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Thermodynamic Interaction Parameters for Bulk and Nano Calcium Acetate (CAc) with N'-Bezylidene-4-Chlorobenzo-Hydrazide (LB) in Mixed EtOH-H_2O Solvents

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Abstract
Characterization of nano calcium acetate (CAc) is done by transmission electron microscopy (TEM), atomic force microscope (AFM) and x-ray diffraction. The thermodynamic parameters for association and complex formation for both bulk CAc (normal) and nano- CAc were evaluated by using condutometric measurements. The association thermodynamic parameters of both bulk -CAc and nano-CAc salts in ethanol (EtOH) + H_2O were calculated in presence of N'-bezylidene-4-chlorobenzohydrazide (LB), non isothermally at different temperatures, 293.15, 298.15, 303.15 and 308.15 K. The thermodynamic solvation parameters for both types of CAc were compared.

1. Introduction

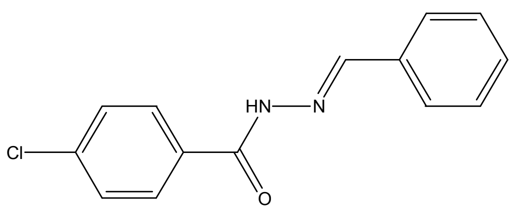
Nanoparticles are very important for medicine and environment, because of their increased behaviours. The increasing in the physical and chemical properties of nanomaterials are due to theirs high surface area and small volume, makes them very reactive, catalytic and able to pass through cell membranes [1]. Uses of calcium acetate in kidney disease, blood levels of phosphate may rise (called hyperphosphatemia) leading to bone problems. Calcium acetate (CAc) binds phosphate in the diet to lower blood phosphate levels [2]. Side effects of this treatment include upset stomach. Calcium acetate (CAc) is used as a food additive, as a stabilizer, buffer and sequestrate for some products. It also neutralizes fluoride in water [3].The difference in solvation parameters between nano and bulk CAc can help us for the uses of this salt in nano form or not. Some salts in nano form shows little solvation behavior in some solvents. Also the analytical determination of this salt and its nano form analytically by using our ligand as try to help in its quantitative determination.

2. Experimental

2.1. Chemicals and Ligand

Calcium acetate monohydrate (CAc) was provided from Al Nasr chemicals Co.

Nano-calcium acetate (CAc) salt was obtained (prepared) by ball milling method using calcium acetate salt. The ball milling was a Retsch MM 2000 Swing mill with 10 cm^3 stainless steel, double-walled tube. Two balls (stainless steel) with diameter of 12 mm were used. Ball milling was performed at 20225 Hz and shaking were used, usually at room temperature without circulating liquid and the temperature did not rise above 30 °C.



N'-benzylidene-4-chlorobenzohydrazide

N'-bezylidene-4-chlorobenzohydrazide, (LB) was prepared by mixing equimolar amounts of 4-chlorobenzohydrazide (0.01 mole; 1.70 gm) and benzaldehyde (0.01 mole; 1.06 gm), in 50 ml ethanol. The reaction mixture is maintained at reflux temprature for 4 hrs. The product is filtered and recrystallized from absolute ethanol and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

2.2. Transmission Electron Microscopy (TEM) Images

Transmission electron microscope is a special kind of electron microscope for imaging of different objects. In contrast to other microscopes the electrons in TEM pass through and interact with atoms of the sample. Due to this interaction the electrons are being scattered. The final image is very complicated interference pattern of incident and diffracted beams. The images were measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of calcium acetate (CAc) obtained in water have spherical shape.

2.3. Condutometric Measurements

A solution of bulk and nano-calcium acetate ($1x10^{-4}$ M) were placed in a titration cell, thermostated at a given temperature and the conductance of the solution was measured [2-21]. The ligand, N'-bezylidene-4-chlorobenzohydrazide (LB) ($1x10^{-3}$ M) was transferred step by step to the titration cell using a precaliberated micropipette and the conductance of the solution was measured after each transfer. The addition of the ligand solution was continued until the total concentration of the ligand was approximately four times higher than that of the metal ions. The complex formation constant K_f, and the molar conductance of the complex ML, were evaluated by computer fitting to the molar conductance mole ratio data. The temperatures used are (293.15, 298.15, 303.15, and 308.15K). The specific conductivity K_s was achieved by using a conductivity bridge of the type (JENCO – 3173 COND).

3. Data Results and Discussion

3.1. Transmission Electron Microscopy (TEM) Images

The photographs from (TEM) are presented for nano-CAc salt .The images show that the nano calcium acetate (CAc) in the form of regular spheres with little diffusion with water solvent, the boundaries were clear as separate spheres and the sizes ranging from 23-59 nm as shown in Fig.1. a, b and c. The electron diffraction image d in Fig .1 indicates the crystal form of the nano calcium acetate , supported by .X-ray diffraction.

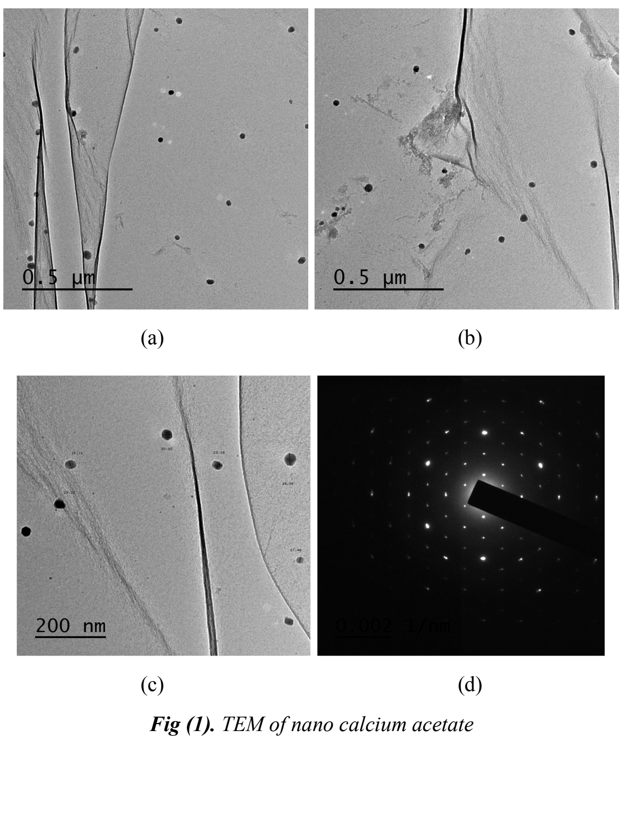
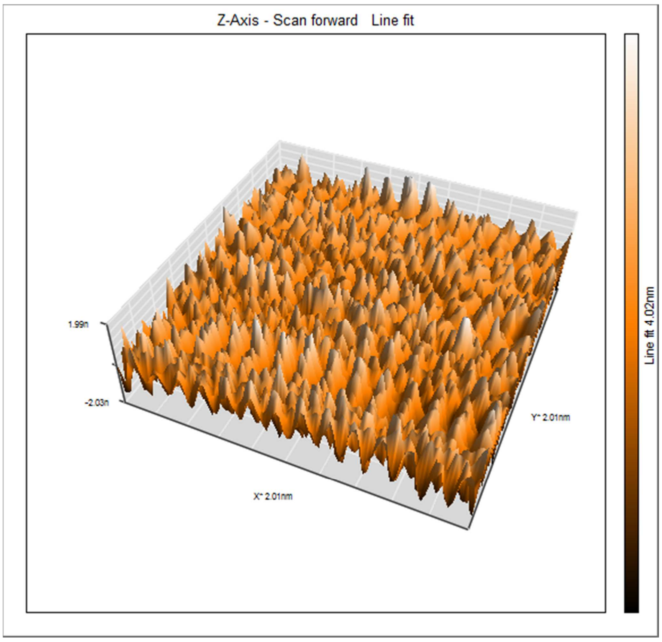


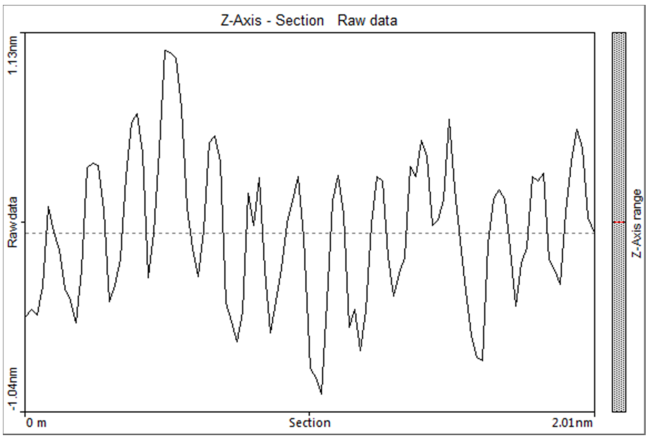
***Fig (1).** TEM of nano calcium acetate*

3.2. Atomic Force Microscope (AFM)

The images of atomic force microscope for nano sample CAc measured in Mansoura University Nanotechnology center using Nanosurf FlexAFM, Switzerland apparatus is shown in Fig.(2).It is seen in Fig.(2) a ,the roughness with average in -1.04 nano meter to +1.13 nano meter of the surface. This surface of the nano CAc has the following properties which clear in Fig.(2) c for forward measuring : roughness average (R_m) -9.44 femto meter , root mean square (R_q) 1180.6 pico meter , peak height (R_p) 1180 pico meter, the peak-valley height (R_y) 2329 pico meter and valley depth lowest level (R_v) -1180.6 femto meter .The mean values for roughness in the forward and backward directions are seen in Fig.(2) d .All AFM images and roughness data proves the homogeneous surface of the nano prepared samples.



(a)



(b)

Name	Value
Ra	428.53pm
Rq	529.79pm
Ry	2329.4pm
Rp	1180.6pm
Rv	-1148.7pm
Rm	-9.44fm

(c)

Tool result

Name	Value
Area	4.063am^2
Sa	502.02pm
Sq	610.38pm
Sy	5.0472nm
Sp	2480.6pm
Sv	-2566.7pm
Sm	-20.009pm

Store

(d)

***Fig (2).** AFM of nano calcium acetate*

3.3. Conductometric Results

The stability of a transition metal complex with ligand N'-bezylidene-4-chlorobenzohydrazide (LB) depends on the number and the type of the donor atoms presented the number and the size of chelate rings formed on the complexation [21-25]. In addition, the stability and the selectivity of the complexities are strongly depend on the donor ability and the dielectric constant of the solvent [25-36], the shape and the size of the solvent molecules [37-45].

3.3.1. Calculation of Thermodynamic Parameters of Association for Bulk and Nano-Calcium Acetate (CAc) in Mixed EtOH-H_2O Solvents

The specific conductance values (K_s) of different concentrations for bulk and nano-calcium acetate (CAc) in EtOH -H_2O mixtures were measured experimentally in absence of ligand N'-bezylidene-4-chlorobenzohydrazide (LB) at different temperatures (293.15, 298.15, 303.15 and 308.15 K). The molar conductance (Λ_m) values were calculated [46-59] using equation (1):

$$\wedge_m = \frac{(K_s - K_{solv}) \times K_{cell} \times 1000}{C} \quad (1)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} (equal 1) is the cell constant and C is the molar concentration of the bulk and nano-CAc solutions.

The limiting molar conductance (Λ_o) at infinite dilutions was estimated for bulk and nano-CAc in EtOH-H_2O mixtures in absence of ligand at different temperatures by extrapolating the relation between Λ_m and $C_m^{½}$ to zero concentration. The relation between Λ_m and $C_m^{½}$ at different temperatures in 40% by volume for EtOH as example is shown in Fig.(3) and Fig. (4) for nano and bulk CAc .

The association constants for nano and bulk (CAc) were calculated from equation (2) in presence of (LB) and tabulated in Table (1) and (2).

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

The free energy of association (ΔG_A) for bulk and nano-CAc in DMF-H_2O mixtures at different temperatures were calculated [60-79] from the association constant (K_A) values by using equation (3) and reported in Table (1) and (2).

$$\Delta G_A = -\ 2.303\ RT \log K_A \quad (3)$$

Where *R* is the gas constant and T is the absolute temperature.

The Gibbs free energies for the solutions of bulk and nano-CAc in EtOH –H_2O at different temperatures were calculated and reported in Table (1) and (2).

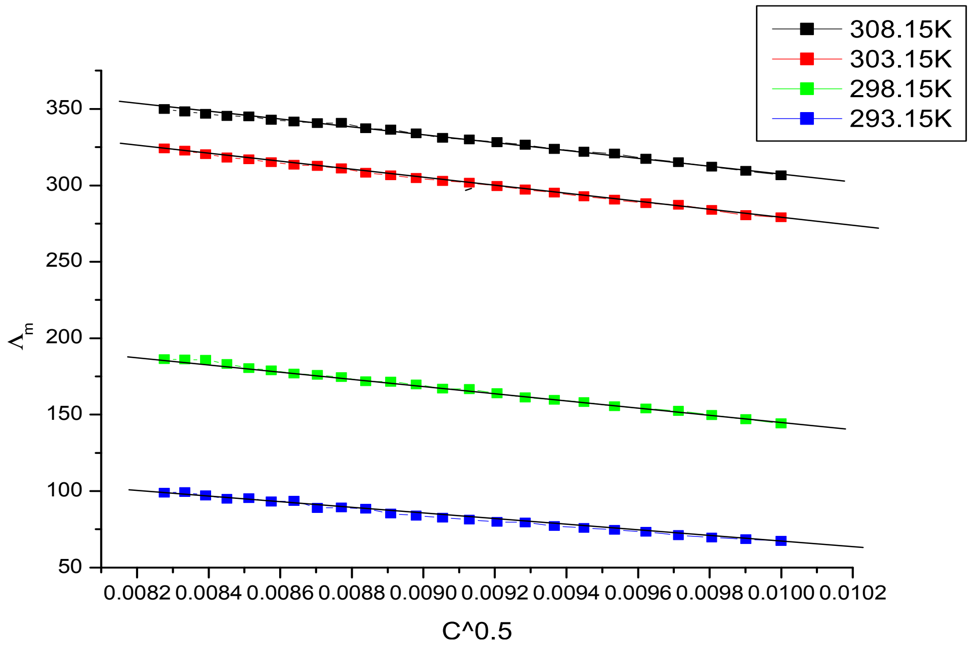


Fig (3). *Molar conductivity of nano calcium acetate-LB complex in 40% EtOH-H_2O solvents at different temperatures.*

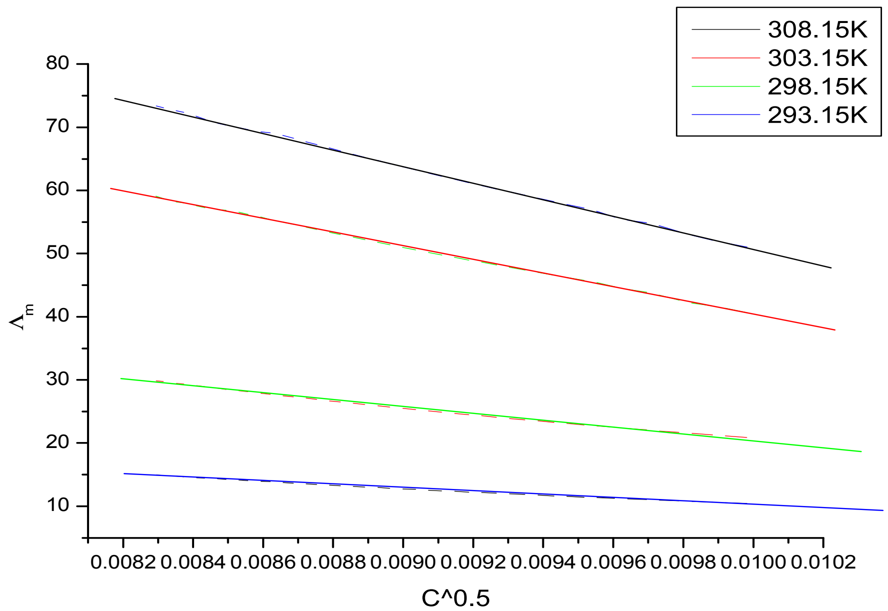


Fig (4). *Molar conductivity of bulk calcium acetate CAc-LB Complex at 40% mixed DMF-water at different temperatures.*

Table 1. *Molar electrical conductance (Λ_m), limiting molar conductance (Λ_0), association constants (K_A) and free energies of association (ΔG),Gibbs Free energy(ΔH) and entropy (Δ S) for 8.41×10^{-6} M nano Ca Ac in mixed EtOH- H_2O solvents at 308.15,303.15,298.15and 293.15K*

C	X_s EtOH	Λ_m Ω^{-1}, Cm^2mol	Λ_0 Ω^{-1}, Cm^2mol	$\gamma_\pm$	$K_A\times10^{-6}$	ΔG_A KJ/mol	ΔH KJ/mol	ΔS KJ/mol.K
8.41×10^{-6}	0.0809	1830.3256 (308.15K)	1760.0014	0.9966	1.7520	-36.4790	-30.9040	0.0610
		1750.3256 (303.15K)	1601.1224		1.5380	-30.3050		0.0620
		.23151466 (298.15K)	1387.5246		3.9630	-32.7070		0.0630
		1293.3265 (293.15K)	1083.8899		2.4900	-35.9010		0.0640
	0.2021	.2321370 (308.15K)	360.2245		9.7900	-32.9540	-31.8430	1.0330
		394.2451 (303.15K)	327.5864		1.0480	-35.1770		1.0500
		211.3210 (298.15K)	187.2451		5.8280	-33.6860		1.0680
		118.3265 (293.15K)	105.3265		5.5430	-33.5590		1.0860
	0.3635	200.2104 (308.15K)	128.3524		4.8470	-39.0610	-31.1220	0.1010
		120.2214 (303.15K)	110.2253		3.8390	-32.6270		0.1030
		100.3251 (298.15K)	98.2241		7.9400	-28.6280		0.1040
		78.0215 (293.15K)	69.3524		5.6290	-33.5980		0.1060

Table 2. *Molar electrical conductance (Λ_m), limiting molar conductance (Λ_0), association constants (K_A) and free energies of association (ΔG_A),Gibbs free energy(ΔH) and entropy (ΔS) for 8.41×10^{-6} M bulk CaAc in mixed EtOH- H_2O solvents at 308.15,303.15,298.15 and 293.15K*

C	X_s EtOH	Λ_m Ω^{-1}, Cm^2mol	Λ_0 Ω^{-1}, Cm^2mol	$\gamma_\pm$	K_A	ΔG_A KJ/mol	Δ H KJ/mol	Δ S KJ/mol.K
8.41×10^{-6}	0.0809	185.2546 (308.15K)	219.8994	0.9966	9.38×10^5	-35.2360	-19.962	0.1140
		156.4587 (303.15K)	189.3325		10.95×10^5	-35.0550		0.1150
		150.1698 (298.15K)	186.3325		13.20×10^5	-34.9390		0.1170
		142.3652 (293.15K)	176.2451		12.98×10^5	-34.3130		0.1160
	0.2021	135.3625 (308.15K)	157.3331		7.80×10^5	-34.7650	-39.134	0.0140
		122.2587 (303.15K)	153.2254		14.16×10^5	-35.7030		0.0110
		107.3265 (298.15K)	136.6985		15.79×10^5	-35.3860		0.0130
		93.2145 (293.15K)	126.2147		23.09×10^5	-35.7180		0.0120
	0.3635	105.3256 (308.15K)	148.3325		28.81×10^5	-38.1130	-23.001	0.6230
		72.3265 (303.15K)	82.2214		6.29×10^5	-33.6580		0.6480
		43.2256 (298.15K)	56.2548		18.16×10^5	-35.7320		0.6520
		35.2875 (293.15K)	71.2145		14.75×10^5	-40.2390		0.6470

3.3.2. Calculation of Thermodynamic Parameters of Complex Formation for Bulk and Nano-Calcium Acetate with N'-Bezylidene-4-Chlorobenzohydrazide (LB) in EtOH -H_2O Mixtures

The specific conductance values (K_s) of different concentrations of bulk and nano-CAc in EtOH -H_2O mixtures were measured experimentally in the presence of ligand (LB) at different temperatures (293.15, 298.15, 303.15, and 308.15K). The molar conductance (Λ_m) values were calculated [21-70] using equation (1).

By drawing the relation between molar conductance (Λ_m) for bulk and nano-CAc in presence of ligand (LB) at different temperatures and the molar ratio of metal to ligand [M]/[L] concentrations, Fig.(3) different lines are obtained with breaks indicating the formation of 1:2 and 1:1 (M:L) stoichiometric complexes ,as done in previous works [71-75].

The formation constants (K_f) for bulk and nano-CAc complexes were calculated for each type of complexes (1:2) and (1:1) (M: L) by using equation (4) [75-79]:

$$K_f = \frac{\wedge_m - \wedge_{obs}}{(\wedge_{obs} - \wedge_{ML})[L]} \quad (4)$$

Where Λ_m is the limiting molar conductance of the bulk and nano-CAc alone, Λ_{obs} is the molar conductance of solution during titration, Λ_{ML} is the molar conductance of the complex at the inflection and [L] is the ligand (LB) concentration.

The Gibbs free energies of formation for each stoichiometry complex (ΔG_f) were calculated by using the equation (5) [10-25]:

$$\Delta G_f = - 2.303\ RT \log K_f \quad (5)$$

The obtained values (K_f) for nano and bulk-CAc stoichiometry complexes and their calculated ΔG_f values at 308.15K as example are presented in Tables.3 -6, respectively.

Table 3. *The formation constants and Gibbs free energies of formation of 1:2 M/LB concentration for nano-CAc in presence of LB at different temperatures in EtOH- H_2O Solvents*

Xs EtOH	T K	Λ_M Ω^{-1}, Cm^2mol	Λ_{ML} Ω^{-1}, Cm^2mol	Λ_{obs} Ω^{-1}, Cm^2mol	$[L]\times10^5$	K_f	ΔG_f KJ/mol	ΔH KJ/mol	ΔS KJ/mol. K
				1447.6520	5.6600	2.47×10^5	-31.8219		0.1520
	308.15	1830.3256	1420.3215	1471.3840	7.4100	9.49×10^4	-28.8894		0.1552
				1495.1160	8.3300	5.38×10^4	-27.0068		0.1582
				1273.2590	5.6600	1.34×10^5	-28.7744		0.1605
	303.15	1750.3256	1210.2551	1301.2480	7.4100	6.66×10^4	-28.4595		0.1532
0.0809				1326.8560	8.3300	4.36×10^4	-26.9296	-51.0720	0.1560
				1117.3430	5.6600	1.17×10^5	-28.9342		0.1709
	298.15	1541.2453	1053.3652	1143.5320	7.4100	5.95×10^4	-26.8003		0.1614
				1184.947	8.3300	3.25×10^4	-26.6215		0.1541
				765.2610	5.6600	1.70×10^5	-30.3579		0.1555
	293.15	1293.3265	710.3365	812.4640	7.4100	6.35×10^4	-27.4193		0.1588
				855.4810	8.3300	3.62×10^4	-25.5889		0.1619
				226.3630	5.6600	6.95×10^5	-34.4691		1.0930
	308.15	319.2315	232.1137	229.7560	7.4100	1.31×10^6	-35.5138		1.1115
				231.9970	8.3300	2.32×10^7	-42.0505		1.1306
				298.1160	5.6600	9.57×10^4	-27.9579		1.1492
	303.15	394.2451	280.3695	302.8480	7.4100	5.49×10^4	-27.9631		1.0937
0.2021				304.7760	8.3300	4.40×10^4	-26.9531	-34.0840	1.1119
				166.6520	5.6600	1.23×10^5	-29.064		1.1300
	298.15	211.3210	160.2541	169.3840	7.4100	6.20×10^4	-26.8992		1.1497
				172.1160	8.3300	3.97×10^4	-27.1323		1.0941
				81.2520	5.6600	2.24×10^5	-31.0534		1.1136
	293.15	118.3265	78.3256	82.5840	7.4100	1.13×10^5	-28.8526		1.1326
				83.9160	8.3300	7.39×10^4	-27.3274		1.1521
				134.8020	5.6600	7.48×10^4	-28.7558		1.2094
	308.15	200.2104	119.3456	137.9110	7.4100	4.53×10^4	-27.0253		1.2297
				141.9950	8.3300	3.09×10^4	-25.6284		1.2506
				91.9200	5.6600	1.39×10^5	-28.8702		1.2710
	303.15	120.2214	88.3265	93.4520	7.4100	7.05×10^4	-28.6046		1.2096
0.3635				94.9840	8.3300	4.55×10^4	-27.0377	-37.6640	1.2299
				81.2520	5.6600	7.85×10^3	-22.2348		1.2522
	298.15	100.3251	38.3254	82.5840	7.4100	5.41×10^3	-20.9542		1.2739
				83.9160	8.3300	4.32×10^3	-21.4505		1.2121
				61.5120	5.6600	1.77×10^4	-24.6526		1.2298
	293.15	78.0215	54.7115	62.4440	7.4100	1.35×10^4	-23.5781		1.2509
				63.3760	8.3300	2.03×10^4	-24.1769		1.2725

Table 4. *The formation constants and Gibbs free energies of formation of 1:1 M/LB concentration for nano-CAc in presence of LB at different temperatures in EtOH- H_2O Solvents*

Xs EtOH	T K	Λ_M Ω^{-1}, Cm^2mol	Λ_{ML} Ω^{-1}, Cm^2mol	Λ_{obs} Ω^{-1}, Cm^2mol	$[L]\times10^5$	K_f	ΔG_f KJ/mol	ΔH KJ/mol	ΔS KJ/mol. K
0.0809	308.15	1410.3265	1300.3652	1306.5900	1.5300	1.09×10^6	-35.6201	-31.9220	0.0897
				1329.9200	1.6700	1.63×10^5	-30.2525		0.0935
				1353.2500	1.8000	6.00×10^4	-27.2754		0.0952
	303.15	1280.3652	1058.3698	1128.3000	1.5300	1.42×10^5	-28.9219		0.0454
				1156.3200	1.6700	7.58×10^4	-28.7921		0.0455
				1175.9800	1.8000	4.93×10^4	-27.2399		0.0464
	298.15	1110.1475	1005.4100	1026.5900	1.5300	2.58×10^5	-30.892		0.0447
				1044.9200	1.6700	9.89×10^4	-28.0369		0.0480
				1063.2500	1.8000	4.50×10^4	-27.4574		0.0458
	293.15	811.3253	500.2154	603.2790	1.5300	1.32×10^5	-29.7209		0.0442
				641.8860	1.6700	7.16×10^4	-27.7159		0.0475
				679.0900	1.8000	4.11×10^4	-25.8957		0.0451
0.2021	308.15	320.1471	310.2541	312.2000	1.5300	6.54×10^4	-28.4112	-29.6070	0.0823
				313.4000	1.6700	5.99×10^4	-27.7295		0.0859
				314.0000	1.8000	5.56×10^4	-27.0863		0.0875
	303.15	303.4127	270.3254	279.5170	1.5300	1.70×10^5	-29.3572		0.0847
				284.2290	1.6700	8.26×10^4	-29.0118		0.0853
				286.5860	1.8000	5.75×10^4	-27.6268		0.0869
	298.15	158.2415	147.54871	152.9920	1.5300	6.30×10^4	-27.3994		0.0859
				155.7240	1.6700	1.84×10^4	-23.9436		0.0896
				158.4560	1.8000	1.09×10^3	-17.9274		0.0854
	293.15	60.4175	48.1313	74.5920	1.5300	3.50×10^4	-26.3767		0.0847
				75.9124	1.6700	3.34×10^4	-25.8247		0.0884
				77.1532	1.8000	3.20×10^4	-25.2901		0.0901
0.3635	308.15	183.7498	102.36524	112.2040	1.5300	4.75×10^5	-33.4951	-32.5870	0.0913
				115.4980	1.6700	3.11×10^5	-31.8841		0.0951
				118.4220	1.8000	2.26×10^5	-30.5654		0.0968
	303.15	98.3549	87.25417	81.8097	1.5300	6.54×10^4	-27.0283		0.0970
				82.4592	1.6700	1.99×10^5	-31.2579		0.0945
				85.9629	1.8000	5.56×10^4	-27.5406		0.0962
	298.15	83.2154	79.24517	74.5920	1.5300	1.21×10^5	-29.0188		0.0957
				75.9124	1.6700	1.31×10^5	-28.7271		0.0996
				77.1532	1.8000	1.61×10^5	-30.7211		0.0949
	293.15	58.3221	49.5497	52.1920	1.5300	6.54×10^4	-27.9502		0.0946
				53.1240	1.6700	5.99×10^4	-27.2722		0.0983
				54.0560	1.8000	5.26×10^4	-26.4986		0.1002

Table 5. *The formation constants and Gibbs free energies of formation of 1:2 M/LB concentration for bulk-CAc in presence of LB at different temperatures in EtOH- H_2O Solvents*

Xs EtOH	T K	Λ_M Ω^{-1}, Cm^2mol	Λ_{ML} Ω^{-1}, Cm^2mol	Λ_{obs} Ω^{-1}, Cm^2mol	$[L]\times10^5$	K_f	ΔG_f KJ/mol	ΔH KJ/mol	ΔS KJ/mol.K
0.0809	308.15	219.8994	182.3354	188.8000	5.6600	8.50×10^4	-29.0844	-49.2310	0.1160
				191.2000	7.4100	4.37×10^4	-26.9350		0.0850
				193.6000	8.3300	2.80×10^4	-25.3900		0.0850
	303.15	189.3325	153.3325	158.6000	5.6600	1.03×10^5	-28.1389		0.1280
				161.2000	7.4100	4.83×10^4	-27.6339		0.0830
				163.8000	8.3300	2.93×10^4	-25.9262		0.0830
	298.15	186.3325	143.3336	152.6400	5.6600	6.40×10^4	-27.4357		0.1200
				155.4300	7.4100	3.45×10^4	-25.4690		0.0870
				157.7500	8.3300	2.38×10^4	-25.8228		0.0820
	293.15	176.2451	138.5478	146.4000	5.6600	6.72×10^4	-28.0185		0.1130
				148.8000	7.4100	3.61×10^4	-26.0194		0.0870
				151.2000	8.3300	2.38×10^4	-24.5619		0.0870
0.2021	308.15	157.3331	126.3325	134.2000	5.6600	1.77×10^4	-25.0592	-22.8790	0.1750
				136.4000	7.4100	1.35×10^4	-23.9735		0.1450
				138.6100	8.3300	1.20×10^4	-23.2879		0.1460
	303.15	153.2254	117.5487	123.7900	5.6600	8.33×10^4	-27.6203		0.1950
				125.8900	7.4100	4.42×10^4	-27.4104		0.1380
				127.9600	8.3300	2.91×10^4	-25.9133		0.1390

Xs EtOH	T K	Λ_M Ω^{-1}, Cm^2mol	Λ_{ML} Ω^{-1}, Cm^2mol	Λ_{obs} Ω^{-1}, Cm^2mol	[L]×10^5	K_f	ΔG_f KJ/mol	ΔH KJ/mol	ΔS KJ/mol.K
				110.5600	5.6600	1.10×10^5	-28.7847		0.1970
	298.15	136.6985	106.3698	112.7300	7.4100	5.09×10^4	-26.4167		0.1490
				114.5500	8.3300	3.25×10^4	-26.6213		0.1400
				98.9900	5.6600	8.19×10^4	-28.5178		0.1720
	293.15	126.2147	93.1142	101.3100	7.4100	4.10×10^4	-26.3336		0.1470
				103.9800	8.3300	2.46×10^4	-24.6428		0.1480
				106.2800	5.6600	9.13×10^4	-29.2675		0.3360
	308.15	148.3325	98.1415	110.4000	7.4100	4.18×10^4	-26.8210		0.2980
				114.8200	8.3300	2.41×10^4	-25.0179		0.3020
				74.4100	5.6600	1.77×10^4	-23.8394		0.3430
	303.15	82.2214	71.3256	75.6100	7.4100	2.08×10^4	-25.4805		0.2800
0.3635				76.8100	8.3300	1.20×10^4	-23.6784	-68.6540	0.2920
				42.0000	5.6600	3.74×10^5	-31.8136		0.3330
	298.15	56.2548	41.3265	43.0000	7.4100	1.07×10^5	-28.2273		0.3050
				44.0000	8.3300	5.50×10^4	-27.9703		0.2880
				42.0400	5.6600	1.77×10^4	-24.6526		0.3210
	293.15	71.2145	39.2154	44.1100	7.4100	1.35×10^4	-23.5781		0.3000
				47.0400	8.3300	3.71×10^4	-25.6471		0.3030

Table 6. *The formation constants and Gibbs free energies of formation of 1:1 M/LB concentration for bulk-CAc in presence of LB at different temperatures in EtOH- H_2O Solvents*

Xs EtOH	T K	Λ_M Ω^{-1}, Cm^2mol	Λ_{ML} Ω^{-1}, Cm^2mol	Λ_{obs} Ω^{-1}, Cm^2mol	[L]×10^5	K_f	ΔG_f KJ/mol	Δ H KJ/mol	Δ S KJ/mol. K
				170.5900	1.5300	3.21×10^5	-32.4867		0.1910
	308.15	196.2231	165.3652	174.9000	1.6700	1.34×10^5	-29.7584		0.1950
				177.8600	1.8000	8.16×10^4	-28.0409		0.1980
				142.9800	1.5300	2.37×10^6	-35.7801		0.2000
	303.15	165.2547	142.3654	146.2500	1.6700	2.93×10^5	-32.2552		0.1910
				148.9800	1.8000	1.37×10^5	-29.8102		0.1950
0.0809				136.4100	1.5300	4.04×10^5	-32.0080	-63.2900	0.2110
	298.15	155.2247	133.3695	138.6000	1.6700	1.90×10^5	-29.6337		0.2020
				140.8300	1.8000	1.07×10^5	-29.6789		0.1920
				132.3200	1.5300	2.44×10^5	-31.2706		0.1950
	293.15	147.1897	128.3365	134.4100	1.6700	1.26×10^5	-29.1166		0.1990
				136.8200	1.8000	6.79×10^4	-27.1215		0.2030
				121.0000	1.5300	6.54×10^4	-28.4112		0.4000
	308.15	135.0215	120.2145	123.2000	1.6700	5.99×10^4	-27.7295		0.4070
				125.4000	1.8000	5.56×10^4	-27.0863		0.4130
				112.0000	1.5300	6.10×10^5	-32.4725		0.4210
	303.15	127.2547	110.3652	113.8600	1.6700	2.30×10^5	-31.6297		0.4010
				115.0900	1.8000	1.43×10^5	-29.9246		0.4080
0.2021				100.8000	1.5300	1.55×10^6	-35.3310	-12.7900	0.4140
	298.15	112.0147	100.3256	102.6000	1.6700	2.48×10^5	-30.2777		0.4220
				103.8200	1.8000	1.30×10^5	-30.1788		0.4020
				89.6000	1.5300	2.07×10^5	-30.8559		0.4080
	293.15	97.0259	87.2549	90.7300	1.6700	1.08×10^5	-28.7455		0.4150
				91.5700	1.8000	7.02×10^4	-27.2039		0.4230
				88.5000	1.5300	5.34×10^6	-39.6938		0.1000
	308.15	109.3256	88.2451	91.2400	1.6700	3.62×10^5	-32.2625		0.1030
				93.6300	1.8000	1.62×10^5	-29.7386		0.1060
				68.4100	1.5300	6.54×10^4	-27.0283		0.1060
	303.15	80.2145	68.3574	69.6000	1.6700	5.12×10^5	-33.6833		0.1020
				70.2000	1.8000	5.56×10^4	-27.5406		0.1040
0.3635				40.2000	1.5300	6.94×10^4	-27.6364	-35.7800	0.1070
	298.15	42.3652	38.1596	41.8000	1.6700	9.30×10^3	-22.2742		0.1100
				42.1000	1.8000	3.74×10^3	-21.0800		0.1060
				33.1200	1.5300	6.54×10^4	-27.9502		0.1030
	293.15	45.2541	32.5487	34.4200	1.6700	5.99×10^4	-27.2722		0.1060
				35.3600	1.8000	1.96×10^5	-29.6994		0.1080

By drawing the relation between log K_f and 1/T, different lines are obtained indicating the formation of 1:2 and 1:1 (M: L) stoichiometric complexes) as explained in previous works [26-60].

From the relation between log K_f and 1/T, ΔH_f can be calculated for each type of complexes, from the slope of each line which equal ($-\Delta H_f/2.303R$). The entropy (ΔS_f) for bulk and nano-CAc stoichiometric complexes were calculated [32, 33] for each type of complexes (1:2) and (1:1) (M:L) by by using Gibbs-Helmholtz equation (6) [60-79]:

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (6)$$

The calculated values of (ΔH_f), ($T\Delta S_f$) and (ΔS_f) for bulk and nano-CAc at different temperatures stoichiometric complexes support the solvation free energy data.

It was found that regular spheres are seen in TEM images for nano CAc which explain that the association of nano CAc is big in solution phase. Therefore the association thermodynamic parameters and the complex formation parameters for nano CAc is bigger than bulk CAc in presence of N'-bezylidene-4-chlorobenzohydrazide (LB) .The association constants and free energies of association for both bulk and nano CAc are bigger than complex formation in presence of N'-bezylidene-4-chlorobenzohydrazide (LB) because both complexation and association are proceed which seen in association parameter. The paper compares the thermodynamic behaviour for nano and bulk CAc .Valuable results were obtained indicating the greater activity for nano salt in absence and presence of ligand (LB).This help for uses of nano CAc better than bulk CAc as food additive , more stabilization of human pressure and to lower more the phosphate level in bodies . Analytically we determine both nano and bulk CAc conductometrically from the association and complex formation thermodynamic parameters given in this work.

4. Conclusion

The association and complex formation parameters for nano calcium acetate are bigger than that of bulk CAc in mexed EtOH-H_2O solvents because of the bigger in both entropies and dissociation degrees for the former. Comparison between the nano and bulk electrolyte thermodynamics are very important to discuss their behaviors in solutions. Uses of nano CAc is preferred than bulk CAc in the used EtOH-H_2O solvents for any application. In this work lot of thermodynamic data was given to illustrate the behaviour in used mixed solvents.

References

[1] David A. Wright and Pamela Welbourn , Cambridge Environmental Chemistry Series, Cambridge University Press , Cambridge UK (2002)

[2] A. E. Williams, in: H. F. Mark, D. F. Othmer, C. G. Overberger, G. T. Seaborg (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 3, 3rd ed., Wiley, New York, 1978, pp. 778–792.

[3] J. L. Opgrande, C. J. Dobratz, E. E. Brown, J. C. Liang, G. S. Conn, J. Wirth, J. Shelton, in: J. I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 4, 4th ed., Wiley, New York, 1992, pp. 103–115.

[4] C. M. Park, R. J. Shechan, in: B. Elvers, S. Hawkins, G. Schultz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, vol. 18, fifth rev. ed , Basel, 1991, pp. 991–1043.

[5] D. E. Read, C. B. Purves, J. Am. Chem. Soc. 74 (1952) 116–119.

[6] E. E. Schrier, M. Pottle, H. A. Scheraga , J. Am. Chem. Soc. 86 (1964) 3444–3449.

[7] E. Suzuki, Y. Taniguchi, T. Watanabe, J. Phys. Chem. 77 (1973) 1918–1922.

[8] K. Yamamoto, N. Nishi, J. Am. Chem. Soc. 112 (1990) 549–558.

[9] P. Debye, E. Hückel, Z. Phys. 24 (1923)185, 305.

[10] Esam A. Gomaa and R. M. Galal, Basic Sciences of Medicine, 1(2), (2012), 1-5.

[11] Esam A. Gomaa, Physics and Chemistry of Liquids, 50(2012)279-283.

[12] Esam A. Gomaa, International Journal of Materials and Chemisty, 2(1), (2012)16-18.

[13] Esam A. Gomaa, American Journal of Environmental Engineering, 2(3), (2012) 54-57.

[14] Esam A. Gomaa. American Journal of Polymer Science, 2(3), (2012), 35-38.

[15] Esam A. Gomaa. Eur. Chem. Bull., 1(2013) 259-261.

[16] Esam A. Gomaa, Elsayed Abou Elleef and E. A. Mahmoud , Eur . Chem. Bull, 2(2013), 732-735.

[17] Esam A Gomaa and Elsayed M.Abou Elleef, American Chemical Science Journal, 3(2013), 489-499.

[18] Esam A. Gomaa, Elsayed M. Abou Elleef, Science and Technology, 3(2013)118-122.

[19] Esam A Gomaa and M. G. Abdel Razek , International Research Journal of Pure and Applied Chemistry,3 (2013)320-329

[20] Esam A. Gomaa, International Journal of Theoretical and Mathematical Physics, 3 (2013) 151-154.

[21] Esam A. Gomaa and B. A. Al Jahdali, Education., 2(3), (2012) 37-40.

[22] Esam A Gomaa, American Journal of Biochemistry, 2(3), 92012), 25-28.

[23] Esam A. Gomaa, Food and Public Health, 2(3), 2012, 65-68.

[24] Esam A. Gomaa, Global Advanced Research Journal of Chemistry and Material Science, 1(2012)35-38.

[25] Esam A. Gomaa, Frontiers in Science, 2(2012)24-27.

[26] Esam A Gomaa, Elsayed M. Abou Elleef, E. T. Helmy and Sh. M. Defrawy, Southern Journal of Chemistry, 21(2013)1-10.

[27] E. A. Gomaa, K. M. Ibrahim, N. M. Hassan, Frontiers in Science, 2 (2012) 76-85.

[28] E. A. Gomaa, K. M. Ibrahim and N. M. Hassan, The International Journal of Engineering and Science (IJES), 3(2014) 44-51.

[29] E. A. Gomaa, H. M. Abu El-Nader and Sh. E. Rashed, The International Journal of Engineering and Science (IJES), 3(2014) 64-73.

[30] E. A. Gomaa, K. M. Ibrahim and N. M. Hassan, Research and Reviews: Journal of Chemistry, 3(2014) 47-55.

[31] Esam A. Gomaa and Elsayed M. Abou Elleef, Thermal and Power Engineering, 3 (2014), 222-226.

[32] Esam A Gomaa, Elsayed M. Abou Elleef, Elsayed T. Helmy, Research and reviews: Journal of Chemistry, 3(2014) 22-27.

[33] Esam A. Gomaa, .Science and Technology, 3(2013)123-126.

[34] E. A. Gomaa, Research and Reviews: Journal of Chemistry, 3(2014) , 28-37.

[35] E. A. Gomaa, A. H. El-Askalany and M. N. H. Moussa, Rev. Roum. Chim, 32 (1987)243.

[36] Esam A Gomaa, Thermochimica Acta, 128(1988)99.

[37] E.A.Gomaa, Indian J.of Tech., 24(1986)725.

[38] Esam A. Gomaa, Thermochimica Acta, 1 42(1989)19.

[39] Esam A. Gomaa, Croatica Chimica Acta, 62(1989)475.

[40] Esam A. Gomaa, Thermochimica Acta, 147(1989)313.

[41] E. A. Gomaa, A. M. Shallapy and M. N. H. Moussa, J. Indian Chem. Soc., 68(1991)339.

[42] E.A.Gomaa, A.M.Shallapy and M. N. H. Moussa , Asian J.of Chem., 4(1992)518.

[43] H. M. Abu El-Nader and E. A. Gomaa, Mansoura Science Bulletin. (A Chem.) Vol. 23 (1) July1996.

[44] J. I. Kim, A. Cecal, H. J. Born, and E.A. Gomaa, Z. Physik Chemic, Neue Folge 110, 209(1978).

[45] J.I. Kim and E. A. Gomaa, Bull.Soci.Chim.Belg.,90(1981)391.

[46] E. A. Gomaa, A.A.El-Khouly and M. A. Mousa, Indian Journal of Chemistry, 23((1984)1033.

[47] E.A.Gomaa,M.A.Mousa and A. A. El-Khouly, Thermochimica Acta, 86 (1985)351.

[48] E.A.Gomaa,M.A.Mousa and A. A. El-Khouly, Thermochimica Acta, 89(1985)133.

[49] Esam A. Gomaa, Thermochimica Acta, 91(1985)235.

[50] Esam A. Gomaa, Thermochimica acta, 128(1988)287.

[51] Esam A. Gomaa, Thermochimica Acta, 140(1989)7.

[52] Esam A. Gomaa, Bull. Soc. Chim. Fr. 5 (1989)620.

[53] Esam A.Gomaa, Bull.Soc.Chim.Fr., 5(1989)623.

[54] Esam A Gomaa, Thermochimica acta, 152(1989)371.

[55] Esam A. Gomaa, Thermochimica Acta, 156(1989)91.

[56] I. S. Shehatta, A. H. El-Askalany and E. A. Gomaa, Thermochimica Acta, 219(1993)65.

[57] E. A. Gomaa and G. Begheit, Asian Journal of Chemistry, 2(1990)444.

[58] A. A. El-Khouly, E. A. Gomaa, and S. Abou-El-Leef, Bull. Electrochem 19, 153 (2003).

[59] A. A. El-Khouly, E. A. Gomaa, and S. Abou El-Leef, Bull. Electrochem 19, 193 (2003).

[60] M. A. Hamada, E. A. Gomaa and N. A. El-Shishtawi, International Journal of Optoelectronic Engineering, 1(2012)1-3.

[61] Kamal M. Ibrahim, Esam A. Gomaa , Rania R. Zaky and M. N. Abdel El-Hady, American Journal of Chemistry,2(2012)23-26.

[62] A. A. El-Khouly, E. A. Gomaa and S. E. Salem, Southern Brazilian Journal of Chemistry, vol. 20 (2012)43-50.

[63] E. A. Gomaa and B. A. M. Al –Jahdali, American Journal of Environmrntal Engineering, 2(2012)6-12.

[64] S.L. Oswal, J.S. Desai, S.P. Ijardar, and D.M. Jain, J. Mol. Liquids 144, 108 (2009).

[65] Y. Marcus. The Properties of Solvents (Wiley, London, 1998).

[66] E. A. Gomaa, A. H. El-Askalany, M. N. H. Moussa, Asian Journal of Chemistry, 4(1992)553.

[67] Esam A. Gomaa, Rev.Roum.de Chimie , 36(1991)11.

[68] Esam A. Gomaa, Journal of King Saud University, 3(1), 1991, 1411.

[69] Esam A. Gomaa, Oriental Journal of Chemistry, 6(1990)12.

[70] E. A. Gomaa, M. A. Hamada and R. Galal, Avances en Quimica, 5(2),117-121(2010).

[71] Esam A. Gomaa, Analele Uni.din Bucuresti-Chimie, vol. 19 no1, pag.45-48 (2010).

[72] Nagah A. El-Shishtawi, Maany A. Hamada and Esam A. Gomaa, Physical Chemistry,1(1),(2011) 14-16.

[73] E. A. Gomaa and B. A. M. Al Jahdali, American Journal of Condensed Matter Physics, 2(1), (2012), 16-21.

[74] Esam A. Gomaa, Elsayed M. Abou Elleef, Ahmed Fekri, Mohamed Khairy anf Reham Abou Karn, Annalen der chemischen Forschung, 2, (2014) 55-64.

[75] Esam A. Gomaa, Elsayed M. Abou Elleef, Kamal S. Shalaby and Shereen E. Salem, Journal of Environment,2 ,4 (2014) 44-53.

[76] Mohamed N. H. Hamed, Esam A. Gomaa and Sameh G. Sanad, International Journal of Engineering Sciences & Research Technology,3, 9 (2014) 97-105.

[77] Mohamed N. H. Hamed, Esam A. Gomaa and Sameh G. Sanad, Indian Journal of Applied Research,4,10(2014)193-197.

[78] Mohamed N. H. Hamed, Esam A. Gomaa and Sameh G.Sanad, International Journal of Engineering and Innovative Technology (IJEIT), vol 4, 2(2014)203-207.

[79] D. Bobicz, W. Grzybkowski, and A. Lwandowski, J. Mol. Liquids 105, 93 (2003).