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DIFFERENTIAL THERMAL ANALYSIS AND PHYSICO-CHEMICAL PROPERTIES OF RUBIDIUM SOAPS IN ALKANOLS

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ABSTRACT

Rubidium soaps (caprylate, caprate) exhibit exotherm and endotherm through differential thermal analysis. The Exotherm and endotherm indicate the crystallization, melting and decomposition states of these soaps ie there exist three temperatures, temperature of crystallization, melting and decomposition. The adsorption excess and surface area covered by 1 g mole micelle for Rubidium soaps in alkanols (methanol, butanol and pentanol) (3.75, 3.86); (4.46, 4.56); (5.62, 5.70)10^{-10} cm ^{2} is calculated using Gibb's adsorption equation. The difference in parachor of soap and solvent, P (soap-solven) K_1 and that of solvent K_2 is determined from Hammic and Andrews' equation.

KEYWORDS: Exotherm, adsorption, endotherm, soaps, crytallisation, melting, decomposition.

INTRODUCTION

Metallic soaps with amphiphilic nature, fundamental importance to investigate these and prove useful in industry, agriculture and medicine as catalyst, inhibitor, fungicide, pesticide, preservative of wood, metallurgical process, greases, intended to improve flow, coating smoothness and thus possess indelible position for human culture.

Mesophase and glass formation in binary systems of caesium and alkali-earth metal butyrates was investigated.[1] Phase diagram of mesogenic binary system of cobalt (II) and univalent metal octanoates was studied.[2] The phase behavior of lithium stearate in cetane and in decalin was investigated.[3] Differential thermal analysis of metal soaps was carried out.[4]

Mesophase and glass formation in binary systems of thallium butyrate with magnesium, calcium or zinc butyrate was investigated.[5]

The criticle micelle concentration (CMC), colloidal nature and other parameters of metallic soaps are influenced by the nature of solvent[6-10], using Szyskowski's empirical equation.

Dependence of CMC values upon the composition of the solvent mixtures and its relation with increasing chain length of the soap anion from surface tension data is reported.[11] In the present investigation we studied the occurrence of various phases of soaps through thermal effect and to ascertain the surface area covered by 1g mole of micelle and variation of parachor of soap with solvent.

MATERIAL AND METHOD

The chemicals of BDH/Analar were used in the experiment. The soaps were prepared, purified, dried and characterized as in article.[12] Differential thermal analysis was carried out on a Stantan thermobalancce using alumina as a reference material. The heating rate was 7.5^0 C /min. The reproducibility of the measurements was checked by repeating the measurements.

RESULTS AND DISCUSSION

The adsorption excess for Rubidium soaps is calculated using Gibb's adsorption equation. Hammic equation too is applied successfully. The results of surface tension can be interpreted easily by Szyszkowski's emprial equatioτn.

$\Upsilon = \Upsilon_0(1 + X L_n Y) - \Upsilon_0 X L_n C,$ _______________ 1

Differenciating equation 1, it gives, $d\Upsilon / dl_n C = - X \Upsilon_0$,

by substituting it in Gibb's adsorption equation, the adsorption excess, τ, (i-e the excess concentration of the solute per unit area of the surface) arrives as follow.

$\tau = -1/R T d\Upsilon/d L_n C = X \Upsilon_0 /RT$

Hence, the surface area, A, covered by the soap micelle formed by 1 g mol micelle of the soap is

$A = RT/X \Upsilon_0.$

The value of A has been calculated from the plot of ϒ vs log C.

The plot of Υ vs log C are characterized by an intersection of two straight lines correspond to CMC. Hence these equations have different values of A_1 and A_2

The approximate values of the surface area occupied by the micelle formed by 1 g mole of micelle of the soap in the solvent are recorded in Table 1.

Table 1: Surface area A 10^{-10} cm^2 from the plots **of Υ vs log C.**

Solvents	Name of the soaps	
	Caprylate	**Caprate**
Methanol	3.75	3.86
Butanol	4.46	4.56
Pentanol	5.62	5.70

The surface area covered by 1 g mole of micelle below CMC increases steadily with the increase in the chain length of soap as well as alcohol.

Parachor

The parachor P of solution is written as

$P = M \Upsilon^{1/4}/D = V \Upsilon^{1/4}$ ---------------------------- 1

Where M, D,V and Υ are respectively the molecular weight ,density, molar volume and surface tension of the solution

Using Hammic and Andrews[13] equation the parachor of the solution can be written as

$P = X P_{soap} + (1- X) P_{solvent}$ ------------------------------ 2

Where P, P_{soap} and $P_{solvent}$ represent parachor of the soap solution, soap and solvent respectively. X is the mole fraction of the soap in solution. The P_{soap} and $P_{solvent}$ are constant, equation 2 becomes as

$P = X [P_{soap} - P_{solvent}] + P_{solvent} = X K_1 + k_2$ --------------------------- 3

Where K_1 is equal to $[P_{soap} - P_{solvent}]$ and K_2 is equal to $P_{solvent}$.

Equation 1 and 2 give $P = V \Upsilon^{1/4} = X K_1 + K_2$

$V \Upsilon^{1/4} = X K_1 + K_2$ ------------------------------- 4

The graph between $\Upsilon^{1/4}$ against X should be linear. Differentiating equation (4)

$d(V \Upsilon^{1/4}) /dX = k_1$------------------------------5

Evidently, $d(V \Upsilon^{1/4}) /dX$ should be equal to K_1 ie $(P_{soap} - P_{solvent})$.

The values of K_1 have been calculated using equation (5) for soap solution. The values of K_1 have been compared with the values obtained graphically by plotting $\Upsilon^{1/4}$ against X_0. The results are given in Table 2. The parachor behavior may be represented by two linear equation having different values of constant, K_1 and K_2 below and above cmc respectively. It is observed that the calculated values of K_1 using equation 5 are in good agreement with the values obtained graphically. Hence Hammic and Andrew's[13] equation can be applied for the soap solutions.

Table 2: K_1 and K_2 from the graph of parachor and mole fraction of the soap.

Solvents	Name of the soaps			
	Caprylate		Caprate	
	K1	K2	K1	K2
Methanol	1266 I 825 II	88.1 I 88.7 II	1066.6I 695.4 II	88.3I 88.9II
Butanol	739.4 I 440 II	203.1 I 203.9 II	642.8 I 434.7II	203.0I 203.8
Pentanol	636 I 340.9 II	242.3 I 242.9 II	641.1 I 436.3II	242.4I 243.3 II

Differential thermal analysis

The results of differential thermal analysis of rubidium caprylate, caprate are shown in fig. 1 and corresponding endotherms and exotherms observed are tabulated in table 3. Endotherms and Exotherms of Rubidium soaps.

Table 3: Endotherm and Exotherm of Caprylate and Caprate.

	Caprylate	Caprate
Endotherms:	25 210m 375]b 390s]b 450d	45 215m 300s 350 450d

	Caprylate	Caprate
Exotherms:	15 c 270 400d 510	30 c 260 365d 510

m = melting, b = boiling, c = crystallisation, s =shoulder and d = decomposition

Caprylate

The exotherm at 15^0C in the differential thermal analysis curve of caprylate fig.1 indicates the crystallization of the soap and the endotherm at 210^0 C corresponds to the melting of the soap. The linear portion of the curve between 210^0C to 260^0 C shows that the temperature of the sample and furnace remain the same and the soap decomposes insignificantly during this range of temperature. The endotherm at 375^0 C along with the shoulder endotherm at 390^0C corresponds to the boiling of the soap. The exotherm at 400^0 C indicates the start of rapid decomposition of rubidium caprylate.

The thermogravimetric analysis of rubidium caprylate reveals that the loss in the weight of the soap is very small up to a temperature of 260^0 C and this is in complete agreement with the linear portion of the cure of differential thermal analysis of the soap fig. 1. The TGA studies show that the loss in weight of the soap is insignificant up to 260^0 C, increases slowly between 260^0 C and 400^0 C, then very rapidly up to 560^0 C and finally shows slow change with further increase in temperature. The results show that the decomposition of the soap also take place along with the boiling ofthe soap. It is also observed that a white crystalline substanc is condensed on the cold part of tube containing the soap surrounded by an inert atmosphere and it is identified as caprylate.

Caprate

The exotherm at 30^0 C in the curve of DTA (differential thermal analysis) of caprate fig .1 reveals the crystallization of the soap.The endotherm at 215^0 C corresponds to the melting of the soap. The linear portion of the DTA curve between 215^0C to 280^0 C shows that the temperature of the sample and furnace remains the same and the loss in weight of the soap is insignificant during this range of temperature. and the soap decomposes insignificantly during this range of temperature. The endotherm at 350^0 C along with the shoulder endotherm at 300^0C corresponds to the boiling of the soap. The exotherm at 400^0 C indicates the start of rapid decomposition of rubidium caprylate. The start of decomposition of soap is indicated by an exotherm at 360^0 C.

The thermogravimetric analysis of rubidium caprate reveals that the loss in the weight of the sample is very small up to a temperature of 220^0 C and remains almost constant between 160^0C to 220^0 C .The results are in complete agreement with the linear portion of the cure of DTA differential thermal analysis of the rubidium caprate fig1. The TGA studies show that the loss in weight of the soap is insignificant up to 220^0 C, increases slowly between 220^0 C and 460^0 C, then very rapidly up to 540^0 C and finally shows no change with further increase in temperature .The results show that the decomposition of the soap also take place alongwith the boiling of the soap. It is also observed that a white crystalline substance is condensed on the cold part of tube containing the soap surrounded by an inert atmosphere and it is identified as caprate.

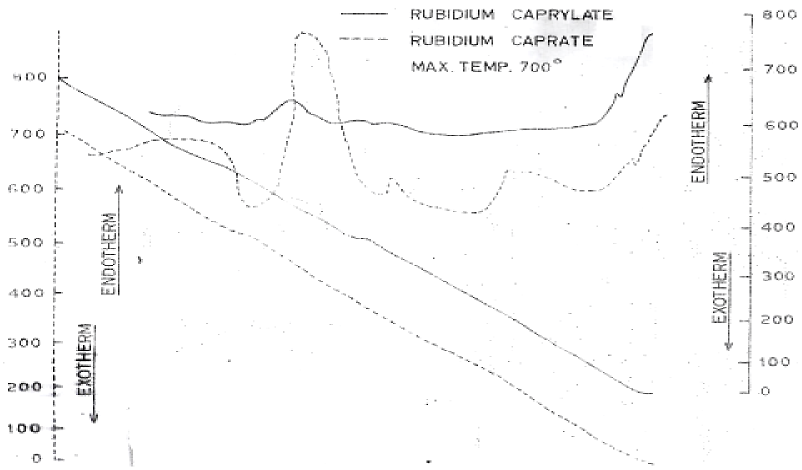

Fig 1: Differential thermal analysis of Rb caprylate and caprate.

CONCLUSION

Differential thermal analysis reveals about the existence of three temperatures, temperature of crystallization, melting of soaps and their decomposition provide the information about their structure. The colloidal chemical nature of the soaps in alkanols at particular concentration ie the occurrence of CMC is revealed by Szyszkowski's emprial equation which is in conformation obtained from other physical properties and surface area covered by this micelle is obtained by Gibb's adsorption equation which is independent to the nature of soap but depends on the nature of solvent. These soaps are of importance for industry, cosmetics and other areas. Hasmmic and Andrewes' equation can be applied successfully to find the variation of parachor of soaps with that of solvent.

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REFERENCES

1. Mirnaya T A, Dradrah V S, Yaremch G G, Mesophase and glass formation in binary systems of caesium and alkali-Earth metal butyrates, Zeitschrift für Naturforschung A, Journal of Physical Sciences, Dec 1999; 54(12): 685-688.
2. Tokmenko Inna I, Miranaya Tatyana A, Yaemchuk Galina G, studied phase diagram of mesogenic binary system of cobalt (II) and univalent metal octanoates, Zeitschrift für Naturforschung A**,** Journal of Physical Sciences, 2011; 66(10-11): 661–667.

3. Vold M J, Vold R D, the phase behavior of lithium stearate in cetane and in decalin was investigated, Journal of colloid science, February 1950; 5(1): 1-19.
4. Hattiangdi G S, Vold M J, Vold R D, Differential thermal analysis of metal soaps, Ind. Eng. Chem., 1949; 41(10): 2320–2324.
5. Mirnaya, T A, et al. "mesophase and glass formation in binary systems of thallium butyrate with magnesium, calcium or zinc butyrate, Russian journal of inorganic chemistry, 1999; 44.5: 775-778.
6. Verma H S and Kumar V, Studies on Surface Tension of Titanium(III) Soaps in Mixed Organic Solvents, Asian Journal of Chemistry, 2008; 20(3): 2445-2450.
7. Varma R P, Singh K and Singh H, studies on surface–tension of manganese soap solutions in organic solvents, Polish journal of chemistry, 1981; 55.5: 1115-1120.
8. Mehrotra K N , Mehta V P and Nagar T N, Studies on surface tension and parachor of copper soap solutions in nonaqueous solvents, J Am Oil Chem Soc, 1970; 47: 329.
9. Mehta V P, Telesara P R, sharma R, Gangwal A and Bhutra R, Surface tension studies of ternary system copper soap plus benzene plus methanol at 313 K, Indian journal of chemistry, 2002; 41A: 1173-1176.
10. Varma R P and Singh H, studies on surface –tension of the system-manganese soaps,1-butanol and para -xylene Annalidi Chimica, 1979; 69(1-2): 1-7.
11. Das D , Surface Tension and parachor studies of lithium soaps in non aqueous media at 313K Int. J. Chem. Sci., 2012; 10(1): 429-436.
12. Mehrotra K N and Saroha S P S, studies on infra red spectra and thermal analysis of rubidium soaps J.Indian Chem.Soc.,1979; VI: 466-469.
13. Hammic D I and Andrews L W, J Chem. Soc., 1929; 754.