Original Research Paper

A Study on PH and Solubility of Aqueous Copper, Zinc, Silver and Cadmium Dodecylsulphates
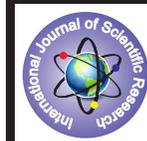
Chemistry

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ABSTRACT

The present study deals with pH and solubility of aqueous solutions of copper, zinc, silver and cadmium dodecylsulphates. pH of the aqueous solutions was measured at 40 ⬜ 0.05°C, whereas solubility of these solutions studied at 30°-50°C. pH measurement was used to evaluate hydrolysis constant, K_H, ionization constant of base, K_b and degree of hydrolysis, X. The results were indicative of the fact that these compounds hydrolyze considerably at the lower concentrations (pre-micellar region). The hydrolysis was however subdued as the concentration of compounds increases and becomes almost negligible in the vicinity of critical micelle concentration, cmc.

The solubility of these compounds was found to increase with increasing temperature and varies as Cu(II)DS > Zn(II)DS > Cd(II)DS > Ag(I)DS. The plots of logarithm of solubility vs. inverse of absolute temperature (log S vs. 1/T) show an intersection nearly at 40°C, the temperature indicating a common Krafft point hinting the onset of micellization. The apparent heat of solution, ⬜Hsol. and entropy of solution, ⬜Ssol. were also computed.

INTRODUCTION

The pH of sodium laurate is determined by Eagland and Franks (1) to ascertain the cmc. The pH is also employed (2) to find out the cmc of magnesium soap in water and methanol. Solubility and pH behaviour of aqueous tetra alkyl ammonium halides have been probed (3). An integrated study on solubility, solubilization and pH of aqueous transition metal dodecylsulphates has been made by Kumar, A. et al. (4). The values of cmc of the compounds under investigation have been reported (5). Mehta et al. (6) carried out investigation on electrometry of alkaline earth metal soap solutions i.e. anionic surfactants and it was pointed out that the cmc's determined by emf method were close to those determined by pH measurements.

Therefore the present investigation on pH and solubility of aqueous dodecylsulphates has been initiated with a view to study different aspects of their solution behaviour.

EXPERIMENTAL
MATERIALS

As the dodecylsulphates of Cu, Zn, Ag and Cd are not commercially available; These were prepared by refluxing the stoichiometric amounts of GR grade copper nitrate/zinc oxide/silver nitrate/cadmium nitrate with sodium dodecylsulphate in toluene for about 5-6 hrs. The coloured compounds thus synthesized washed with benzene-methanol solvent mixture. Well dried compounds were repurified by recrystallisation technique. The crystalline greenish blue copper, brownish black silver, pale white cadmium and white zinc dodecylsulphates so obtained were found to decompose in the vicinity of 250°C (observed by thermal analysis) and the structure of the purified products was ascertained using physicochemical techniques like elemental analysis and infrared spectroscopy. The percentage CHNS data support the proposed structural formulae of transition metal dodecylsulphates.The similarity of the infrared spectra of sodium dodecyl and transition metal dodecylsulphates makes it not unrealistic to expect that this staggered structure also occurs in the transition metal dodecylsulphates.

METHODS

The pH values of salt solutions were determined with a pH-meter (Systronics, pH-meter 324) using combined glass and calomel electrodes in a thermostatically controlled bath at 40° ± 0.05°C. The asymmetric potential was adjusted by buffer solution of pH 9.2 obtained from B.D.H. The accuracy of the results was further checked by determining the pH of the standard solutions.

To measure solubility of aqueous transition metal (Cu, Zn, Ag and Cd) dodecylsulphates at different temperatures (30 - 50°C, the saturated solutions of the compounds were prepared by vigorous shaking of the excess compounds in distilled water (taken in 25 ml stoppered wide mouth bottles, also known as gravity bottles, kept in a thermostatic bath). Clear supernatant saturated solution was taken out as the equilibrium approached (after almost ½ hr). The time taken for equilibrium, as mentioned to be almost in the vicinity of ½ hour, for the surfactant systems of aqueous transition metal dodecylsulphates was cited based on our observation (4) with these systems pursued by some other researchers in our laboratory.

RESULTS AND DISCUSSION
pH Measurements:

The data on pH of the aqueous solutions of transition metal (copper, zinc, silver, cadmium) dodecylsulphates are recorded in tables 1 and 2. The plots of pH vs. concentration (pH-C) used to show a rapid fall in pH upto cmc (fig. 1) and the change is not much appreciable beyond the cmc.
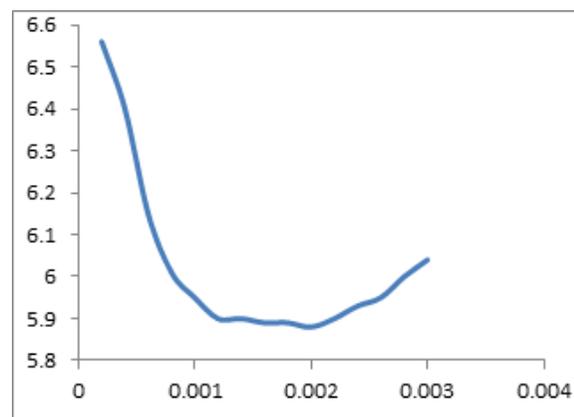

Fig 1- The Plot of pH vs. concentration, C (moldm⁻³) for Cadmium dodecylsulphates at 400C.

The data on cmc (Table 3) as deduced from the plots of specific conductance, k as a function of concentration, C (5) exhibit an intersection of two straight lines (cmc point) indicating the onset of micellization. The data (Table 3) taken from our earlier study (5) also suggest that cmc is found to increase with increasing temperature and concentration. The pH and solubility methods however do not furnish sharp changes at cmc as pH-C and solubility-C plots are

known to give a parabola so the exact values of cmc's were determined by conductivity method (5).

The transition metal dodecylsulphates may be represented by a condensed formula, (C12H25SO4)2 M and C12H25SO4M. Here, M refers to copper, zinc, cadmium in the former case and silver in the latter case. The compounds may be shown to hydrolyze as under,

$$(C_{12}H_{25}SO_4)_2\ M + 2\ H_2O \rightleftharpoons M\ (OH)_2 + 2C_{12}H_{25}SO_4\ H$$

(M = Cu, Zn, Cd)   (Weak base) (Acidic moiety)

$$C_{12}H_{25}SO_4\ M + H_2O \rightleftharpoons M\ OH + C_{12}H_{25}SO_4\ H$$

(M =Ag)   (Weak base) (Acidic moiety)
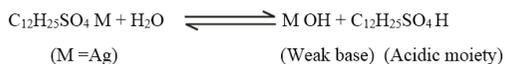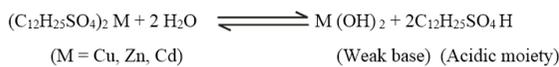
The expression $pH = 7 - \frac{1}{2}pk_b - \frac{1}{2}\log C$ was used to compute the

dissociation constant (Kb) of the weak base. The hydrolysis constant, KH (KH = KW/Kb) and degree of hydrolysis, X {X = √(Kh/C)} of these aqueous solutions are also evaluated (Tables 1, 2). The degree of hydrolysis (X) is found to decrease with increasing surfactant concentration upto cmc and variation is negligible for post micellar region.. The parameters (Tables 1, 2) are suggestive of the fact that hydrolysis of transition metal dodecylsulphates occurs mainly at lower concentrations (premicellar region) whereas the hydrolysis gets subdued as the concentration increases and becomes almost negligible in the vicinity of cmc.

Solubility Measurement:
The solubility of aqueous solutions of transition metal dodecylsulphates (Table 4) has been measured at different temperatures (30 – 500C). The solubility of these compounds in water is found to increase with increasing temperature (endothermic dissolution). The variation of solubility for different compounds is observed as : Cu(II)DS > Zn(II)DS > Cd(II)DS > Ag(I)DS. It is however noticeable that logS vs. 1/T plots (fig 2) for all the compounds show an intersection nearly at 400C, indicating a common Kraft point beyond which the onset of micellization occurs.
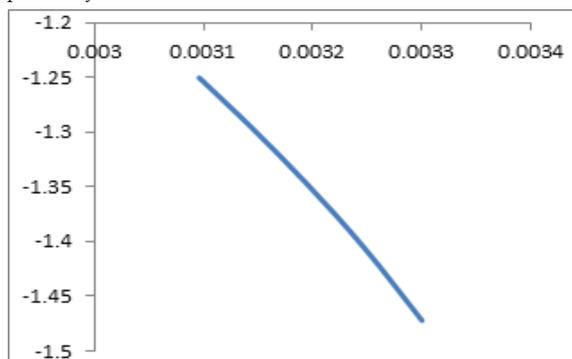
Fig 2: The Plot of log S vs. 1/T of Copper dodecylsulphates at different temperatures (30-500C).
The following Van't Hoff's reaction isochore expression has been used to compute the apparent heat of solutions, ΔHsol

as
$$\Delta H_{sol} = RT^2\left[\frac{d\ln s}{dt}\right]$$

Here, 's' is the solubility in mol dm–3 whereas other terms carry usual significance. Different values of below and above the Krafft point (Table 5) also confirm micellization

$$\Delta S_{sol} = RT^2\left[\frac{\Delta H_{sol}}{T}\right]$$

ls in water. Positive enthalpy (Table – 5) (below and above the Krafft point) also dothermic dissolution. The expression, , is used to evaluate the change in entropy (Table – 5) for the dissolution process. The mixing of singly dispersed molecules below cmc is completely random in analogy to normal solutions. On the contrary, micelle formation involves complete orientation and non-mixing of solvents with compound and micelle core. The results have been supported by positive entropy change for dissolution, ΔSsol (Table-5) for these systems. It may thus be stated that the solubility of these compounds differ from those of simple substances in as much as the polar solvent penetrates into their polar end groups and the lattice approaches its maximum degree of disorder at higher temperatures. This results in swelling and finally dissolution of the molecules in a polar solvent. In the above expression it has been assumed that the process of dissolution of these compounds is an isothermal equilibrium process and so the free energy change is zero. However the formations of micelles (micellization) and breaking off micelles (Dynamic Equilibrium) set in beyond the Krafft point i.e. at further elevated temperature (400C onward). Thus the positive entropy (below and above the Krafft point) may be attributed to the ongoing randomness observed both for pre- and post micellar regions. The degree of randomness may though be different for different regions (giving different positive ΔSsol for these regions).

Table-1: pH, ionization constant of base, Kb, hydrolysis constant, KH and degree of dissociation, X of copper and zinc dodecylsulphates at 40°C.

Conc. (mol dm⁻³)	CuDS				ZnDS			
	pH	$K_b \times 10^{-7}$	$K_H \times 10^{22}$	$X \times 10^9$	pH	$K_b \times 10^{-3}$	$K_H \times 10^{18}$	$X \times 10^8$
0.0002	5.02	4.56	2.19	1.05	6.82	11.45	0.87	6.61
0.0004	4.95	3.15	3.17	8.90	6.76	7.55	1.32	5.74
0.0006	4.85	3.32	3.01	7.08	6.71	6.34	1.58	5.13
0.0008	4.77	3.60	2.78	5.89	6.65	6.26	1.59	4.46
0.0010	4.70	3.98	2.52	5.02	6.60	6.31	1.58	3.97
0.0012	4.69	3.47	2.88	4.89	6.58	5.76	1.73	3.79
0.0014	4.69	2.98	3.36	4.89	6.58	4.94	2.02	3.79
0.0016	4.68	2.73	3.66	4.78	6.58	4.32	2.31	3.79
0.0018	4.70	2.21	4.52	5.01	6.59	3.67	2.72	3.88
0.0020	4.69	2.08	4.81	4.90	6.59	3.30	3.03	3.89
0.0022	4.68	1.98	5.05	4.79	6.60	2.87	3.48	3.98
0.0024	4.68	1.82	5.49	4.78	6.61	2.51	3.98	4.07
0.0026	4.74	1.27	7.87	5.50	6.65	1.93	5.18	4.40
0.0028	4.77	1.03	9.71	5.69	6.68	1.56	6.41	4.70
0.0030	4.84	0.69	14.49	6.95	6.70	1.33	7.52	5.00

Table-2: pH, ionization constant of base, Kb, hydrolysis constant, KH and degree of dissociation, X of silver and cadmium dodecylsulphates at 40°C.

Conc. (mol dm⁻³)	AgDS				CdDS			
	pH	$K_b \times 10^{-7}$	$K_H \times 10^{22}$	$X \times 10^{10}$	pH	$K_b \times 10^{-4}$	$K_H \times 10^{20}$	$X \times 10^9$
0.0002	5.33	1.09	9.17	20.00	6.56	3.79	26.40	36.30
0.0004	5.03	2.18	4.59	10.00	6.40	3.96	25.20	25.10
0.0006	4.89	4.19	2.39	6.31	6.15	8.35	12.00	14.00

0.0008	4.71	4.75	2.10	5.12	6.01	11.94	8.37	10.00
0.0010	4.67	4.57	2.19	4.68	5.95	12.60	7.94	8.00
0.0012	4.64	4.36	2.29	4.37	5.90	13.20	7.58	7.00
0.0014	4.65	3.57	2.80	4.47	5.90	11.30	8.85	7.05
0.0016	4.64	3.28	3.05	4.37	5.89	10.30	9.71	7.05
0.0018	4.64	2.92	3.42	4.36	5.89	9.20	10.87	7.04
0.0020	4.65	2.51	3.98	4.46	5.88	8.68	11.52	7.03
0.0022	4.64	2.38	4.20	4.37	5.90	7.20	13.89	7.08
0.0024	4.66	1.99	5.03	4.58	5.93	5.75	17.39	8.00
0.0026	4.69	1.60	6.25	4.90	5.95	4.84	20.66	8.00
0.0028	4.73	1.24	8.06	5.37	6.00	3.57	28.01	10.0
0.0030	4.79	0.88	11.36	6.15	6.04	2.77	36.10	10.10

Table– 3: The values of critical micelle concentration, cmc (mol dm-3) at different temperatures (30 – 50ºC).

Compounds	cmc (mol dm^{-3}) × 10^4				
	30ºC	35ºC	40ºC	45ºC	50ºC
CuDS	5.60	5.80	7.30	7.60	7.90
ZnDS	11.20	12.00	13.40	14.60	16.00
AgDS	13.25	13.40	13.60	13.65	14.30
CdDS	7.00	19.00	12.00	13.70	15.10

Table– 4 : Solubility data for transition metal dodecylsulphates in water at different temperatures (30 – 50ºC).

Compounds	Solubility (mol dm^{-3}) × 10^2				
	30ºC	35ºC	40ºC	45ºC	50ºC
CuDS	3.37	3.93	4.49	5.06	5.62
ZnDS	1.70	1.98	2.27	2.55	2.83
AgDS	0.54	0.63	0.72	0.81	0.90
CdDS	1.56	1.82	2.08	2.34	2.60

Table–5: Thermodynamic parameters of transition metal dodecylsulphates below and above the Krafft point (40ºC).

Compounds	ΔH_{sol}(KJmol^{-1})		ΔS_{sol}(JK^{-1}mol^{-1})			
	Below Krafft Point	Above Krafft Point	30ºC	35ºC	45ºC	50ºC
CuDS	21.49	19.79	70.91	69.76	62.23	61.26
ZnDS	21.85	19.34	72.08	70.91	60.78	59.83
AgDS	21.52	19.61	70.97	69.82	61.64	60.68
CdDS	21.54	19.59	71.06	69.91	61.58	60.62

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