Effect of Ovalbumin, Gelatin & Transfusion Gelatin on Micellization of Non-ionic Surfactants

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The lowering in critical micelle concentration of non-ionic surfactants has been observed in the order: ovalbumin > gelatin > transfusion gelatin. The results have been explained on the basis of electrostatic mechanism involving a weak positive charge due to oxonium ions on the micelles and negative charge sites on protein molecules.

THE effect of added salts[1-4], aliphatic alcohols[5-7], hydrocarbons[8-10] and of non-electrolytes[11-14] on micellization of surfactants has been extensively studied. The effect of added proteins, viz. ovalbumin, gelatin and transfusion gelatin, on the micellar behaviour of non-ionic surfactants, viz. Nonex 501, Nonidet P40 and Nonidet P42, has now been studied and the results reported in this note.

Nonex 501 (methoxy polyoxyethylated glycol laurate), Nonidet P40 (100% polyethylene oxide condensate) and Nonidet P42 (condensation product of dioctylphenol and ethylene oxide) were BDH products. Transfusion gelatin (TG) was obtained in the form of 6% isotonic saline solution from NCL, Poona. Ovalbumin was prepared in the laboratory according to the procedure of Sorensen and Hoyrup[15]. All solutions were prepared in doubly distilled water. The critical micelle concentration (c.m.c.) values of non-ionic surfactants alone as well as in the presence of varying amounts of proteins were determined by measuring surface tension at $25° \pm 0.1°$ by du Nouy's method.

The plots of surface tension (ovalbumin) versus log concentration (C in g/dl) of Nonidet P40 exhibit breaks which obviously correspond to the c.m.c. values of Nonidet P40. The c.m.c. values calculated from these breaks are given in Table 1. The c.m.c. values obtained similarly in the presence of other proteins are also given in Table 1. The sharp breaks in these plots representing the c.m.c. values become less pronounced as the concentration of the protein is increased. The breaks almost disappear when the [protein] is about 0.05 g/dl for ovalbumin and 0.1 g/dl for gelatin and transfusion gelatin. Obviously, at these concentrations, the c.m.c. values cannot precisely be deduced.

An examination of the c.m.c. values in Table 1 reveals that the values decrease in the presence of proteins. The lowering of the c.m.c. of non-ionic surfactant by added proteins is due to electrostatic mechanism involving a weak positive charge on the micelles and oppositely charged sites (negative) on protein molecules, in accordance with the observations of Klurschmit[16] and Hsiao et al.[17].

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Some Special Features of the Reaction Between Aluminium & Orthophosphate Ions

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Equilibrium pH titration curves of aluminium ions with orthophosphate ions suggest variscite to have the composition $AlPO_4.2H_2O$. This has been further confirmed by its IR spectrum. The titration curves also depict the existence of a new compound $Na_3Al(PO_4)_2$. IR spectra of strengite, mansfieldite and scordite show that position of lattice water in these minerals as well as in variscite is alike.

VARISCITE and strengite are the normal phosphates of Al^{3+} and Fe^{3+} with chemical composition corresponding to the formulae $AlPO_4.2H_2O$ and $FePO_4.2H_2O$ respectively. Assuming six coordination for Al^{3+}, Swenson et. al.[1] argued that $H_2PO_4^-$ replaces one water molecule from $[Al(H_2O)_4$-

TABLE 1 — c.m.c. Values of Non-ionic Surfactants in the Presence of Varying Amounts of Proteins

[Protein] g/dl	c.m.c. $\times 10^3$ (g/dl)		
	Nonidet P40	Nonidet P42	Nonex 501
0.0	13.26	37.59	5.62
OVALBUMIN			
0.01	11.42	31.60	5.01
0.02	9.44	26.60	4.73
0.05	—	—	—
GELATIN			
0.02	11.55	33.5	5.16
0.04	10.53	28.2	4.60
0.08	9.18	25.8	4.47
0.10	—	—	—
TRANSFUSION GELATIN			
0.02	12.23	34.47	5.31
0.04	11.22	30.73	4.87
0.08	10.00	28.20	4.73
0.10	—	—	—

$(OH)_2]^+$ ion to give variscite $[Al(H_2O)_3(H_2PO_4)(OH)_2]$. The coordinated water as given in this formula does not occur in variscite crystals and hence Cole and Jackson[2] suggested it can always be omitted. When a suspension of ferric hydroxide was mixed with soluble phosphate of similar pH, the pH of the mixture increased with the adsorption of phosphate. It was assumed[3] that OH^- ion from the hydroxide has been exchanged for $H_2PO_4^-$ giving strengite, $Fe(OH)_2H_2PO_4$, an analogue of variscite. From our experimental evidences variscite and strengite may be regarded as $MPO_4.2H_2O$ (M=Al, Fe).

To an aliquot of aqueous $0.01M$ $AlCl_3$ solution, taken in several Pyrex bottles increasing amounts of the sodium orthophosphate solution were added. The bottles were then stoppered and sealed. After a period of 24 hr, 3 months and 6 months, the pH of the contents of each bottle were measured with a Beckmann pH-meter (model H-2). From the data so obtained titration curves were constructed (Fig. 1).

The pH titration curve for solutions kept for 24 hr shows fall in pH in the initial stages of the reaction (Fig. 1, curve a), followed by a sharp inflection, where the normal aluminium phosphate is expected to be formed. Indeed a precipitate was thrown out, having composition similar to that of variscite. Even the X-ray powder patterns of precipitate and variscite were identical thereby revealing that two have identical structure.

The fall in pH is attributed to the assimilation of basic aluminium ions by the solid phase is an adsorptive process, and is not due to compound formation with definite stoichiometric relationship between the reactants.

pH titration curve obtained after three months (Fig. 1, curve b) represents the equilibrium titration
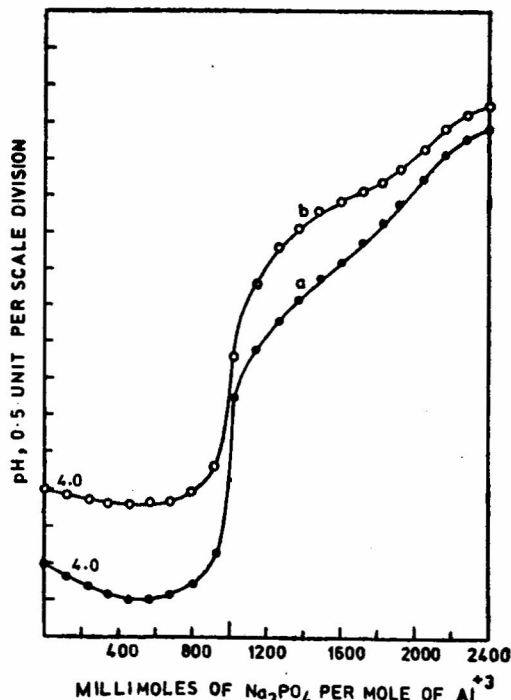

Fig. 1 — Potentiometric titration curves [Measurements made (a) 24 hr after the additions, (b) after 3 months. Initial pH is indicated on the curves]

because no further change in pH titration curve is observed even when measurements were made after 6 months. The fall in pH by 0.5 unit observed in curve a decreased to 0.2 unit in curve b. It is not difficult to see in terms of mechanism of the fall in pH previously described, when this fall decreased in a sufficiently long interval of time. On keeping the precipitate in contact with the mother liquor, the aluminium phosphate crystals 'ripen', i.e. their structure becomes better and still better organized. The main feature of this ripening process is a progressive removal of OH^- ions incorporated earlier into the solid phase and the replacement of these OH^- ions by PO_4^{3-} ions present in the mother liquor. The re-entry of OH^- ions in the solution phase raises its pH. The decrease in pH even in equilibrium titration curve is due to the fact that adsorptive process by the solid phase for the assimilation of basic aluminium ion will always be there.

In the pH titration curves a second inflection corresponding to two moles of orthophosphate is due to the formation of $Na_3Al(PO_4)_2$. This significant observation was missed by earlier workers.

Infrared* spectra (KBr) of variscite, mansfieldite, strengite and scordite were taken with a view to confirming the nature of water molecules. Variscite shows an intense absorption band at 1570 cm^{-1} which is absent in the dehydrated sample indicating the presence of lattice water[4]. Variscite does not show any band in the region 800-1000 cm^{-1}, ruling out the possibility of $[Al(OH)_2]^+$ in variscite. Hence the structural formula of variscite corresponds to $AlPO_4.2H_2O$ and not $Al(OH)_2H_2PO_4$ (Ref. 5 and 6). The fact that two molecules of water are readily[7] lost from variscite on heating at 110° is also in agreement with the formation $AlPO_4.2H_2O$.

These observations are in agreement with earlier reported work[7,8], where an orthorhombic crystal structure for variscite has been suggested with unit cell containing eight molecules of $AlPO_4.2H_2O$. Each Al^{3+} ion is octahedrally surrounded by four phosphate tetrahedra and two water oxygens.

IR spectra of other minerals also show a similar absorption band due to bending mode of lattice water[4] molecules around 1600 cm^{-1}. No absorption band was observed in the region 800-1000 cm^{-1}. Evidently the other three minerals strengite, mansfieldite and scordite have structural formulae $FePO_4.2H_2O$, $AlAsO_4.2H_2O$ and $FeAsO_4.2H_2O$ respectively. These observations are in agreement with that of Kelber and Weiner[8] who found that these minerals have a structure similar to variscite except that in the latter two cases octahedra is a little distorted.

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*Detailed IR spectra available from the author on request.

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Kinetic Evidence for Radical Anions in the Oxidation of p-Nitrotoluene & 2,4-Dinitrotoluene by Alkaline Hexacyanoferrate(III) in Aqueous Dimethyl Sulphoxide

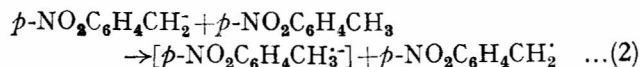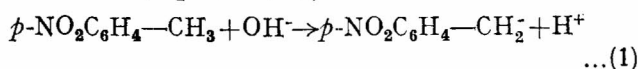P. S. RADHAKRISHNAMURTI & S. N. MAHAPATRO

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Stoichiometry in the oxidation of p-nitrotoluene by alkaline ferricyanide in aqueous DMSO is 1:3 under excess or low base concentration whereas in the case of 2,4-dinitrotoluene the stoichiometry is 1:1 in deficient base which becomes 1:2 in excess base. This has been rationalized on the basis of formation of radical ion in the case of p-nitrotoluene at all [base] whereas in the case of 2,4-dinitrotoluene only feeble [base] generates the radical ion.

RECENTLY we have reported the kinetics of oxidation of p-nitrotoluene in aqueous DMSO by alkaline ferricyanide[1]. We had explained the oxidation process as involving a rate determining abstraction of an electron from the carbanion formed in a fast step from p-nitrotoluene and the base. A thorough study of these reactions showed that the stoichiometry was 1:3 and not 1:6 (p-nitrotoluene: ferricyanide) as it should have been in the presence of excess oxidant.

This is a pointer to the fact that, in addition to the oxidation process which uses the carbanion that is formed, there is a parallel reaction of radical ion formation (Eqs. 1 and 2).

$$p\text{-}NO_2C_6H_4\text{---}CH_3 + OH^- \rightarrow p\text{-}NO_2C_6H_4\text{---}CH_2^- + H^+ \quad \ldots(1)$$

$$p\text{-}NO_2C_6H_4CH_2^- + p\text{-}NO_2C_6H_4CH_3$$
$$\rightarrow [p\text{-}NO_2C_6H_4CH_3^{\bar{\cdot}}] + p\text{-}NO_2C_6H_4CH_2^{\bar{\cdot}} \quad \ldots(2)$$

Due to this parallel reaction, the p-nitrotoluene species that is used for oxidation is about half that of the total concentration and the rest half being used for radical ion formation, whose concentration becomes constant after certain period.

Hence the overall stoichiometry of 1:3 is actually 1:6 when the used up concentration of p-nitrotoluene for oxidation is taken into account for stoichiometric computation. This is quite in conformity with the nature of ferricyanide as a one-electron oxidant.

Evidences for radical ion formation in basic systems have been well summarized by Russel and

Janzen[2]. The important point noted in the present investigation is even though an oxidant is present to react firmly with the carbanion there exists a parallel reaction of spontaneous breakdown of the carbanion into radical ion.

Another important point is that radical ions are stable in partially aqueous system for nitroaromatics even though the base is not so strong as in a non-aqueous system like t-butanol or t-butanol-DMSO.

According to Russel and Janzen[2] in the spontaneous disproportionation of p-nitrotoluene in basic solution, 50% of the initial p-nitrotoluene is recovered. This checks remarkably well with our finding that actually 50% of initial [p-nitrotoluene] is available for oxidation by ferricyanide while the rest is converted into radical anion.

We have confirmed the above reasoning by further experiments with 2,4-dinitrotoluene. The rate constants for 2,4-dinitrotoluenes at varying [substrate] and [base] are given in Tables 1 and 2. For purposes of comparison the rate constants reported for p-nitrotoluene oxidation are also included. The reactivity order is 2,4-dinitrotoluene > p-nitrotoluene which is quite plausible on the basis of acidity considerations. The reaction of 2,4-dinitrotoluene with ferricyanide is first order each in the substrate and in the oxidant. Dependence on [OH⁻] is unity. The stoichiometry with excess oxidant is 1:1 and the product is 2,4-dinitrobenzyl alcohol unlike p-nitrobenzoic acid in p-nitrotoluene oxidation. The stoichiometry for the single step of oxidation is 1:1, in consonance with our earlier work that the effective concentration of 2,4-dinitrotoluene for oxidation is just half the total concentration of 2,4-dinitrotoluene and the other half is converted

TABLE 1 — SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF 2,4-DINITROTOLUENE BY FERRICYANIDE

{Solvent: aq. DMSO (50%, v/v); [ferricyanide] = $0.0011M$; [KCl] = $0.025M$; [NaOH] = $0.002M$; temp. = 35°}

[Substrate] M	k_2 litre mole⁻¹ sec⁻¹
0.001267	0.1714
0.002417	0.1586
0.003297	0.1675
0.004548	0.1694

TABLE 2 — DEPENDENCE ON [OH⁻] IN THE OXIDATION OF 2,4-DINITROTOLUENE BY FERRICYANIDE

{Solvent: aq. DMSO (50%, v/v); [ferricyanide] = $0.0011M$; [substrate] = $0.0012M$; [KCl] = $0.025M$; temp. = 35°}

[NaOH] M	k_2 litre mole⁻¹ sec⁻¹
0.002	0.167
0.005	0.432
0.007	0.731
0.011	1.210

k_2 for the p-nitrotoluene oxidation by ferricyanide in 50% aq. DMSO, $0.1M$ NaOH at 45°C is 0.03834 litre mole⁻¹ sec⁻¹ (loc. cit.).