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Conductometric Studies of Calcium Ions with Kryptofix 221 in Mixed MeOH-DMF Solvents at Different Temperatures

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Abstract On using conductometric technique, the apparent association constant (K_A) of Ca $(NO_3)_2$ were measured in mixed MeOH-DMF mixed solvents at 0, 20, 40 , 60 ,80 and 100% MeOH (by volume) and different temperatures (298.15, 303.15, 308.15 and 313.15K) in absence and presence of . Kryptofix- 221 [4, 7, 13, 16, 21- pentaoxa-1.10-diazo-bicyclo (8,8,5) tricosane]. From the experimental results, the molar conductivities ($\wedge$) were calculated and limiting molar conductivities ($\wedge_0$) were calculated by using Shedlovsky and Fouss – Kraus extrapolation methods. The molar solvated ($\vee$), Van der Waals ($\vee_w$) and electrostriction ($\vee_e$) were evaluated. The association constants K_A for $Ca(NO_3)_2$ were calculated by using simple equation derived from Ostwald, Arrhenius and Fuoss-Shedlovsky theories. From the association constants the different thermodynamic parameters were evaluated and the results obtained were discussed. The free energy of association (ΔG_A), free energy necessary for complexation ($\Delta G_{complex}$) and enthalpy (ΔH) were determined. It was concluded that the maximum complexation between calcium ions and Kryptofix-221 were by using 80% and 100%. MeOH in the mixtures. Where as the least complexing ability at 40% and 60% by volume of MeOH .This work give data can help for the analytical determination of calcium in blood and water samples.

Keywords Association Constants, Activity Coefficients, Different Volumes, Free Energies of Association, Solvation Enthalpies, Calcium , Kryptofix 221

1. Introduction

Calcium is an essential element in living organism.It plays an important role in the metabolism of nitrogen in some plants, where a deficiency of calcium leads to poor absorption of nitrogen. Lack of calcium nutrition leads to a reduction in the number and size of chloroplants.Cacium in the most abundant inorganic element in the higher animals, and is located principally in the bones and teeth as apatite, a calcium mineral.Bllod is also a huge reservoir of calcium in animals. Calcium is distributed throughout all tissues where it has special roles in controlling g nerve impulse transmission, muscle action, blood cotting and cell permeability. Calcium deficiency is exhibited by the outset of rickets, failure of blood-clotting, nervous disorder andconvulsive muscular contractions. Vitamin D greatly improves the absorbability of calcium ion. Large intakes of calcium lead to excessive calcification and kidney stones.

Almost all natural waters, including seawater, contain either or both calcium carbonate and calcium sulphate.

Many organisms concentrate calcium in their shells or skeletons. For example calcium carbonate is formed in shells of oysters. Calcium has significant applications in the production of alloys with lead and aluminium and in industrial products of metals from its oxides.It is also used as deoxidizer with iron, steel and its alloys.[1,2]. The main target is to data help for calcium analysis.

The association of salt solutions were studied by Barthel [3] and Deepa[4]. The ion solvent interactions were explained in different electrolytes and polymers using conductivity, relaxation and FTIR measurements[1].

Schori et al.[5,6] used conductivity as an electrical method for studying complexation of Na^+ with some crown ethers in DMF and in diemthoxyethane solutions.

Different Fuoss theories, Fuoss-Shedlovsky, Fuoss-Kraus and Fuoss-Debye theories[7,8]were used for the estimation of the association constants (K_A) for symmetric electrolytes (1:1 electrolytes).

We apply here simple equation for determining K_A for asymmetric 1:2 salts in solutions based on Fuoss-Shedlovsky and Ostwald law[8]. Evaluation of individual ionic molar volumes[9], preferential solvation of drugs[10] partial molar volumes[11], ligands used for selective metal extraction[12],

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ionic salvation[13], potntiometric study[14] and specific salvation[15] are some trends of this area of physical inorganic chemistry.

2. Experimental

Kryptofix 221 (Fig.1) was supplied from Fluka Co., whereas $Ca(NO_3)_2$ was supplied from BDH. The water content of $Ca(NO_3)_2$ was determined by using (Mettler DL-18) Karl-Fisher titrator and it was found to be less than ±0.01%. methanol (MeOH) and N,N-dimethylformamide (DMF) used were from BDH. All the conductometric titrations were manipulated using $1x10^{-3}$ mol/l $Ca(NO_3)_2$ and $1x10^{-4}$ molal of Kryptofix 221 as stock solutions. The specific conductivity (K_S) measurements were achieved at different temperatures using a conductometer of the type YSI model-35 connected with an ultra thermostatic water bath of the type Kottermann-4130.

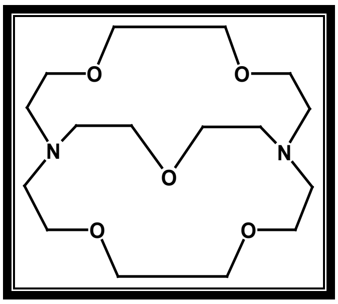

Figure 1. Kryptofix-221 [4,7,13,16,21-pentaoxa-1.10-diazo-bicyclo [8,8, 5] tricosane]

The densities were measured by weighing 1 ml solution in weighing bottle using four digital weighing balance of the type Mettler Toledo DA analytical balance.

3. Results and Discussion

The molar volumes of $Ca(NO_3)_2$ stork solution (V_M) were calculated by dividing the molecular weight of the salt by the measured densities. From the packing density (P) as reported by Kim[16,17], i.e., the relation between Van der Waals volume (V_W) and the molar volume (V_M) for large molecules (M.W. above 40) the Van der Waals volumes for $Ca(NO_3)_2$ were evaluated (equation 1)[16,17].

$$P = \frac{V_M}{V_W} = 0.661 \pm 0.017 \qquad (1)$$

The electrostriction volume (V_e), which is the volume compressed by the solvent can be calculated by using equation (2) [18] as follows:

$$V_e = V_W - V_M \qquad (2)$$

All the evaluated different volumes for calcium nitrate in mixed MeOH-DMF solvents were tabulated in Table (1) at 298.15, 303.15, 308.15 and 313.15 K.

The specific conductance (K_S) of different dilutions of $Ca(NO_3)_2$ in mixed solvents as well as in the presence of Kryptofix 221 were measured experimentally, from which the molar conductance (Λ) were calculated. The limiting molar conductance (Λ_o) of these solutions were obtained by extrapolating the relation between Λ and square root of concentration to zero concentration. The association constant K_A of different 1:1 (symmetric) electrolytes can be estimated by using Fuoss-Shedlovsky equations [19,20].equation (3)

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C.\Lambda.\gamma_\pm^2 S(Z)\right) \qquad (3)$$

Where

$$S(Z) = \left[\frac{Z}{2} + \left(1 + \left(\frac{Z}{2}\right)^2\right)^2\right], \; Z = S(\Lambda_o)^{-3/2}(C\Lambda_o)^{1/2}$$

$$S = a\,\Lambda_o + b, \; a = 8.2x10^5(\varepsilon.T)^{1/2}$$

$$b = \frac{0.825}{\eta^o(\varepsilon T)^{1/2}}$$

ε is the dielectric constant, η_o is the viscosity of the solvent, T absolute temperature and S(Z) is the Fuoss-Shedlovsky factor.

With the use of equation (3) for 1: 2 electrolytes, small values are obtained for K_A. Therefore another simple equation can be applied by following equations (4-8)

$$A^{+2} + 2\,B^- \overset{K_A}{\rightleftharpoons} AB_2 \qquad (4)$$

$$K_A = \frac{1-\alpha}{(2\alpha)^2.C_m\alpha} = \frac{1-\alpha}{4C_m^2.\alpha^3} \qquad (5)$$

$$\alpha \text{ (dissociation degree)} = \frac{\Lambda.S(Z)}{\Lambda_o} \qquad (6)$$

$$K_A = \frac{1 - \frac{\Lambda S(Z)}{\Lambda_o}}{4C_m^2\left(\frac{\Lambda.S(Z)}{\Lambda}\right)^3} \qquad (7)$$

$$K_A = \frac{\Lambda_o^2(\Lambda_o - \Lambda)}{4C_m^2\gamma_\pm^2\Lambda^3 S(Z)^2} \qquad (8)$$

Thus equation (8) can be applied for $Ca(NO_3)_2$ as dilute solution because this equation depends on Fuoss-Shedlovsky and Ostwald dilution laws.

The different Λ, Λ_o for $Ca(NO_3)_2$ solutions were evaluated at concentration equal $8x10^{-5}$ as inflection point and zero concentration, respectively.

K_A association for $Ca(NO_3)_2$ in absence and presence of Kryptofix 221 were evaluated and their values are given in Tables 2 and 3, knowing that S(Z) factor for all solutions were found to be approximately one.

The Gibbs free energies of association were calculated by applying equation (9) [20-23] in absences and presences of Kryptofix 221 in mixed MeOH-DMF solvents at different temperatures and their values are shown also in Tables (2) and (3).

$$\Delta G_A = -RT \ln K_A \qquad (9)$$

From the difference between association Gibbs free energies in presence and absence of the ligand (Kryptofix 221), the Gibbs free energies for complexations were evaluated and listed in Table (3).

Table 1. Molar volumes (V_M), Van der Waals volumes (V_M), electrostriction volumes (V_e) and solvated radii R_s for $Ca(NO_3)_2$ in mixed MeOH-DMF solvents at different temperatures

Vol%	V_M(cm^2/mol)				V_w(cm^2/mol)				V_e(cm^3/mol)				R_s (A^o)			
(ϕ) MeOH	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0	173.05	173.89	174.89	176.89	114.38	114.94	115.6	116.35	-58.67	-58.95	-59.29	-59.67	4.09	4.1	4.11	4.12
20	178.01	179.31	180.3	181.17	117.66	118.52	119.17	119.75	-60.35	-60.79	-61.13	-61.42	4.13	4.14	4.15	4.16
40	180.73	181.7	183.1	184.16	119.46	120.1	121.03	121.73	-61.27	-61.6	-62.07	-62.43	4.153	4.16	4.17	4.18
60	190.32	191.5	192.67	194.1	125.8	126.58	137.35	128.3	-46.52	-46.92	-65.32	-65.8	4.22	4.23	4.24	4.25
80	198.28	199.85	210.17	202.99	131.06	132.1	132.97	134.17	-67.22	-67.75	-68.2	-68.82	4.28	4.29	4.30	4.31
100	213.29	215.05	216.04	217.47	140.79	142.15	142.8	143.75	-72.5	-72.9	-73.24	-73.72	4.39	4.40	4.41	4.42

Table 2. Molar conductance (Λ), limiting molar conductance ($Λ_o$), activity coefficient ($γ_±$), association constant (K_A) and Gibbs free energies of association ($Δ G_A$) for $Ca(NO_3)_2$ in absence of Kryptofix in mixed MeOH-DMF solvent at different temperatures

Vol.% (ϕ) MeOH	T	Λ	$Λ_o$	$γ_±$	K_A(x10^{-6})	$ΔG_A$ (k.J/mole)
0	298.15	130	140	0.9423	981	-34.204
	303.15	170	200	0.944	2676.643	-37.308
	308.15	205	255	0.944	4135.660	-39.038
	313.15	170	205	0.9497	3241.575	-39.038
20	298.15	124	143	0.9380	1045.895	-34.364
	303.15	188	230	0.991	4496.876	-38.616
	308.15	197	250	0.940	4788.522	-39.414
	313.15	160	200	0.9370	4344.911	-39.800
40	298.15	156	168	0.9342	998.266	-34.208
	303.15	232	280	0.937	3352.078	-37.875
	308.15	266	335	0.936	4586.085	-39.303
	313.15	224	280	0.9331	4381.307	-39.822
60	298.15	145	156	0.9312	988.899	-34.228
	303.15	222	270	0.934	3580.272	-38.041
	308.15	242	300	0.933	4132.008	-39.036
	313.15	216	272	0.9300	4641.931	-39.937
80	298.15	126	141	0.9300	1683.263	-35.543
	303.15	266	276	0.932	3709.634	-38.131
	308.15	252	315	0.930	4410.564	-39.203
	313.15	220	257	0.9271	4448.200	-39.855
100	298.15	115	130	0.9282	1889.301	-35.829
	303.15	180	212	0.921	2839.127	-37.457
	308.15	212	265	0.928	4006.364	-38.957
	313.15	202	255	0.9250	3715.38	-39.393

Table 3. The values of limiting molar conductance ($Λ_o$), molar conductance (Λ), activity coefficient ($γ_±$), association constant (K_A) Gibbs free energy of association ($ΔG_A$) and compelxation free energies ($ΔG_c$) for $Ca(NO_3)_2$ in (MeOH-DMF) in presence of Kryptofix-221

Vol.% (ϕ) MeOH	T	Λ	$Λ_o$	$γ_±$	K_A(x10^{-6})	$ΔG_A$ (k.J/mole)	$ΔG_c$,kJ/ mole
0	298.15	478.8	580	0.9457	3376	-37.26	-3.064
	303.15	478	565	0.9442	2823	-37.44	-1.34
	308.15	450	585	0.9451	5129	-39.62	-5.83
	313.15	475	600	0.9921	4427	-39.84	-8.11
20	298.15	372.5	495	0.9441	5835	-38.62	-4.321
	303.15	385	500	0.9426	5175	-38.97	-3.54
	308.15	350	460	0.9410	5522	-39.77	-3.65
	313.15	360	500	0.9402	7268	4114	1.340
40	298.15	41.7	46.5	0.9350	1320	-34.94	-6.920
	303.15	33	80	0.9550	4510	-38.62	-7.48
	308.15	37	67	0.9462	1907	-37.05	-2.248
	313.15	39	94	0.9513	4467	-39.87	0.51
60	298.15	43.8	49.5	0.9324	1533	-35.31	-1.083
	303.15	24	77	0.9590	9213	-40.42	-2.383
	308.15	52.5	82	0.9394	11.41	-35.73	-3.297
	313.15	52	109	0.9453	3042	-38.87	-1.101
80	298.15	62	73	0.9315	2508	-36.53	-9.880
	303.15	52	140	0.9537	6021	-39.35	-1.039
	308.15	63	95	0.9361	1001	-35.40	-3.800
	313.15	54.5	117	0.9438	3274	-38.91	-7.92
100	298.15	63	74	0.9464	2548	-53.69	-17.868
	303.15	63.5	64.5	0.9549	2571	-48.15	-10.196
	308.15	64.1	75	0.9558	2610	-55.50	-16.607
	313.15	64.2	75.2	0.9572	2618	-56.47	-17.072

Table 4. Solvation enthalpies of $Ca(NO_3)_2$ in presence and absence of Kryptofix 221 (in k.J/mole)

Vol.% (ϕ) MeOH	ΔH (without ligand)	ΔH in presence of (Kryptofix-221)
0%	-54.173	-53.263
20%	-50.395	-26.546
40%	-102.926	-52.741
60%	-107.763	-43.929
80%	-52.685	-54.407
100%	-27.977	-73.905

The enthalpies of solvation for Ca $(NO_3)_2$ in absence and presence of Kryptofix 221 were obtained graphically from the relation between log K_A against $\frac{1}{T}$ with slope equal $-\frac{\Delta H}{2.303\ R}$. The evaluated data were listed in Table (4) in absence and presence of ligand.

It was concluded from the given tables that the maximum complexation between calcium ions and Kryptofix-221 were by using 80% and 100%. MeOH in the mixtures. Where as the least complexing ability at 40% and 60% by volume of MeOH. This behaviour was indicated from ΔG_C and ΔH values cited in Tables 3 and 4, respectively.

4. Conclusions

We tried in this work to give data that can help for biological and analytical determination of calcium ions in blood,tissues,water and industrial samples.The free energy values for calcium ions are great in 80% MeOH-DMF and pure MeOH, whereas the conductance values are great in 20 % MeOH-DMF and pure DMF.These data explains the ion solvent interaction trend in the same order. All the thermodynamic parameters for calcium ions are greater in presence of Krytofix 221 than in absence of it, favouring more complexing character and ease of detection on using Kryptofix221. The ligand used can be extracted by chloroform and by evaporating the solvent the solid can be obtained for further use.

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