Asian Journal of Chemistry Vol. 11, No. 4 (1999),1455 –1458

A Comparative Study on Solubilities and Refractive Indices of Aqueous Solutions of Sodium and Calcium Salts of α-Amino Fatty Acids

R.P. VERMA*, J. PARSHAD and SURENDER KUMAR
Department of Chemistry, D.A.V. College, Muzaffarnagar-251 001, India

Solubilities and refractive indices of sodium and calcium salts of α-amino isovaleric, α-amino β-hydroxy butyric and α-amino iso caproic acids have been studied. Solubilities, apparent heat and entropy of solution suggest the existence of aggregates of salt above K.P. (323 K) in water. The C.M.C. has been determined by refractive index using Lorentz-Lorenz equation. The values of molar refraction of soap, $[R]_2$, of calcium salts are found higher than sodium salts.

INTRODUCTION

A number of metal salts of amino carboxylic acids have been used as plasticizers[1], heat stablizers[2], detergents[3–5], cosmetics[6], shampoos, synthetic toilet soap[7], dentifries[8] etc. In view of the above important utility and the fact that the references on the physical properties of these salts are rare, the present study has been initiated. Solubilities and refractive indices of these soaps in water have been studied in order to compare their micellar behaviour.

EXPERIMENTAL

α-Amino isovaleric, α-amino β-hydroxy butyric and α-amino isocaproic acids were obtained from Sigma Chemical Co., U.S.A. Sodium hydroxide and calcium carbonate were of AR grade. Double distilled water was used through out the work.

Freshly prepared sodium hydroxide and calcium hydroxide solutions were added dropwise in aqueous solutions of amino acids containing a drop of phenolphthalein till a pale pink colour was obtained to prepare sodium and calcium salts of amino acids respectively. The solution was then concentrated to yield a white crystalline salt. It was further recrystallized with water and dried in an air oven (373–378 K).

The methods of determination of solubility and refractive index were the same as reported earlier[9–11]

RESULTS AND DISCUSSION

Solubility: The solubility of sodium and calcium salts of α-amino acid

increases with increase in temperature. When the salt is heated in water, the opening of lattice due to thermal agitation of chain permits entry between the chain of solvent molecules. The increased disorder in the lattice due to this penetration of solvent causes a breakdown in the structure of the salt which dissolves in the form of micelles[12].

It is observed that the solubility of sodium salt is higher than that of calcium salt. However the solubility of both sodium and calcium salts of α-amino acids vary in the following order.

α-amino isocaproate < α-amino isovalerate < α-amino-β-hydroxy butyrate.

The apparent heat of solution, ΔH_{sol} was calculated from the Van't Hoff reaction isochore.

$$\Delta H_{sol} = RT^2 \left[\frac{d \ln S}{dT} \right]$$

Where S is the solubitlity in mol kg^{-1} and other terms have their usual meaning.

The value of ΔH_{sol} (Table-1) has been calculated from slopes of linear plots of log S vs 1/T. The appreciable difference in the value of ΔH_{sol} below and above the K.P. (323 K) confirm the formation of micelle. However, the values of ΔH_{sol} for sodium salt are higher than calcium salt below K.P. except α-amino iso caproic acid below K.P. and α-amino isovaleric acid above K.P. which shows the reverse order.

Another factor which affects the solubility of soap is the entropy of soap in solution, ΔS_{sol} (Table-1) can be calculated as

$$\Delta S_{sol} = \frac{\Delta H_{sol}}{T}$$

The variation of ΔS_{sol} is similiar to the behaviour of ΔH_{sol}.

TABLE-1
VALUE OF ΔH_{Sol} (KJ $mols^{-1}$) AND ΔS_{Sol}(J $K^{-1}mol^{-1}$) OF SODIUM AND CALCIUM SALTS OF α-AMINO FATTY ACIDS IN WATER

	Below K.P.				Above K.P.		
	ΔH_{sol}	ΔS_{sol}			ΔH_{sol}	ΔS_{sol}	
		308	313	318		328	333
Sodium							
α-amino isovaleric acid	17·28	56·10	55·20	54·34	11·49	35·03	34·50
α-amino β-hydroxy butyric acid	16·81	54·59	53·71	52·87	9·19	28·02	27·60
α-amino isocaproic acid	11·21	39·64	39·00	38·39	17·23	52·54	51·75
Calcium							
α-amino iso valeric acid	11·21	39·64	39·00	38·39	13·40	40·86	40·25
α–amino β-hydroxy butyric acid	10·97	35·63	35·01	34·51	6·13	18·68	18·40
α–amino iso caproic acid	13·34	43·33	42·64	41·97	14·93	45·53	44·85

TABLE-2
REFRACTIVE INDEX OF SODIUM AND CALCIUM SALTS OF α-AMINO FATTY ACIDS IN WATER AT 308K.

Concentration C (mol dm^{-3})	α-amino iso valeric acid		α-amino β-hydroxy butyric acid		α-amino iso caproic acid	
	Refractive Index (n)	Molar Refraction of the soap $[R]_2$	Refractive Index (n)	Molar Refraction of the soap $[R]_2$	Refractive Index (n)	Molar Refraction of the soap $[R]_2$
			Sodium			
0.002	1.3221	33.16	1.3222	60.08	1.3322	68.40
0.004	1.3321	35.80	1.3323	63.26	1.3324	71.20
0.006	1.3323	38.65	1.3326	67.00	1.3326	74.08
0.008	1.3324	41.45	1.3328	70.69	1.3329	77.16
0.010	1.3325	41.95	1.3330	72.50	1.3331	80.06
0.015	1.3327	42.10	1.3335	73.20	1.3336	79.10
0.020	1.3330	42.45	1.3339	74.00	1.3341	77.78
			Calcium			
0.002	1.3321	72.10	1.3322	85.04	1.3323	113.40
0.004	1.3323	75.16	1.3324	88.40	1.3325	116.02
0.006	1.3324	78.09	1.3326	91.60	1.3328	118.62
0.008	1.3326	81.08	1.3328	95.06	1.3331	121.20
0.010	1.3328	84.20	1.3331	98.40	1.3334	123.82
0.015	1.3332	84.20	1.3336	98.96	1.3340	123.80
0.020	1.3335	83.79	1.3340	96.22	1.3346	120.43

Refractive Index: Refractive index n increases with increase in concentration. The n-C plots show a change at a definite concentration, *i.e.*, 0·01 M of salt for all the salts called C.M.C. However the values of n of calcium salts are higher than sodium salts. The refractive indices data have been analysed using Lorentz–Lorenz equation.

$$[R] = \frac{n^2 - 1}{n^2 + 2} = \frac{X_1M_1 + X_2M_2}{d}$$

where n and d are respectively the refractive index and the density of solutions, X_1 is mole fraction of solvent of molecular weight M_1 and X_2 is the mole fraction of the solute of molecular weight M_2.

The molar refraction of solution [R] is also expressed by the equation

$$[R] = X_1[R]_1 + X_2[R]_2$$

where $[R]_1$ and $[R]_2$ are molar refraction of the solvent and solute respectively.

The value of $[R]_2$ (Table-2) have been calculated using refractive index data. These values vary too much with the salt-concentration below C.M.C. due to the existence of molecularly dispersed salt. When the concentration of the salt increases, the size of the micelle also increases but after a certain concentration there is no further interaciton so that the values of $[R]_2$ do not vary appreciably. It is observed that the value of $[R]_2$ is higher for calcium salt than sodium salt.

ACKNOWLEDGEMENT

The author would like to thank Prof. K.N. Mehrotra for his help and support and the college authorities for providing laboratory facilities.

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(*Received*: 12 May 1999; *Accepted*: 28 July 1999) AJC-1814