Conductometric Studies for Association Reaction of some Amino Acid Complexes in Water

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ABSTRACT

Molar conductivities of dilute solutions for the complexes: Co(II)(alanine + valine), Ni(II)(valine + serine), Ca(II)(alanine + serine), Mg(II)(valine + serine) in water were measured in the temperature range from (293.16–313.16K). The ionic molar conductivity (Λ), the association constant (K_A), distance parameter (R), and ($\sigma\Lambda$) at best fit values were determined by treating experimental data with Lee-Wheaton conductivity equation. Thermodynamic quantities for the ion association reaction were derived from the temperature dependence of K_A . The obtained results provide information on ion – ion and ion-solvent interactions.

Keywords: Amino acid, conductivity, mixed ligand amino acid complexes, lee-wheaton equation, thermodynamics.

: Co(II)(alanine + valine), Ni(II)(valine + serine), Ca(II)(alanine + serine), Mg(II)(valine + (293.16–313.16K) serine) (R) (K_A) (Λ) ($\sigma\Lambda$)

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INTRODUCTION

Many amino acids and their derived complexes were prepared and identified by using different methods (ex: spectral (U.V,IR), magnetic susptibility, elemental analysis and X-ray diffraction], since amino acids as ligands contain two donor atoms (N and O), therefore the complexes of amino acids with metals are interesting to study. The complexes of Co(II), Zn(II) with mixed ligands of amino acids (systine, histidine, systine methyl ester and histidine methyl ester) were prepared and identified by elemental analysis, electrochemical conductivity, magnetic measurements and IR spectra and they have shown a tetrahedral shape (Rabindra *et al.*, 2005).

Complexes of Fe(II), Cr(II), Ni(II), Co(II) and Cu(II) were prepared using Schiff bases by the condensation of lyosine with 2-acetyl pyridine, and analyzed by elemental analysis, electrical conductivity, magnetic susptebelity and spectral methods (IR and UV). The results show that Co(II) and Ni(II) complexes are tetrahedral while Fe(III) and Cr(III) complexes are octahydral, while Cu(II) complex is square planer. In addition, the study includes the measurement of vibrational spectra and equivalent conductance at infinite dilution (Λ°), association constant (K_A) at 298K using mixed solvent 50% (v\v) (diethylformamide-water) (Hosny and El-Dossoki, 2008). In differential pulse polarographic study, the complexes of Cu (II) with mixed ligands composed of amino acids (therionine, valine, isolyosine) with tartarate were prepared, the formation constantans and equilibrium constants were also calculated for these complexes (Killa *et al.*,1992). The study of Cd (II) with Vit.C (ascorbic acid) with amino acids (Serine and L-Lysine) and other complexes were prepared and measured by voltametric technique at pH 7.3 at two temperatures (25 and 37°C) and molar percent 1:1:1,1:1:2,1:2:1. The stability constants follow the sequence:

L-Lys. < L-Orn. < L-Ser. < L-Phe. < L-Glu. < L-Asp. Depending on steric effect and the basisity of ligands, the equilibrium constants for the complexes range were between (2.23-11.33), and the thermodynamic parameters were also calculated (Khan and Khanam, 2008).

EXPERIMENTAL

Conductivity water was prepared by redistilling water three times with the addition of little amount of potassium permanganate and a small pellets of (KOH) (Palmer,1954) ,the specific conductance of water was less than 1-2 × 10⁻⁶ (S.cm⁻¹). The complexes of Fe(II), Ca(II), Ni(II) with histidine and glycine were prepared by mixing 0.0012 mole of each hydrated salts (FeCl₂, CaCl₂, NiCl₂) in 25 ml of conductivity water with 0.0037 mole of the amino acid (Glycine or Histidine) in 25 ml of conductivity water and refluxed for about two hours on a water bath. On cooling, each complex was precipitated, then the product was dried under vacuum over anhydrous calcium chloride. Magnetic electronic spectra, (UV-Vis Shimadzu,1650), Infrared (biotech engineering management Co. LTD.UK FTIR-600) measurement was used for the analysis of the complexes.

A general method has been used for measuring the conductance of the electrolytes, the conductivity cell was washed, dried and then weighed empty and kept at a constant temperature (\pm 0.1°C) using a water circulating ultra thermostat type VH5B radiometer. A certain amount of solution was injected into the conductivity cell and the conductivity of solution was measured by WTW Inolab 740 computerized conductivity meter. Another known amount of solution was injected by a syringe of 1ml and the measurement was repeated. Generally about (15) addition have been made by weighing the amount for each one.

$$+2$$
 Cl_2

M=II(Ni), Co(II), Ca(II), Mg(II)

Proposed structure of the complex under study

RESULTS AND DISCUSSION

Conductometric data were treated using (LW) equation in which a wide dielectric range for electrolytes solution can give detailed information concerning ion-ion and ion-solvent interaction. For unsymmetrical electrolyte 2:1 a program (RM1) is used to analyze the concentration- conductivity measurements in which the input data are (T, D, η) where T is temperature in Kelvin, D and η are the dielectric constant and viscosity (poise) of the solvent at (37 °C).

Lee and Wheaton obtained an equation of unsymmetrical electrolytes of the form (Lee and Wheaton, 1979):

$$\lambda i = \lambda i^{o} \left[1 + Z_{j} \sum_{P=2}^{S} X_{j}^{P} \sum_{V=1}^{S} tv X_{V}^{P} \left[A^{P}_{v}(t)(\beta k) + B^{P}_{v}(t) (\beta k)^{2} + C^{P}_{v}(t) (\beta k)^{3} \right] - \frac{Z_{j}(Kt)}{2(I+t)} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \Pi_{j}^{(5)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k)^{2} + \frac{1}{2} \left[I + V_{j}^{(1)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k) + V_{j}^{(2)}(t) (\beta k) \right] \right]$$

all the terms are defined in the original paper (Lee and Wheaton (1978). The program (RM1) is used to determine values of K_A , $\lambda^o_{MX}^+$ and R where K_A is the association constant; R is the average center to center distance for the ion pairs; λ^o , is the ionic equivalent conductance of each ion in solution. A multi parameter "Least square" curve fitting procedure is used to give the lowest value of curve fitting parameter, $\sigma(\Lambda)$, between the experimental and calculated values. An iterative numerical method which was found to be very successful has been used to find the minimum($\sigma\Lambda$).

$$\sigma \Lambda = \left\{ \sum_{n=1}^{NP} \left(\Lambda_{\text{calc.}} - \Lambda_{\text{exp.}} \right)^2 / NP \right\}^{1/2}$$

Tables (A) (1-4) and figures (A)(1-4) show the relations between (Λ) and concentration (\sqrt{c}) for the studied complexes at different temperatures.

A general look at the tables of the solution complexes of amino acids with $\{Co(II), Ni(II), Ca(II) \text{ and } Mg(II)\}$ at different temperatures shows that the equivalent conductance (Λ) increases with increasing temperatures, which may be due to the dissociation of the

amino acids complexes at high temperatures leading to the formation of intermediate compounds which reduce the values of equivalent conductance.

Fig. (A)(1-4), show the application of Kohlrawsh equation for the complexes under study at different temperatures, in which the relation between equivalent conductances against the square roots of concentration gives a hyperbolic relation which indicates that the solutions of the complexes behave as week electrolytes in this concentration range.

Tables (1-4) show that the equivalent conductances differ by increasing or decreasing temperature, this can be attributed to the breaking and formation of hydrogen bonding and increasing the kinetic energy of the molecules and decreasing viscosity (Dabbagh and Akrawi, 1992), the relation between equivalent conductance and temperature is illustrated by the equation (Robinson and Soykes, 1959):

$$\Lambda$$
 (t) = Λ (25C)[1+B(T-25)]

 Λ = the equivalent conductance at temperature (t)

 Λ (25) = the equivalent conductance at (25C)

Lee-Wheaton equation for unsymmetrical electrolyte (2:1) at different temperatures and at pH7 were applied, the results which include the concentration and equivalent conductance were analyzed by using a computer program after giving the values of temperature (T)K, viscosity (η) pois and dielectric constant (D) to determine the ionic molar conductivities λ_M^{2+} , λ_{MX}^{+} , association constant K_A for the ion pairs. The mean distance between ions in solution (R) and the standard deviation σ (Λ) between the experimental and calculated values of (Λ). Tables B(1-4) show the results of analysis of the complexes at different temperatures.

Table A 1: Molar concentration (M) and Equivalent conductance of Mg-Complexes with alanine and valine in water at different temperatures

283.16 °K	Y₀ 9	288.16 °K	У₀9	293.16 °K	Ж∘9	303.16 °K	У 9	313.16 °K	Y₀ 9
C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	$\Lambda_{\rm equiv.}$ (ohm ⁻¹ .equiv ⁻¹
0.1982	155.287	0.1989	149.247	0.1989	145.759	0.1981	151.837	0.1996	146.315
0.3877	146.936	0.3903	142.198	0.3939	140.078	0.3897	145.689	0.3925	142.138
0.5710	144.779	0.5750	140.862	0.5773	137.849	0.5738	142.903	0.5774	139.416
0.7460	143.427	0.7526	140.847	0.7543	136.554	0.7521	142.271	0.7569	138.060
0.9163	142.969	0.9229	140.306	0.9253	136.179	0.9245	141.703	0.9304	137.570
1.0793	142.687	1.0865	140.355	1.0895	135.838	1.0909	141.164	1.0989	137.416
1.2376	142.212	1.2464	140.003	1.2469	135.541	1.2509	140.697	1.2616	136.733
1.3919	141.888	1.4007	139.217	1.3996	135.394	1.4066	139.694	1.4186	136.053
1.5395	141.284	1.5497	139.061	1.5476	135.047	1.5572	139.356	1.5706	135.932
1.6814	140.949	1.6925	138.844	1.6905	134.577	1.7029	138.884	1.7187	135.570
1.8200	140.657	1.8309	138.453	1.8290	134.226	1.8440	138.013	1.8619	135.080
1.9539	140.235	1.9666	138.053	1.9623	133.819	1.9809	137.816	2.0004	134.475
2.0837	140.136	2.0974	137.415	2.0918	133.464	2.1138	137.430	2.1351	133.954
2.2101	139.811	2.2236	137.085	2.2175	132.907	2.2431	136.971	2.2663	133.696
2.3317	139.599	2.3467	136.768	2.3395	132.868	2.3685	136.737	2.3934	132.957

Table A 2: Molar concentration (M) and Equivalent conductance of Ca- Complexes with valine and serine in water at different temperatures

283.16 °K	Y₀ 9	288.16 °K	Y₀ 9	293.16 °K	Y₀ 9	303.16 °K	Y₀ 9	313.16 °K	Y₀ 9
C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹	C×10 ⁴ (mole\L)	A _{equiv.} (ohm-1 .equiv-1 .cm ²)	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹
0.1982	151.250	0.1967	146.249	0.1988	145.843	0.2003	150.814	0.2006	150.106
0.3890	142.092	0.3873	139.830	0.3885	141.010	0.3934	143.363	0.3941	143.819
0.5733	138.675	0.5714	137.513	0.5720	138.911	0.5776	141.111	0.5813	140.207
0.7522	137.599	0.7499	136.004	0.7491	137.497	0.7551	140.378	0.7625	139.012
0.9222	137.177	0.9224	135.513	0.9197	137.007	0.9256	139.907	0.9371	138.731
1.0874	137.022	1.0894	134.942	1.0833	136.625	1.0904	139.861	1.1051	138.444
1.2498	136.016	1.2492	134.483	1.2409	136.592	1.2491	139.295	1.2682	137.595
1.4044	135.288	1.4048	134.184	1.3932	136.020	1.4033	138.958	1.4266	137.040
1.5541	134.602	1.5553	133.739	1.5407	135.651	1.5528	138.136	1.5795	136.756
1.7001	133.406	1.6997	132.966	1.6841	135.384	1.6965	137.635	1.7278	136.304
1.8419	132.828	1.8405	132.848	1.8217	135.039	1.8355	137.566	1.8719	135.423
1.9792	131.576	1.9767	132.541	1.9547	134.502	1.9694	137.098	2.0119	134.949
2.1127	130.695	2.1097	132.244	2.0843	134.197	2.1000	136.666	2.1480	134.776
2.2424	129.908	2.2384	132.015	2.2103	133.964	2.2267	136.527	2.2795	134.361
2.3688	129.358	2.3635	131.796	2.3325	133.779	2.3494	136.206	2.4071	133.354

Table A 3: Molar concentration (M) and Equivalent conductance of Co- Complexes with alanine and serine in water at different temperatures

283.16 °K	y₀ 9	288.16 °K	y∘ 9	293.16 °K	9 oK	303.16 °K	У₀9	313.16 °K	Y₀ 9
C×10 ⁴ (mole\L)	Aequiv. (ohm-1 .equiv-1 .cm ²)	C×10 ⁴ (mole\L)	$\Lambda_{\rm equiv.}$ (ohm-1 .equiv-1 .cm ²)	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)
0.2008	121.981	0.2034	121.988	0.2022	126.621	0.2008	122.568	0.2020	125.282
0.3940	115.475	0.3966	117.994	0.3958	123.285	0.3957	115.719	0.3952	119.923
0.5795	114.148	0.5829	115.786	0.5814	121.402	0.5811	112.858	0.5828	118.391
0.7571	113.587	0.7632	115.300	0.7587	119.935	0.7627	111.444	0.7636	117.868
0.9277	113.175	0.9353	114.931	0.9302	119.324	0.9392	110.729	0.9380	117.266
1.0926	113.036	1.1021	114.777	1.0965	119.010	1.1102	109.889	1.1055	116.694
1.2514	112.674	1.2639	114.329	1.2569	118.948	1.2758	109.733	1.2676	116.359
1.4058	112.390	1.4195	114.127	1.4109	118.361	1.4351	109.052	1.4247	115.815
1.5540	111.968	1.5690	113.765	1.5601	117.938	1.5881	108.937	1.5759	115.485
1.6979	111.699	1.7146	113.436	1.7041	117.657	1.7373	108.212	1.7225	114.952
1.8366	111.341	1.8538	113.282	1.8430	117.471	1.8813	107.902	1.8647	114.766
1.9706	111.135	1.9874	113.213	1.9775	117.064	2.0208	107.633	2.0017	114.401
2.1014	110.841	2.1188	112.798	2.1083	116.681	2.1561	107.107	2.1356	113.786
2.2284	110.618	2.2443	112.506	2.2347	116.568	2.2875	106.885	2.2646	113.705
2.3511	110.587	2.3675	112.353	2.3579	116.415	2.4158	106.662	2.3906	113.152

Table A 4: Molar concentration (M) and Equivalent conductance of Ni- Complexes with valine and serine in water at different temperatures

283.1	283.16 °K	288.1	8.16 °K	293.16 °K	Y∘ 9	303.16 °K	Y₀ 9	313.16 °K	9° K
C×10 ⁴ (mole\L)	A _{equiv.} (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	Aequiv. (ohm ⁻¹ .equiv ⁻¹ .cm ²)	C×10 ⁴ (mole\L)	$\Lambda_{ m equiv.}$ (ohm-1 .equiv-1 .cm ²)	C×10 ⁴ (mole\L)	Aequiv. (ohm-1 .equiv-1 .cm ²)	C×10 ⁴ (mole\L)	$\Lambda_{ m equiv.}$ (ohm-1 .equiv-1 .cm ²)
0.1973	131.695	0.2017	137.929	0.2898	93.715	0.2015	139.019	0.1993	130.459
0.3889	125.404	0.3945	129.727	0.5657	89.391	0.3952	130.247	0.3913	124.949
0.5734	122.961	0.5817	126.364	0.8316	87.178	0.5811	124.908	0.5787	122.697
0.7498	122.039	0.7614	125.434	1.0881	86.387	0.7617	123.412	0.7569	121.543
0.9227	122.039	0.9328	124.896	1.3329	906:58	0.9340	122.591	0.9309	121.394
1.0880	120.861	1.0982	124.295	1.5735	85.477	1.1023	122.467	1.0985	121.077
1.2479	120.398	1.2589	123.917	1.8033	862.398	1.2644	122.191	1.2606	120.972
1.4027	119.767	1.4139	123.420	2.0259	84.900	1.4204	121.852	1.4175	120.634
1.5536	119.196	1.5642	123.066	2.2417	84.756	1.5706	121.290	1.5686	120.170
1.6996	118.761	1.7084	122.922	2.4490	84.524	1.7166	121.171	1.7156	120.075
1.8403	118.489	1.8490	122.498	2.6512	84.302	1.8584	120.803	1.8577	119.772
1.9762	118.255	1.9843	122.209	2.8467	84.134	1.9954	120.679	1.9954	119.524
2.1085	118.095	2.1157	122.184	3.0358	83.834	2.1281	120.058	2.1279	119.363
2.2361	118.061	2.2426	121.954	3.2198	83.702	2.2562	119.893	2.2577	119.148
2.3596	117.606	2.3659	121.726	3.3986	83.564	2.3817	119.663	2.3835	118.943

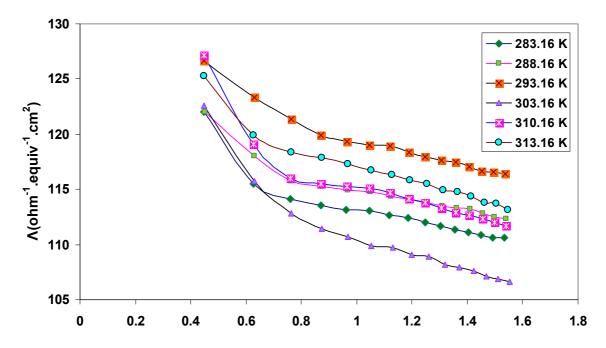


Fig. A(1): The relation between the square root of concentration and the equivalent conductance of Co(II) with alanine and valine at different temperatures

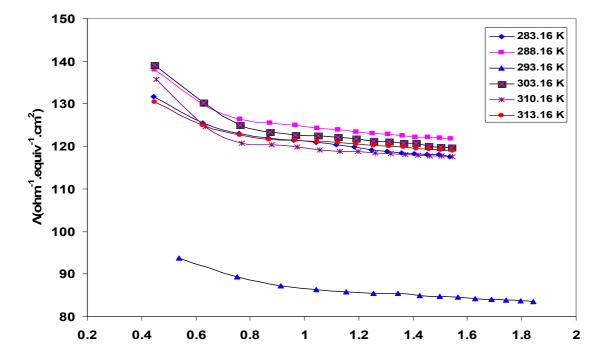


Fig. A(2): The relation between the square root of concentration and the equivalent conductance of Ni (II) with valine and serine at different temperatures

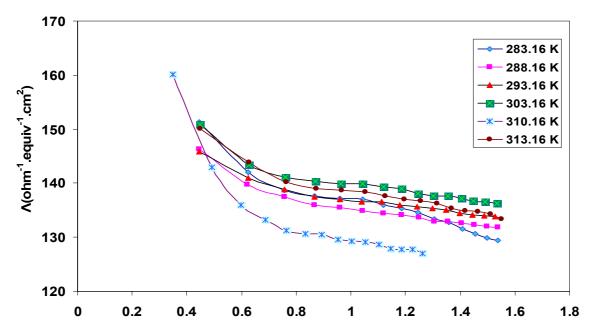


Fig. A(3): The relation between the square root of concentration and the equivalent conductance of Ca (II) with alanine and serine at different temperatures

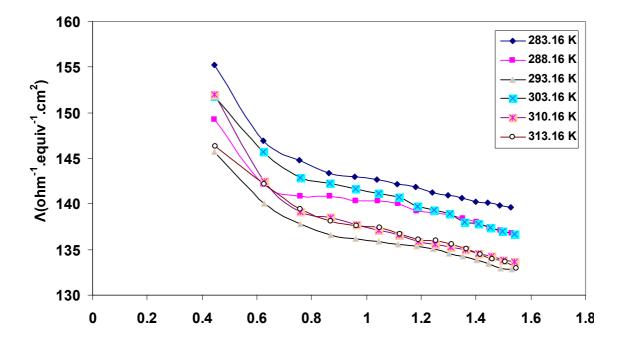


Fig. A (4): The relation between the square root of concentration and the equivalent conductance of Mg(II) with valine and serine at different temperatures

Results of Application of Lee-Wheaton Equation to the Complex Solutions of Cobalt, Nickel, Calcium and Magnesium with Amino Acids:

Lee-Wheaton equation for unsymmetrical electrolytes (2:1) was applied to the complexes under study mentioned above at different temperatures (283.16, 288.16, 293.16, 303.16, 310.16, and 313.16) at pH7. The experimental results which contain the concentrations and the equivalent conductances were analyzed by a computer program. The results of analysis give information about the ionic equivalent conductance ($\Lambda_{\rm M}^{+2}$, $\Lambda_{\rm M}^{+}$), association constant ($K_{\rm A}$), the distance between ions in solution (R) and the value of standard deviation ($\sigma\Lambda$) as shown in the tables B(1-4) for the complexes under study (Dabbagh and Akrawi, 1992)

From the above tables, the values of K_A decrease with increasing temperatures, this can be attributed to the increase of the kinetic energies of the molecules and to the break of electrostatic forces due to the short range reactions (Yokoyama and Kon, 1991), except at (310.16K) for cobalt complex. The values of K_A for cobalt complexes were higher than that of nickel complexes, the ionic radius of cobalt is lower than that of nickel and besides the methyl group of alanine molecule, which have an electron donating character, more than methoxy group in serine molecule. The values of K_A for magnesium complexes were more than that of calcium complexes because the magnesium complexes contain valine and serine while calcium complexes contain alanine and serine as ligande and because the isopropyl group in valine has more electron donating character than methyl group in alanine in calcium complexes, so the reaction will be more active and then will be more associative. The values of λ_M^{2+} for Co and Ni complex ions behave similarly and their values are around 50-60, while for Ca and Mg complex ions have higher values are around 80-180, according to the periodic properties between alkali earth metals and transition metals. The values of R (the distance parameter) were more than the Bierrium value which means that the complex ions were separated by solvent molecules (SSIP) and this depends on the metal ion and the amino acid nature that formed the complex to some extent. The values differ from one complex in to another depending on the interactions in solution.

Table B (1): The results of analysis for the values of λ_M^{+2} , λ_M^{+} , R, K_A and $\sigma\Lambda$ for aqueous solution of Co(II) complexes with alanine and valine at different temperatures

T (K)	K _A	$\lambda^{o}M^{+2}$	λ°MX ⁺	R(A°)	σΛ
283.16	962.94	52.20	2.90	22.3	0.038
288.16	470.0	49.09	14.30	26.9	0.017
293.16	220.30	50.00	0.80	8.0	0.008
303.16	145.39	39.09	0.11	10.1	0.021
310.16	234.39	70.09	1.26	6.9	0.016
313.16	144.60	45.40	0.80	10.1	0.011

Table B (2): The results of analysis for the values of λ_M^{+2} , λ_M^{+} , R, K_A and $\sigma\Lambda$ for aqueous solution of Ni(II) complexes with valine and serine at different temperatures

T (K)	K _A	$\lambda^{o}M^{+2}$	λ°ΜΧ ⁺	R(A°)	σΛ
283.16	392.20	54.29	5.59	16.7	0.013
288.16	259.82	52.40	0.60	9.5	0.037
293.16	191.50	51.0	0.40	8.6	0.010
303.16	114.43	51.0	0.13	10.2	0.031
310.16	77.58	50.5	2.38	7.5	0.036
313.16	70.1	49.30	0.24	9.0	0.015

Table B (3): The results of analysis for the values of λ_M^{+2} , λ_M^{+} , R, K_A and $\sigma\Lambda$ for aqueous solution of Ca(II) complexes with alanine and Serine at different temperatures

T (K)	K _A	$\lambda^{o}M^{+2}$	λ°MX ⁺	R(A°)	σΛ
283.16	163.10	64.80	5.79	9.8	0.029
288.16	132.95	63.60	0.20	6.2	0.018
293.16	109.95	64.57	0.11	10.0	0.016
303.16	91.90	67.59	0.15	10.1	0.018
310.16	85.63	59.80	2.00	9.0	0.062
313.16	79.84	66.90	0.16	8.7	0.023

Table B (4): The results of analysis for the values of λ_M^{+2} , λ_M^{+} , R, K_A and $\sigma\Lambda$ for aqueous solution of Mg(II) complexes with Valine and serine at different temperatures

T (K)	K _A	$\lambda^{o}M^{+2}$	λ°MX ⁺	R(A°)	σΛ
283.16	179.47	71.00	0.30	5.6	0.029
288.16	147.39	70.00	1.5	6.7	0.012
293.16	124.19	65.40	0.11	4.6	0.013
303.16	113.11	69.90	0.03	14.1	0.017
310.16	95.90	65.09	0.40	10.8	0.027
313.16	86.49	65.60	0.22	5.2	0.015

Calculation of the thermodynamic parameters (ΔH , ΔG , ΔS):

The relation of lnK_A against 1\T was shown in figure B (1-4) and the relation between them was illustrated by Vant-Hoff equation (Eggers *et al.*, 1964).

$$\ln K_{A} = \frac{\Delta H}{RT} + C$$

The relation gives a straight line for complex solutions:

This behavior will be illustrated by the fact that the results of association depends on two opposite effects. The first one was the formation of ion pairs separated by solvent molecules

(SSIP) and the other was the formation of contact ion pairs (CIP) (Dawod, 1995). The values of ΔH were calculated from Vant –Hoff equation and ΔG from the equation :

$$\Delta G = -R T \ln K_A$$

While ΔS values were calculated from the equation :

$$\Delta G = \Delta H - T \Delta S$$

From the tables below, the values of ΔH (enthalpy of association) were negative which show that the operation was hydration ,while ΔG (Gibbs free energy) has a negative values which depends upon the kind of ions (Al-Tamer, 1999) and in agreement with the relation $\Delta G = -RTLnK_A$ which means that the reaction was spontaneous towards association (Doe *et al.*, 1990; Al-Mustawi, 2002), and the values of ΔS were also negative due to the negative values of ΔH which leads to the ordering of the system as a result of association under the influence of solvation and columbic effect in spontaneous continuum media (Nancollas, 1960).

Table C (1): Thermodynamic parameters of Cobalt complexes with alanine and valine

T (K)	-ΔH (KJ.mol ⁻¹)	-ΔG (KJ.mol ⁻¹)	-ΔS (J.mol ⁻¹ .K ⁻¹)
283.16	37.611	16.173	75.710
288.16		14.734	79.390
293.16		13.137	83.483
303.16		12.552	82.659
310.16		14.080	75.867
313.16		12.940	78.781

Table C (2): Thermodynamic parameters of Nickel complexes with valine and serine

T	-ΔΗ	-ΔG	-ΔS
(K)	(KJ.mol ⁻¹)	(KJ.mol ⁻¹)	(J.mol ⁻¹ .K ⁻¹)
283.16	35.631	14.055	76.197
288.16		13.320	77.426
293.16		12.796	77.893
303.16		11.947	78.124
310.16		11.217	78.714
313.16		11.065	78.446

Table C (3): Thermodynamic parameters of Calcium complexes with alanine and serine

T	- ΔH	-ΔG	-ΔS
(K)	(KJ.mol ⁻¹)	(KJ.mol ⁻¹)	(J.mol ⁻¹ .K ⁻¹)
283.16	16.244	11.983	15.048
288.16		11.715	15.717
293.16		11.455	16.336
303.16		11.393	16.001
310.16		11.475	15.376
313.16		11.404	15.455

Table C (4): Thermodynamic parameters of Magnesium complexes with valine and serine

T (K)	-ΔΗ (KJ.mol ⁻¹)	-ΔG (KJ.mol ⁻¹)	-ΔS (J.mol ⁻¹ .K ⁻¹)
283.16	16.000	12.218	13.356
288.16		11.955	14.037
293.16		11.748	14.504
303.16		11.922	13.452
310.16		11.759	13.674
313.16		11.612	14.012

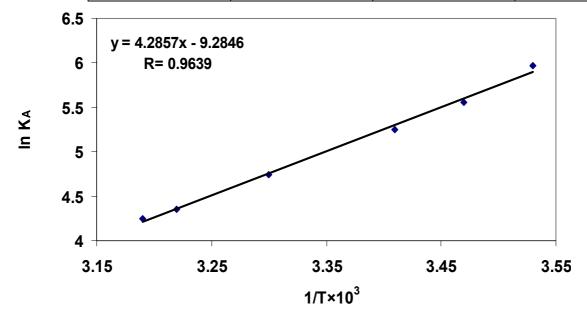


Fig. B (1): The relation of LnK_A and $1\T$ for aqueous solution of cobalt complex with alanine and valine

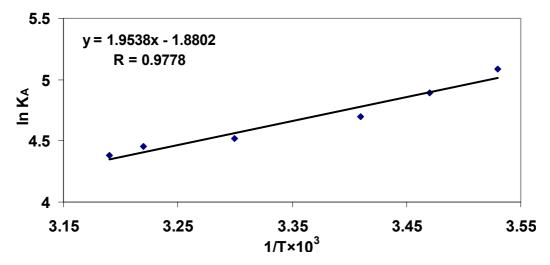


Fig. B (2): The relation of LnK_A and $1\T$ for aqueous solution of Nickel complex with valine and serine

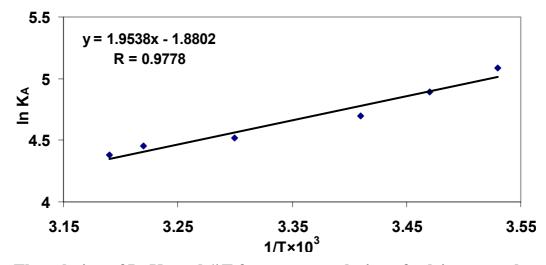


Fig. B (3): The relation of LnK_A and $1\T$ for aqueous solution of calcium complex with alanine and s

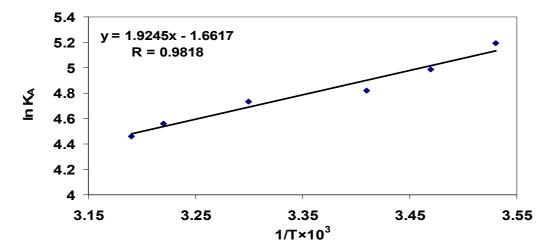


Fig. B (4): The relation of LnK_A and 1\T for aqueous solution of magnesium complex with valine and serine

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