° values in many solvents, since the theoretical equation of ΔH° contains $(1 + \delta\ln D / \delta\ln T)$ term, where D is the solvent dielectric constant. Thus, the experimental value of $(1 + \delta\ln D / \delta\ln T)$ makes the theoretical ΔH° value positive $(1 + \delta\ln D / \delta\ln T) (-1)$, contrary to the expectation¹⁶. The negative value of ΔG° indicates that the process is spontaneous.

The complexes of barbituric acid with alkaline earth metals (Mg²⁺, Ca²⁺ and Ba²⁺ as chlorides):

Have been prepared for the first time and the following measurements were carried out to characterize them: Infrared spectra, Halogen-test, Job-method, Electronic spectra.

The IR spectra of both ligand and complexes are shown in figures (3,4), and the details of the stretching vibration bands is discussed as follows:

O-H Stretching Vibration (H-bonding):

In the region (3478-3474 cm⁻¹) an intense broad band was observed in the infrared spectra for ligand and complexes (Table 4.4). This band was assigned to the stretching vibration of hydrogen bonding^(17a) (intra-H-bonding with ortho group).

N-H Stretching Vibration:

The spectra of barbituric acid show a single free N-H stretching band in the region⁽¹¹⁴⁾ (3100-3300 cm⁻¹) of the ligand spectra (Table 4).

The infrared spectra of the complexes (II, III, IV) showed that the previous $\nu(N-H)$ band weakened indicating a loss of hydrogen from (N-H) after coordination of ligand with the metal^(17b).

Carbonyl (C=O) Stretching Vibration:

The spectra of barbituric acid show a single strong band at 1718 cm^{-1} which may be assigned to the stretching of C=O group. This band weakened in the complexes and new bands appear at ($1619, 1618, 1703\text{ cm}^{-1}$) in magnesium complex, calcium complex and barium complex respectively. The shifting of $\nu\text{C=O}$ to lower wavelength numbers in the complexes of alkaline earth metals studied during the present investigations, supports the coordination of C=O group to the metal ion^(17c).

M-N Stretching Vibration:

The absorption band of $\nu(\text{M-N})$ for the complexes of Mg(II), Ca(II) and Ba(II) at ($469, 497$ and 440 cm^{-1}) respectively as shown in Table (4.4) indicate the coordination of metal with ligand^(17d).

M-O Stretching Vibration:

The absorption band for $\nu(\text{M-O})$ appear in the region ($650\text{-}350\text{ cm}^{-1}$)^(17d). The infrared spectra of the complexes of Mg(II), Ca(II) and Ba(II) show the absorption band in the region ($532\text{-}628\text{ cm}^{-1}$) which indicate the coordination of metal with ligand^(17d).

Halogen-test:

Test for chloride with AgNO_3 gives white precipitate which indicate the presence of free chloride (outside the coordination sphere)^(18a,b)

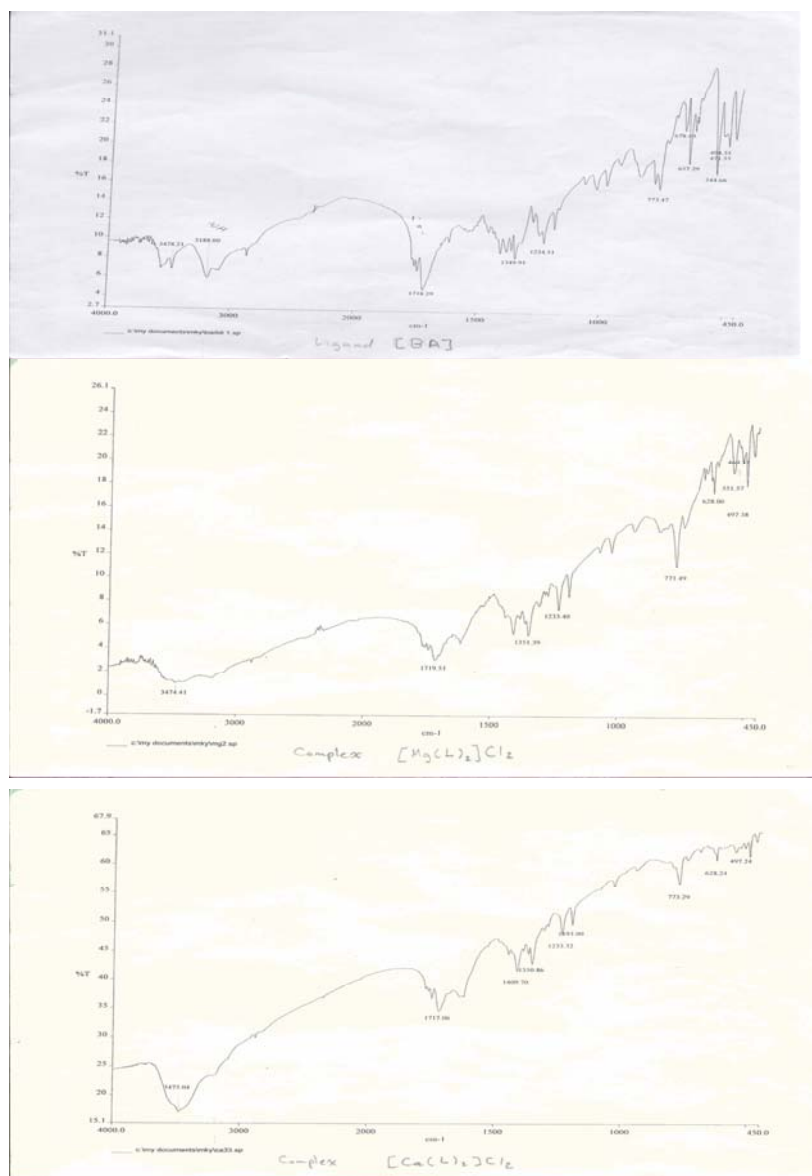


Figure (3): The IR spectra for ligand (BA) and [Mg(L)₂]Cl₂, [Ca(L)₂]Cl₂ complexes

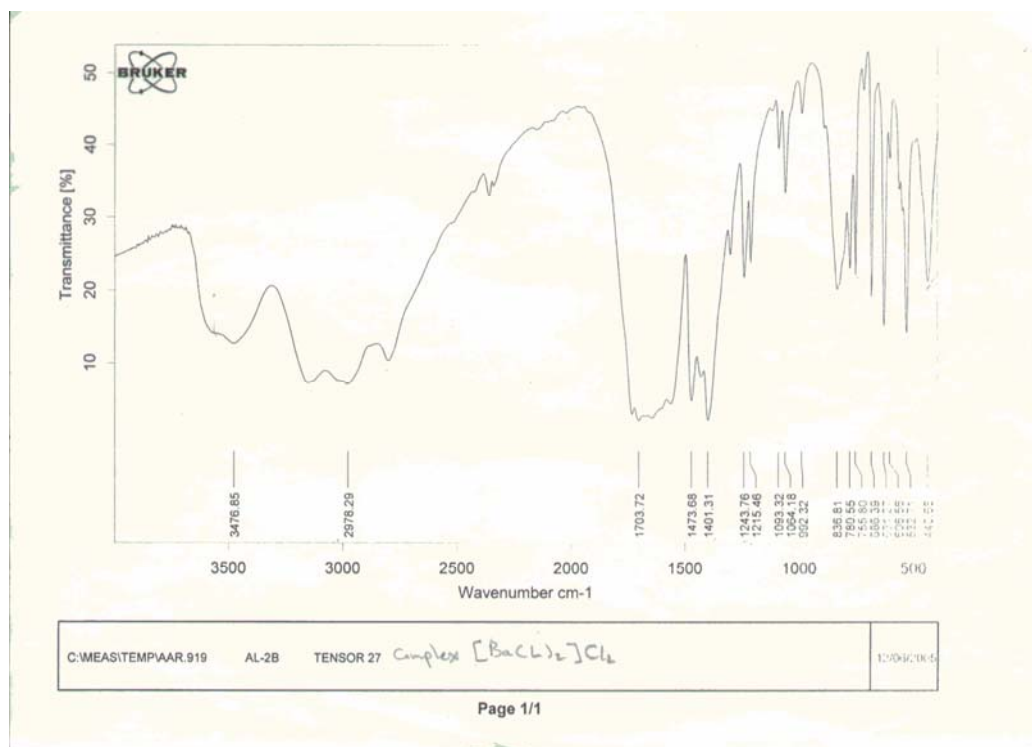
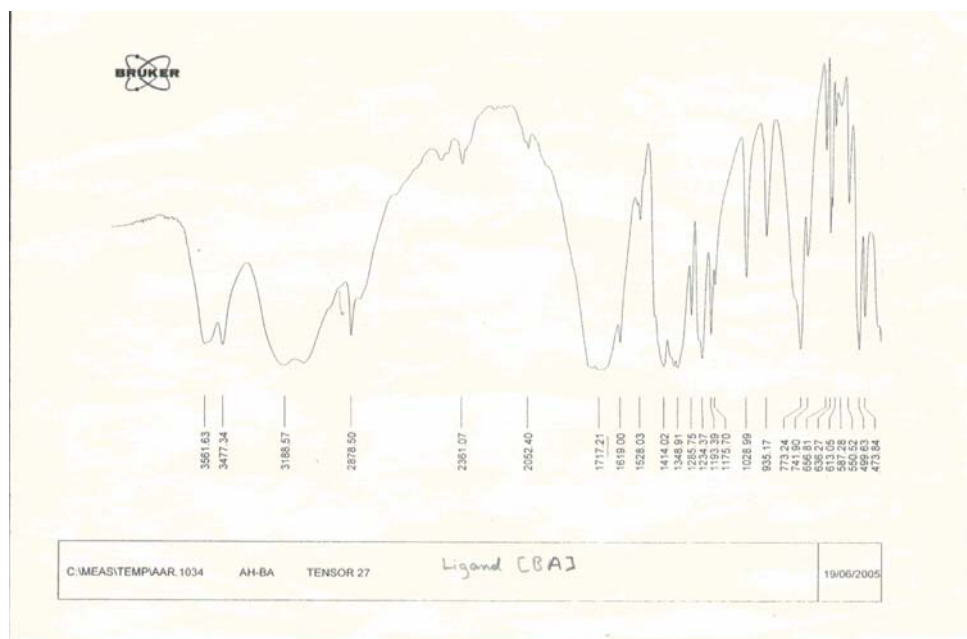


Figure (4): The IR spectra for ligand (BA) and [Ba(L)₂]Cl₂ complex

Infrared spectra (cm⁻¹) for barbituric acid (L) and its metal complexes are presented in Table (4):

Table (4): Infrared spectra (cm^{-1}) for barbituric acid (L) and its metal complexes

No.	Compound	$\nu(\text{H-bond})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
I	L	3478	3188	1718		
II	$[\text{Mg}(\text{L})_2]\text{Cl}_2$	3474	3188(w)	1719, 1619	469	628
III	$[\text{Ca}(\text{L})_2]\text{Cl}_2$	3475	3188(w)	1717, 1618	497	628
IV	$[\text{Ba}(\text{L})_2]\text{Cl}_2$	3477	3188(w)	1717, 1703	440	606, 632

(w) = weak

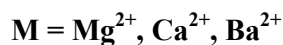
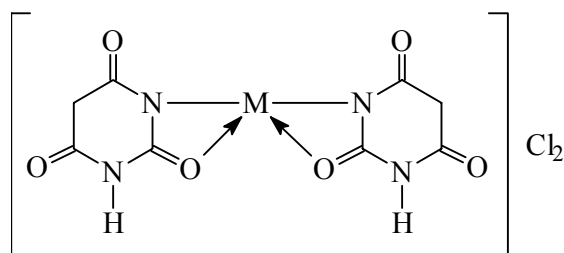
The UV-Visible spectra for barbituric acid as ligand and its complexes (nm) are presented in Table (5)

Table (5): The UV-Visible spectra for barbituric acid as ligand and its complexes (nm)

No.	Compound	Wavelength (nm)		
I	L	215	256	
II	$[\text{Mg}(\text{L})_2]\text{Cl}_2$	235	267	426, 481 (c.t.)
III	$[\text{Ca}(\text{L})_2]\text{Cl}_2$	236	307	459 (c.t.)
IV	$[\text{Ba}(\text{L})_2]\text{Cl}_2$	245	326	467 (c.t.)

c.t. = charge transfer absorption band.

The expected structure of the complexes:

**Figure (5): The expected structure for the complexes of barbituric acid**

Conductivity Measurements of Complexes (II, III, IV) in Water at Different Temperatures:

All the complexes (II, III, IV) have been measured in deionized water

at different temperature (288.16-318.16 K). The results obtained are illustrated in Figures (6-8).

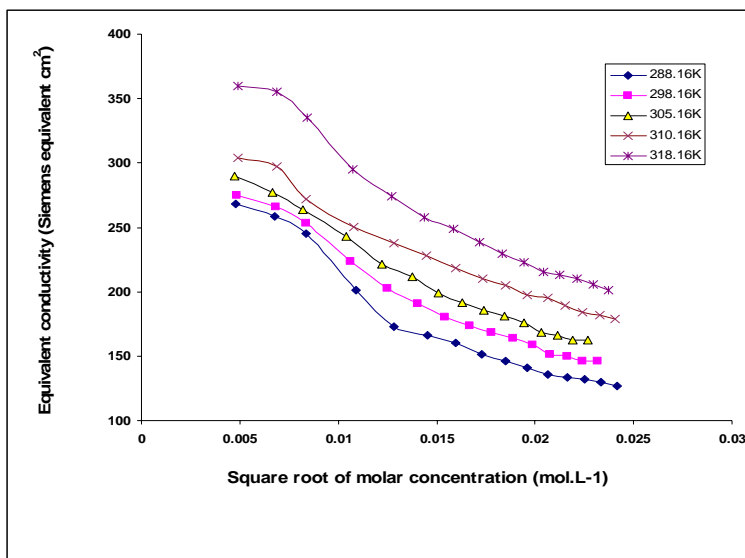


Figure (6): Plot of equivalent conductivity against square root of molar concentration of $[\text{Mg}(\text{L})_2]\text{Cl}_2$ in water at different temperatures

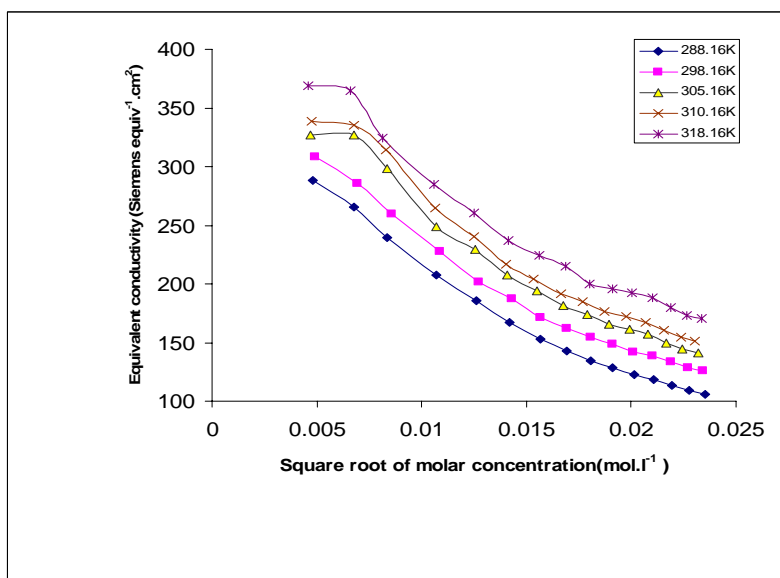
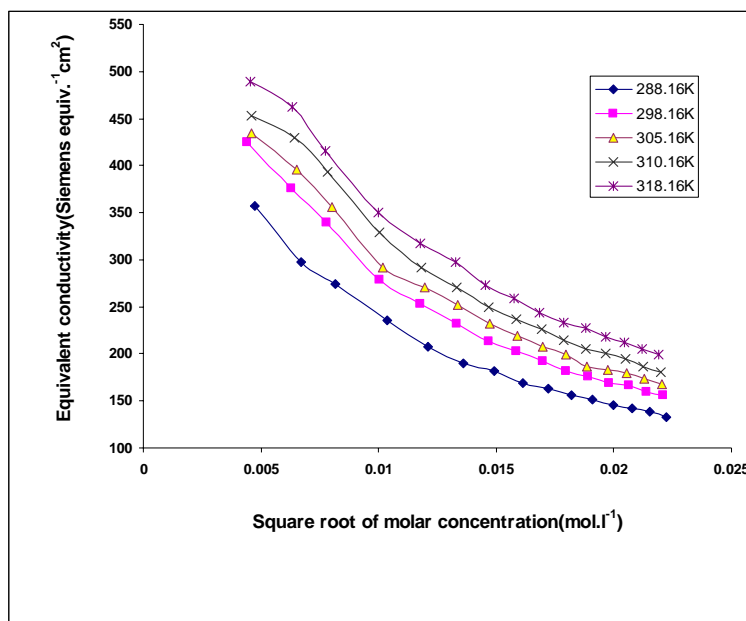


Figure (7): Plot of the equivalent conductivity against square root of molar concentration of $[\text{Ca}(\text{L})_2]\text{Cl}_2$ in water at different temperatures



Figure(8):Plot of the equivalent conductivity against molar concentration of $[\text{Ba}(\text{L})_2]\text{Cl}_2$ in water at different temperatures

From the above Tables and Figures it is found that $\Lambda_{\text{equiv.}}$ decrease with the increasing of the concentration of all the complexes. The equivalent conductivity for each of the complexes is directly proportional with temperatures according to equation (4).

Interpretation of Conductivity Measurements of Barbituric acid-Alkaline Earth Metals in Water at Different Temperatures:

Computer programme (RM1) for asymmetrical electrolytes is used to analyze the concentration-conductivity measurements for the complexes: $[\text{Mg}(\text{L})_2]\text{Cl}_2$, $[\text{Ca}(\text{L})_2]\text{Cl}_2$ and $[\text{Ba}(\text{L})_2]\text{Cl}_2$ in conductivity water. In which the input data are (T, D, η) where T is the temperature in Kelvin,

D and η are the dielectric constant and viscosity (poise) of the solvent at that temperature¹⁸ z_i and λ_i for each ionic species; $K_A^{(1)}$, $K_A^{(2)}$, $\lambda_{\text{MX}^+}^0$, $\lambda_{\text{M}^{2+}}^0$ and R according to L-W equation for MX_2 electrolyte^{9,10}.

Tables (6-8) show the best fit parameters of analysis of conductance data using L-W equation. This analysis show that all the complex cations associated with anions to form a new species $(\text{MX})^+$:

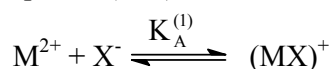


Table (6): Best fit parameters of analysis of conductance data for [Mg(L)₂]Cl₂ in water at different temperatures

Temp. (K)	K _A ⁽¹⁾	K _A ⁽²⁾	λ _{MX⁺} ^o	λ _{M²⁺} ^o	R (A°)	σs(Λ)
288.16	2800	< 1.0	0.9	191	8.0	0.931
298.16	2280	< 1.0	0.9	219	8.0	0.970
305.16	1976	< 1.0	0.9	225	8.0	0.743
310.16	1755	< 1.0	0.9	225	8.0	0.268
318.16	1506	< 1.0	0.9	229	8.5	0.241

Table (7): Best fit parameters of analysis of conductance data for [Ca(L)₂]Cl₂ in water at different temperatures

Temp. (K)	K _A ⁽¹⁾	K _A ⁽²⁾	λ _{MX⁺} ^o	λ _{M²⁺} ^o	R (A°)	σs(Λ)
288.16	4415	< 1.0	0.1	289	8.5	0.726
298.16	4155	< 1.0	0.1	290	7.5	0.327
305.16	3980	< 1.0	0.1	310	7.0	0.717
310.16	3870	< 1.0	0.1	313	9.0	0.462
318.16	3730	< 1.0	9.0	325	7.0	0.846

Table (8): Best fit parameters of analysis of conductance data for [Ba(L)₂]Cl₂ in water at different temperatures

Temp. (K)	K _A ⁽¹⁾	K _A ⁽²⁾	λ _{MX⁺} ^o	λ _{M²⁺} ^o	R (A°)	σs(Λ)
288.16	5650	< 1.0	52.0	332	8.0	0.367
298.16	5455	< 1.0	25.0	398	8.5	0.290
305.16	5000	< 1.0	5.0	420	8.5	0.658
310.16	4800	< 1.0	1.0	441	7.0	0.513
318.16	4550	< 1.0	1.0	454	7.0	0.829

The results of analysis, Tables (9-11) show that the values of λ_{M²⁺}^o for [Mg(L)₂]Cl₂, [Ca(L)₂]Cl₂ and [Ba(L)₂]Cl₂ increase with the increasing of temperature. Generally the values of λ_{M²⁺}^o for the three complexes follow the sequence λ_{M²⁺}^o [Ba(L)₂]²⁺ > λ_{M²⁺}^o [Ca(L)₂]²⁺ > λ_{M²⁺}^o [Mg(L)₂]²⁺ since Mg²⁺ is the smallest cation and has the smallest solvated-ion mobility.

For the three complexes, λ_{MX⁺}^o are smaller than λ_{M²⁺}^o this is attributed to the fact that the solvation of MX⁺ ion is more than M²⁺ ion.

The values of K_A⁽¹⁾ are decreasing with the increasing of temperature of the three complexes. This may be due to the effect of short range interaction and the hydrogen bonding formed at low temperature^{17a,19}.

Also the values of K_A⁽¹⁾ follow the sequence K_A[Ba(L)₂]Cl₂ > K_A[Ca(L)₂]Cl₂ > K_A[Mg(L)₂]Cl₂.

The cation forms a more stable ion-pair as the cation solvation becomes weaker i.e if the ion-solvation stronger the stability of ion-pair becomes smaller²⁰. The values of the distance parameter (R) are found to be (7-9 A°) for all the complexes which indicate the formation of SSIP. Finally the values of σs(Λ) indicate the good

applicability of the equation used for the analysis of the barbituric acid complexes.

The plot of $\ln K_A$ against $1/T$ for barbituric acid complexes are shown in Figure (9).

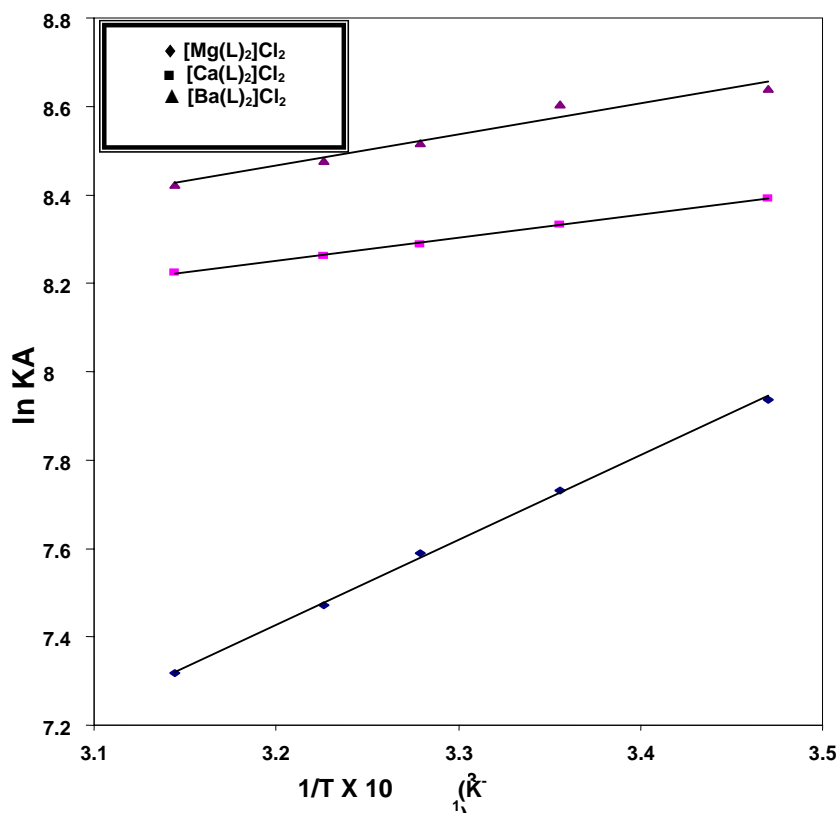


Figure (9): Plot of $\ln K_A$ against $1/T$ for barbituric acid complexes with (Mg, Ca, Ba) in water

Calculation of the Thermodynamic Parameters (ΔG° , ΔH° and ΔS°) of Barbituric Acid Complexes:

The thermodynamic parameters (ΔG° , ΔH° and ΔS°) are calculated as

mentioned before. Tables (9-11) show the calculated values.

Table (9): Thermodynamic parameters from the ion-association constant of $[\text{Mg}(\text{L})_2]\text{Cl}_2$ in water at different temperatures

Temp. K	$-\Delta G^\circ$ kJ.mol^{-1}	$-\Delta H^\circ$ kJ.mol^{-1}	ΔS° $\text{J.K}^{-1}.\text{mol}^{-1}$
288.16	19.016	15.844	11.007
298.16	19.167		11.143
305.16	19.254		11.172
310.16	19.263		11.023
318.16	19.355		11.035

Table (10): Thermodynamic parameters from the ion-association constant of $[\text{Ca}(\text{L})_2]\text{Cl}_2$ in water at different temperatures

Temp. K	$-\Delta G^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	$-\Delta H^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	ΔS° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
288.16	24.215	4.351	68.934
298.16	23.246		63.372
305.16	22.595		59.785
310.16	22.156		57.406
318.16	21.502		53.907

Table (11): Thermodynamic parameters from the ion-association constant of $[\text{Ba}(\text{L})_2]\text{Cl}_2$ in water at different temperatures

Temp. K	$-\Delta G^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	$-\Delta H^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	ΔS° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
288.16	24.926	5.855	66.182
298.16	24.005		60.873
305.16	23.217		56.895
310.16	22.733		54.417
318.16	22.021		50.811

It was found that the values of ΔH° of ion-association in water for all the complexes are negative since ions are rigid and associated in a coulombic interaction in a dielectric continuum media¹⁵. The value of ΔG° are negative indicating that the process occurs spontaneously.

The positive values of ΔS° for the complexes in water have been considered as due to the decrease in the orientation of solvent molecules when the ion-pair form, i.e: is explained by the fact of the solvation of M^{2+} is weakened by the ion pairing of MX^+ ¹⁶.

The plot of Walden-product against reciprocal dielectric constant is shown in Figure (10). it is clear that $\Lambda_0\eta$ decreases with the decreasing of

the dielectric constant. This variation in Walden-product reflects the change of the total solvations²¹. The decrease of the Walden-product indicates an increase of the total solvation with decreasing of the dielectric constant²². The increase of dielectric constant of the solvent will increase the solvating power of that solvent, this causes the ion to move with only the primary solvation shell in the solvent and the effect of the secondary solvation appears to be very small²³.

The plot of Walden-product against the reciprocal of temperature is shown in Figure (11) which indicates that Walden-product in this work is temperature dependence.

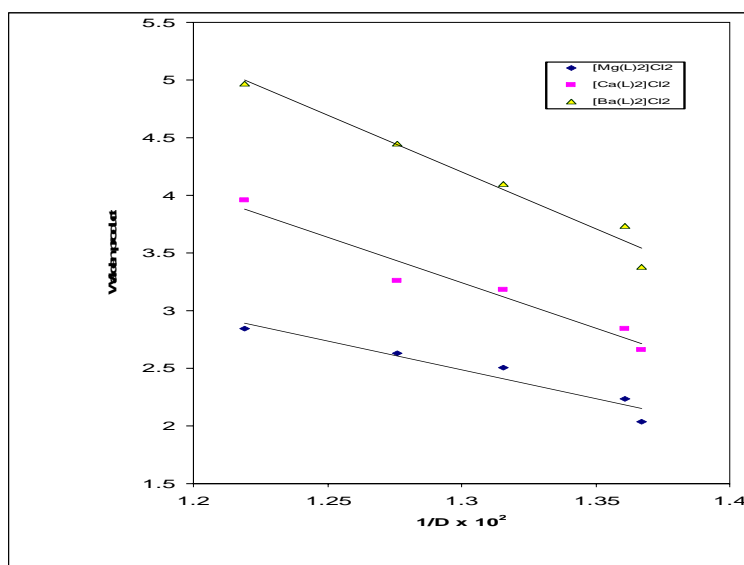


Figure (10): Plot of Walden-product against $1/D$ for Barbituric acid complexes in water at different temperatures

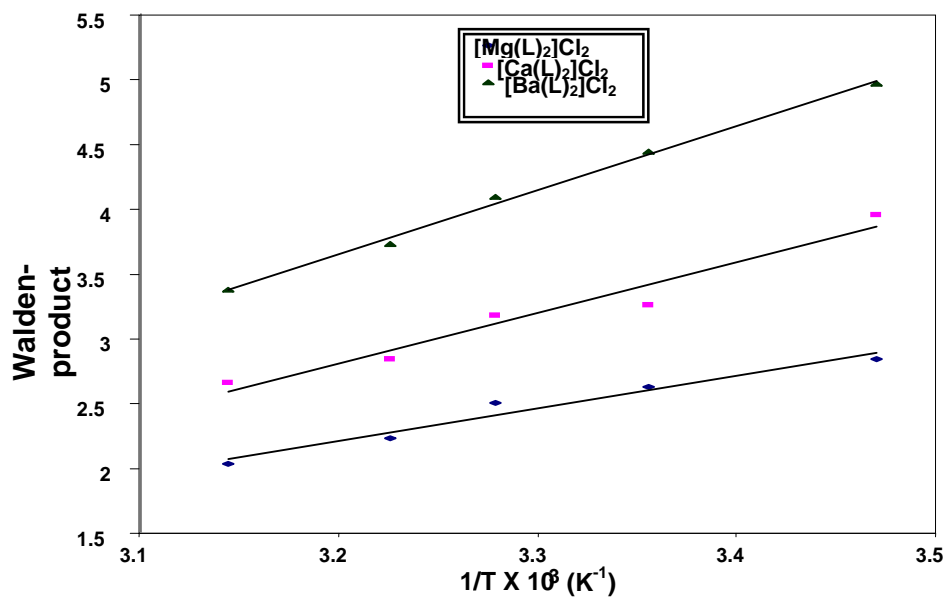


Figure (11): Plot of Walden-product against $1/T$

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