A Comprehensive Study of Thermodynamical Parameters and Solvation Number of Some Organic Acid Salts in Non- Aqueous Medium

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Abstract

Acoustic signals couple to liquids via fundamental parameters such as density and viscosity. Variations in the relevant liquid parameters may result in the variations of thermodynamic parameters such as Internal pressure and Free volume. The variation in the sample properties is investigated to understand the structural influence of the solute on the solvent. In the present study, measurements of ultrasound velocities, densities and viscosities over a concentration range 0.001m to 0.15m of non-aqueous formamide solutions of calcium salts of some organic acids in the temperature range ^{0}C to 55^{0}C have been made to compute thermodynamical parameters to reveal the nature of interactions between the components of the solutions. Further, the compressibility behaviour in a solution throws light on the solute- solvent interactions. The solvation number has been calculated to determine the interactions taking place in the solutions. The result obtained from compressibility method is seen to agree well with the results from different theoretical and experimental methods.

Keywords: Internal pressure, free volume, solvation number, formamide, calcium salts of some organic acids.

Introduction

Liquids owe their fascinating features to their molecular interaction energies of the order of thermal energies, which fluctuate rapidly. In order to understand the liquid state, it is therefore necessary to investigate the fluctuations in the properties of liquids. Sonic waves, which couple fundamental thermodynamic parameters and transport properties, constitute a valuable tool for the studies of large variety of molecular processes.

The samples chosen are calcium salts of carboxylic acids and its derivatives. The non-aqueous solutions of the salts in formamide are electrolytic in nature. The study of molecular interactions existing in the non-aqueous solutions of calcium salts has been made through ultrasonic velocity measurements. The formulae and the structure of the samples are listed in (Table1).

Experimental Procedure and Computation

Solutions of different molalites are prepared using AR grade Calcium salts in Formamide. The density(ρ), the viscosity(η) and the sound velocity (u) are measured the using 25 ml specific gravity bottle, Cannon Fenske viscometer and Mittal Interferometer operating at 2MHz with accuracies of ±0.001gm/cc, ±0.01% and ±2m/s. Internal pressure (p_i), free volume (V_f) and Solvation number (n_s) are calculated using the following formulae,

Internal pressure(p_i) = $bRT(k\eta/u)^{1/2} [\rho^{2/3} / M_{eff}^{7/6}]$atms

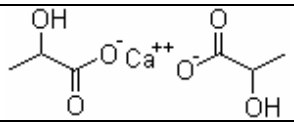
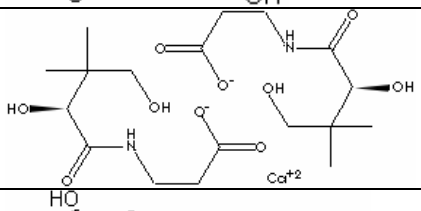
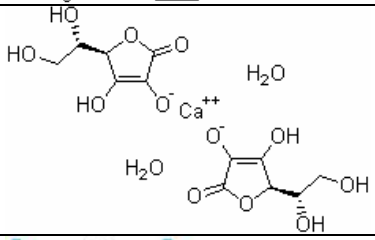
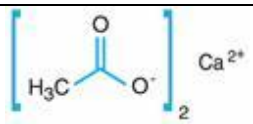
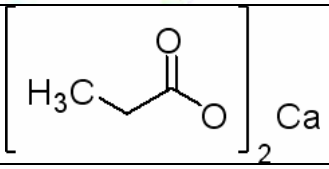
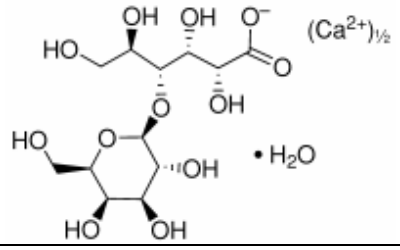
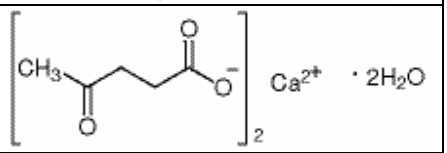
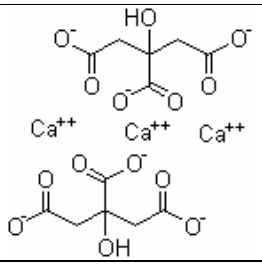
Free volume (V_f) = $(M_{eff} u/k)^{3/2}$ cc

Solvation number (n_s) = $(n_f/n_i)(1-(\beta/\beta_0))$

Where,

b is the packing factor, R is the gas constant, T is the temperature in Kelvin
K is the constant value 4.28 x 10^9, M_{eff} is effective the molecular weight,
β , β_0 is the adiabatic compressibility of the solutions and the solvent
n_f , n_i is the number of moles of solvent formamide and number of ions solvated.

Table – 1
Samples

Sl.No	Name of the electrolytes	Molecular formula	Molecular structure
1	Calcium L- Lactate hydrate	$C_6H_{10}O_6\ Ca.H_20$	
2	D- Calcium Pantothenate	$C_{18}H_{32}N_2O_{10}\ Ca$	
3	Calcium L – Ascorbate dihydrate	$C_{12}\ H_{14}\ Ca\ O_{12}\ 2H_2O$	
4	Calcium Acetate	$C_4H_6\ CaO_4$	
5	Calcium Propionate	$C_6H_{10}CaO_4$	
6	Calcium Lactobionate monohydrate	$C_{12}\ H_{21}O_{12}\ 0.5\ Ca\ H_2O$	
7	Calcium Levulinate	$C_5\ H_7\ 0.5Ca\ O_3\ H_2O$	
8	Calcium Citrate Tetra hydrate	$Ca_3\ (C_6H_5O_7)\ 4H_2O$	

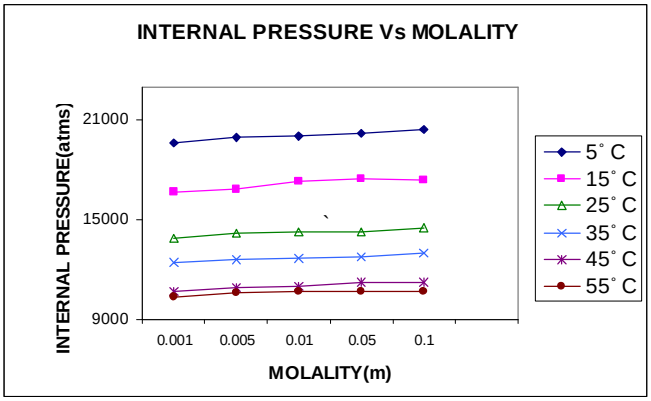
Results and discussion

Internal pressure is the resultant of forces of attraction and the forces of repulsion between molecules in a liquid and its role in transport properties has been emphasized by Surya Narayana[1]. The internal pressure is also a measure of cohesive force in a solution and is considered as a rational basis to understand thermodynamics of electrolytic solutions[2]. The values of internal pressure (p_i) and free volume (V_f) are presented for temperatures ranging from 5^0C to 55^0C and various concentrations in Tables 2 and 3.The free volume and internal pressure are qualitatively complimentary . Formamide is a protic polar solvent, existing as dimer having a cage structure[3]. Addition of salts either promote or disrupt the Hydrogen bonded structure of the formamide, thereby strengthening or weakening the structure of the solvent.

Internal pressure is found to be increasing with molality at all temperatures. The rise in internal pressure with concentration indicates that there is a strong ion solvent interaction occurring in the solution. In the present investigation, the internal pressure shows an increasing trend with respect to molalities in calcium lactate solution at different temperatures as shown in (Figure 1). This increasing trend suggests the presence of strong solute-solvent interactions or increase in the cohesive energy of the system. Hence, this may be attributed to the structure enhancing nature of the solutes in the solvent[4] Calcium ascorbate and calcium acetate are also observed to have an increasing trend with concentration exhibiting a structure stabilizing nature. However, a dip in the increasing values of internal pressure with concentration is observed for calcium ascorbate (0.1m, 45°C) and calcium acetate (0.01m, 5°, 15°C). This may be due to weakening of interactions at specific concentrations and temperature suggesting the loosening of structures due to lowering of cohesive energy. Calcium panthonate solution (0.05m), calcium propionate (0.01m) and calcium citrate (0.0075m) show similar behaviour at temperatures from 5°C to 55°C exhibiting structure weakening nature.

Figure – 1

Calcium Lactate



Calcium levulinate at 0.10m below 35°C shows such weakening of structure. Calcium lactobionate exhibits an increasing trend of internal pressure with concentration at room temperature (35°C) generally showing structure enhancing behaviour. But lowering of cohesive energy at higher temperatures 45°, 55°C and at higher concentrations 0.05m and 0.10m is indicated by the dip in its general trend. The decreasing trend in internal pressure suggests that the solute has the tendency of breaking of the structure of the solvent. The internal pressure is found to decrease with temperature in all solutions. This is attributed to the fact that when temperature is increased, the ions move away from each other; the interaction between the ions is decreased, further leading to the decrease in the cohesive forces and hence a decrease in internal pressure[5]. Thus, internal pressure is a factor, which varies due to all the internal interactions. The decreasing values of free volume with molalities and the change or the increase in free volume in its decreasing trend is in agreement with the structure making / breaking behaviour of the solutes.

Table - 2

Internal pressure (π_i) (Atms)

	Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
CALCIUM LACTATE	0.001	19601	16713	13850	12459	10662	10331
	0.005	19970	16835	14206	12627	10894	10580
	0.01	20033	17311	14293	12719	11010	10696
	0.05	20172	17470	14300	12777	11236	10715
	0.1	20463	17391	14551	12965	11233	10675
CALCIUM PANTOTHENATE	0.001	19517	16653	13849	11950	10589	9995
	0.005	19679	16893	13902	12427	10986	10365
	0.01	20180	17109	14067	12402	11037	10549
	0.05	19250	16493	13686	12195	11020	10121
	0.1	21271	17778	14222	12352	10732	10146
CALCIUM ASCORBATE	0.001	18706	15922	13825	12155	10656	10093
	0.005	18999	16418	13869	12434	10807	10250
	0.01	19496	16490	13984	12443	10997	10287
	0.05	20317	17026	14488	12760	11207	10401
	0.1	20898	17732	14611	12792	10975	10527
	0.15	22405	18834	15218	13496	11440	10657
CALCIUM ACETATE	0.001	18333	15345	13043	12051	10295	10061
	0.005	19082	16086	13470	12258	10458	10298
	0.01	19292	16424	13749	12596	10872	10458
	0.05	20110	17188	14312	12960	11167	10843
	0.1	20247	17233	14429	13167	11324	11084
	0.15	20425	17515	14566	13366	11574	11290
CALCIUM PROPIONATE	0.001	19317	16310	13625	12338	10935	10352
	0.005	19537	16917	13805	12347	10879	10263
	0.01	19481	16561	13639	12415	10832	10145
	0.05	20020	16996	14182	12506	11077	10226
	0.1	20820	17223	14398	12724	11036	10461
	0.15	20974	17373	14588	12726	11014	10494
CALCIUM LACTOBIONATE	0.001	18448	15876	13622	12265	10444	10013
	0.005	18806	15908	13684	12290	10588	10128
	0.01	18982	16250	13702	12452	10885	10221
	0.05	19527	16700	13992	12471	10875	10202
	0.1	21452	17725	14571	13046	11403	10167
CALCIUM CITRATE	0.001	19018	15902	13399	12086	10413	9898
	0.005	19824	16507	14074	12575	11026	10541
	0.0075	18892	15829	13573	12413	10780	10153
	0.01	19391	16402	13824	12443	9594	10399
	0.0125	19267	16251	13707	11433	10764	10117
CALCIUM LEVULINATE	0.001	18909	16205	13591	12183	10415	10067
	0.005	19362	16640	13804	12346	10863	10556
	0.01	19469	16645	14065	12403	11029	10680
	0.05	19825	16821	14277	12639	11155	10752
	0.1	19420	16608	14159	12624	11343	10866
	0.15	20581	17419	14416	12896	11558	10561

Table - 3
Free volume E–8m^3

	Molality(m)	5˚ C	15˚ C	25˚ C	35˚ C	45˚ C	55˚ C
CALCIUM LACTATE	0.001	0.812	1.442	2.773	4.149	7.187	8.550
	0.005	0.767	1.410	2.568	3.983	6.730	7.947
	0.01	0.758	1.294	2.519	3.880	6.523	7.683
	0.05	0.733	1.248	2.965	3.814	6.096	7.612
	0.1	0.690	1.247	2.337	3.601	6.025	7.592
CALCIUM PANTOTHENATE	0.001	0.827	1.463	2.775	4.696	7.336	9.427
	0.005	0.804	1.398	2.738	4.168	6.550	8.428
	0.01	0.745	1.342	2.375	4.175	6.441	7.971
	0.05	0.828	1.449	2.664	4.275	6.267	8.734
	0.1	0.576	1.083	2.308	3.816	6.342	8.124
CALCIUM ASCORBATE	0.001	0.940	1.673	2.793	4.471	7.200	9.155
	0.005	0.896	1.524	2.762	4.172	6.894	8.289
	0.01	0.829	1.504	2.697	4.162	6.541	8.638
	0.05	0.718	1.340	2.375	3.778	6.057	8.197
	0.1	0.643	1.158	2.260	3.660	6.297	7.716
	0.15	0.513	0.950	1.840	3.088	5.474	7.330
CALCIUM ACETATE	0.001	0.996	1.869	3.293	4.587	7.981	9.259
	0.005	0.884	1.624	3.021	4.362	7.620	8.631
	0.01	0.857	1.525	2.425	4.015	6.783	8.238
	0.05	0.759	1.337	2.528	3.705	6.290	7.415
	0.1	0.747	1.332	2.484	3.557	6.075	7.003
	0.15	0.727	1.272	2.427	3.418	5.733	6.651
CALCIUM PROPIONATE	0.001	0.848	1.549	2.913	4.273	6.667	8.520
	0.005	0.819	1.391	2.798	4.260	6.774	8.741
	0.01	0.825	1.478	2.904	4.195	6.884	9.034
	0.05	0.757	1.363	2.564	4.076	6.377	8.770
	0.1	0.663	1.294	2.427	3.868	6.396	8.139
	0.15	0.641	1.237	2.299	3.780	6.334	7.966
CALCIUM LACTOBIONATE	0.001	0.976	1.685	2.914	4.346	7.636	9.373
	0.005	0.921	1.723	2.872	4.312	7.321	9.055
	0.01	0.895	1.566	2.700	4.143	6.733	8.814
	0.05	0.807	1.420	2.344	4.083	6.634	8.714
	0.1	0.594	1.158	2.276	3.447	5.602	8.584
CALCIUM CITRATE	0.001	0.890	1.672	3.059	4.541	7.693	9.698
	0.005	0.784	1.490	2.632	4.017	6.458	7.996
	0.0075	0.904	1.687	2.928	4.167	6.902	8.949
	0.01	0.839	1.514	2.769	4.127	9.772	8.311
	0.0125	0.848	1.554	2.838	5.310	6.902	9.016
CALCIUM LEVULINATE	0.001	0.904	1.582	2.361	4.435	7.710	9.240
	0.005	0.843	1.459	2.802	4.258	6.788	8.002
	0.01	0.827	1.460	2.645	4.182	6.509	7.736
	0.05	0.777	1.404	2.159	3.950	6.229	7.527
	0.1	0.820	1.446	2.563	3.937	5.899	7.267
	0.15	0.684	1.244	2.413	3.667	5.547	7.855

Solvation Number

Intermolecular interactions determine solubility. The study of solvation number is used to interpret ion-solvent interactions. The solvation number is defined as the number of solvent molecules per ion, which remain attached to a given ion long enough to experience its translational movements. The values of solvation number for various values of temperatures and molalities are presented in Table 4. The decrease in the solvation number with increasing concentration reveals that either there is not enough solvent for all the ions or preferably ion pairing has occurred. The positive solvation number for the solutions suggests that the compressibility of the solution at high temperatures may be less than that of solvent. However, the fall in solvation number at high temperatures and the rise in solvation number from negative maximum towards zero at low temperatures may be attributed to the decreasing ion-solvent interactions but with further increase in concentration, it remains constant. This may be due to the dominant effect of intermolecular attraction of solutes over ion- solvent interactions.

The general observations on solvation number of the system studied in relation to temperature and molality may be summarized as follows.

- The solvation number is positive above room temperature and is negative below room temperature.
- Gradual increase of solvation number from lower to higher concentrations is observed.
- The solvation number values are approximately found to be zero near higher concentration of 0.1m and 0.15m mostly at lower temperature.
- The sign of the solvation number indicates the relative values of compressibility of solution and the solvent.

The negative values of solvation number at temperatures emphasize that the solutions are more compressible than the solvent. This may be attributed to the mobility of the ion being low at the low temperatures. Therefore solution is more compressible than the solvent and hence the negative sign for the solvation number. Positive solvation number suggests that compressibility of the solution at high temperatures at all molalities will be less than that of the solvent supporting the fact that ions gain high mobility and have more probability of contacting solvent molecules. Therefore an increase in interaction between ion and solvent molecules is expected. Zero value of solvation number indicates that no change occurs in the compressibility value of the solvent when the solution is formed [6]. The rise in solvation number from negative value towards zero at low temperatures and fall in solvation number at higher temperature with increasing concentration may be attributed to decreasing solute-solvent interaction.

The constant values of solvation number at higher concentrations and higher temperatures may be due to the strong ion-ion attractions between the electrolyte molecules than the ion-solvent interactions[7]. The perusal of Table 5 shows that the number of solvent molecules in the coordination sphere varies with anions [8]. The values of the solvation number of Ca^{2+} in formamide obtained in the present study agree well with the solvation numbers reported from other methods Table 6.

Conclusion

The effect of the salts on the structure of the solvent is investigated by the study of internal pressure and free volume at various temperatures and concentrations. The solvation number of calcium ion calculated from the present compressibility study for sample solutions agree well with the reported values from other methods.

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Table - 4
Solvation Number

	Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
CALCIUM LACTATE	0.001	-168	-94	-244	34	250	377
	0.005	-133	-17	-36	28	73	91
	0.01	-34	5	-12	-6	24	35
	0.05	-9	1	-1	3	3	7
	0.1	-3	2	1	3	4	5
CALCIUM PANTOTHENATE	0.001	-818	-391	-168	-84	153	366
	0.005	-138	-51	10	-8	61	123
	0.01	-30	-6	12	22	48	47
	0.05	-6	2	1	-4	11	6
	0.1	1	4	4	4	8	18
CALCIUM ASCORBA	0.001	-449	77	-481	21	254	274
	0.005	-110	-38	-25	15	73	70
	0.01	-43	-10	-8	59	10	44
	0.05	-5	5	-15	9	2	28
	0.1	5	3	7	11	11	5
	0.15	4	6	5	6	8	8
CALCIUM ACETATE	0.001	-268	-88	-247	-486	84	-63
	0.005	-44	25	-6	-21	53	84
	0.01	-4	19	9	11	32	75
	0.05	-8	-1	-2	1	6	10
	0.1	-2	1	0	4	5	9
	0.15	0	-1	-1	1	2	4
CALCIUM PROPIONATE	0.001	-640	-396	-298	200	754	817
	0.005	-228	-53	-53	76	165	243
	0.01	-64	-42	-5	53	110	110
	0.05	-12	3	-2	10	18	24
	0.1	-10	0	-2	4	12	4
	0.15	-6	-3	-1	7	9	4
CALCIUM LACTOBIONATE	0.001	-534	-417	-457	117	603	1151
	0.005	-91	-44	-83	83	74	248
	0.01	-91	-12	-10	9	62	88
	0.05	-10	-5	-5	8	23	31
	0.1	-4	4	2	7	7	17
CALCIUM CITRATE	0.001	-629	-97	-327	-149	114	381
	0.005	-84	-7	-9	8	49	101
	0.0075	-57	-18	-35	-4	30	70
	0.01	-33	3	-14	20	28	51
	0.0125	-41	-3	-33	0	12	18
CALCIUM LEVULINATE	0.001	-255	-281	-260	-153	214	230
	0.005	-18	-32	-37	3	68	-48
	0.01	-17	6	-11	18	52	8
	0.05	-4	-1	-3	-1	8	10
	0.1	-1	6	-1	2	3	1
	0.15	0	1	0	2	3	2

Table 5
The solvation number for Ca^{2+} ion in formamide at 35^{O}C and 0.1m for all the samples

Sample	Solvation number
Calcium levulinate	2
Calcium lactate	3
Calcium pantothenate	4
Calcium acetate	4
Calcium propionate	4
Calcium lactobionate	7
Calcium ascorbate	11

Table 6
The solvation number of Ca^{2+} reported from different studies in different solvents.

Study	Solvation number.
From Aqueous solutions at 25^{O}C [9]	4
$CaClO_4$ in DMPA at 298 (from Raman spectroscopy)[10]	6
Calcium ion in DMS (LAXS)[11]	6
Ca^{2+} in Aq. Ammonium solutions (QM/MM simulation)[12]	7.2
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