

EFFECT OF ELECTROLYTES ON NON - IONIC SURFACTANT MICELLES AT DIFFERENT TEMPERATURES

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ABSTRACT

The micelles size and intrinsic viscosity of a non - ionic surfactant composed of nonylphenol polyoxypropylene and polyethylene blocks (NPE-1800) were studied. The variables are temperature, nature and concentration of added electrolytes (KCl, K_2SO_4 , $NaNO_3$ and $MgCl_2 \cdot 6H_2O$). The size of the micelle decreases with increasing of temperature and concentration of electrolyte. Also, the polydispersity and the large size of the micelle influences the solution viscosity.

Keywords, Non-Ionic surfactants, Micelle, Electrolytes, Viscosity

INTRODUCTION

The effect of electrolytes on physicochemical characteristics of non-ionic surfactants have attracted the attention of many researchers [1,2].

Phenomenologically the explanation of the influence of electrolyte on the properties of the non-ionic surfactants must be sought in terms of specific ion binding and modification of the solvency by salt, termed as salting out or salting in . But , owing to electrostatic interactions between adsorbed components, the properties of anionic and cationic surfactant are dependent on the concentration and type of inorganic electrolyte present in solution [3, 4].

A hydrodynamic technique that can be applied to obtain information on the size and shape of the micelle is viscometry . The viscosity of a surfactant solution is sensitive to the size and shape of the micelles , since the average size of the micelle probably increases with increase of the micellar concentration [5].

In this paper the effect of different concentrations of various electrolytes on the viscosity and size of the micelle at different temperatures of a non-ionic surfactant namely nonylphenol- polypropylene polyethylene blocks have been studied.

MATERIALS AND METHODS

The general formula of the non-ionic surfactant is

nonylphenol- polypropylene polyethylene blocks (NPE - 1800). The complete analysis and structure of NPE - 1800 has been described elsewhere [6]. The electrolytes , KCl (Fischer Sci. Co.), K_2SO_4 , $MgCl_2 \cdot 6H_2O$, $NaNO_3$ and KNO_3 (BDH) , were of AR grade and used without further purification .

Viscosities were measured with an Ubbelohde suspended level dilution viscometer . Solutions were filtered prior to the measurements .

RESULTS AND DISCUSSIONS

Thermodynamics and hydrodynamics of large micelles:

For dilute surfactant solutions in which the intermicellar interaction are not important , the micelle size distribution is given by [7, 8]

$$x_g = x_1 \exp [- g (u_g^\circ - u_1^\circ)/kT] \quad (1)$$

Where x_g is the molefraction of micelles of size g , x_1 is the molefraction of the singly dispersed amphiphiles, u_g° is the standard chemical potential per surfactant, molecule incorporated into the micelle, u_1° is the standard chemical potential of the surfactant in water, k is the Boltzmann constant and T is the absolute temperature .

When the standard chemical potentials are such as

four cylindrical micelles and when the total surfactant concentration x is large compared to that of the single dispersed amphiphile x_1 , the size distribution equation has been simplified to [9].

$$x_g = (1/k) \exp[-g/k(x - x_{cmc})], g > g_s \quad (2)$$

$$\exp\{-g_s(u_c^0 - u_1^0)/kT\} / \exp\{-g_s u_s^0 - u_1^0/kT\} \quad (3)$$

$$x_{cmc} = \exp[-(u_c - u_1)/KT] \quad (4)$$

In equation (2-4) g_s is the aggregation number of the largest spherical micelle beyond which the addition of further amphiphiles gives rise to cylindrical micelles and u_c^0 is the standard chemical potential of a surfactant present in the largest spherical micelle respectively. The parameter K represents the relative preference for cylindrical micelles compared to the spherical one.

So, the difference in the standard chemical potentials $(u_c - u_1)$ could be calculated from equations (2-4). These values represent the change that occurs in the process of transferring a spherical micelle to a cylindrical one.

According to the size distribution of cylindrical micelles represented in equation (2), the dependence of the weight and number average of aggregation number of the micelle are:

$$g_w = g_s + 2 [K(x - x_{cmc})]^{1/2} \quad (5)$$

$$g_n = g_s + [K(x - x_{cmc})]^{1/2} \quad (6)$$

Equations (5, 6) show that the theoretically predicted polydispersity index g_w / g_n is large and tends to 2.

The axial ratio of a cylindrical micelle of aggregation number g and axial ratio (L/d) is

$$L/d = \left[\frac{(g v_o - 4/3 \pi L_o^3 / \pi L_o^2) + 2(L_o + \delta)}{2(L_o + \delta)} \right] \quad (7)$$

In equation (7), V_o and L_o are the volume and the length of the hydrocarbon tail of the amphiphile

respectively and δ is the effective length of the polar head group including adsorbed counterions and water of hydration. The smallest value is about 2.5 water molecules per ethylene oxide, may be significant in relation to the requirements of preventing secondary association [9]. Therefore in the present work the value of δ depends mainly on the length of the polyethylene oxide (about 40 units) and adding the length of solvation could be negligible compared to the total length of EO units.

The exact conformation of the oxyethylene chain length in NPE - 1800 micelle is not known. At the extremes, the chain might be fully extended, sometimes called the Zig-Zag conformation [10, 11] which would add about 14.4 nm for 40 oxyethylene units or it might form a random coil [12] (adding about 6.7 nm). A third conformation which has been suggested for the oxyethylene chain is the meander conformation [10], this would add about 0.18 nm. For simplicity, the value of 7.2 nm for the average length of oxyethylene chain has been taken in the present calculation.

The relative viscosity η_r of the cylindrical micellar solution can be computed using equation [13] (8)

$$\eta_r = 1 + v_c \phi + K_1(v_c \phi)^2 + K_2(v_c \phi)^3 \quad (8)$$

The subscript c on the shape factor (v_c) denotes the fact that the average micelle size g_w and, v_c depends on the total surfactant concentration.

The term $K_1(v_c \phi)^2$ accounts for the hydrodynamic interaction and the coefficient K_1 is estimated to be about (0.75) [13], While the term $K_2(v_c \phi)^3$ arises due to direct micelle to micelle interactions and will be neglected for dilute surfactant solution. The volume fraction ϕ of the micelles in solution can be calculated from the expressions.

$$\phi = (10/55.5 Ms) (C - C_{cmc}) (V_s/V_w) \quad (9)$$

Where V_s and V_w are the volumes of the surfactant and of the water molecule respectively. From liquid density one could calculate the volume of NPE - 1800 as 583.1 (nm)^3 and the water molecule as 3.0 (nm)^3 ; Ms , the molecular weight of the surfactant is taken as 3000.

The intrinsic viscosity $[\eta_c]$ is related to the shape

factor (v_c) by the expression

$$[\eta_c] = v_c \phi / (C - C_{cmc}) \quad (10)$$

Because of concentration dependence of the average micellar size (g_w) and the shape factor (v_c), the equation (10) can be alternatively expressed in term of intrinsic viscosity as

$$\eta_r = 1 + [\eta_c] (C - C_{cmc}) + 0.75 [\eta_c]^2 (C - C_{cmc})^2 \quad (11)$$

Calculation of $[\eta_c]$, g_w / g_s and K

The values of $[\eta_c]$, g_w/g_s and K have been calculated for NPE-1800 in aqueous and electrolytic solution over the temperature range 25 to 40 C. Some of these data are summarized in Tables (1a-d).

Table (1a). Values of ϕ , $[\eta_c]$, G_w / G_s and K for NPE - 1800 in presence of different concentration of $MgCl_2 \cdot 6H_2O$ at 25 °C ϕ = the volume fraction of the surfactant micelle, $[\eta_c]$ = the intrinsic viscosity, G_w/G_s = the aggregation number of cylindrical and spherical micelle and K = the relative preference for the cylindrical micelles compared to the spherical micelle.

Table (1 - a) , 1 M of $MgCl_2 \cdot 6H_2O$

Conc. g/dl.	ϕ	$[\eta_c]$	G_w / G_s	$K \times 10^{-9}$
2.4	0.0209	18.004	51.89	0.383
3.0	0.0261	15.394	44.76	0.227
4.2	0.0366	18.971	54.43	0.241
4.8	0.0418	17.430	50.36	0.180
5.4	0.0470	21.382	60.55	0.232

Table (1 - b) , 2 M of $MgCl_2 \cdot 6H_2O$

Conc.

Conc. g/dl.	ϕ	$[\eta_c]$	G_w / G_s	$K \times 10^{-9}$
2.4	0.0209	10.430	29.64	0.121
3.0	0.0261	10.739	30.66	0.104
3.6	0.0314	11.931	34.49	0.111
4.8	0.0418	11.548	33.28	0.771
5.4	0.0470	11.784	34.02	0.717

Table (1- c) , 3M of MgCl₂ . 6H₂O

Conc. g/dl.	ϕ	$[\eta_c]$	G_w / G_s	$\times 10^{-9}$
1.8	0.0157	10.457	29.73	0.163
3.0	0.0261	11.567	33.43	0.124
3.6	0.0314	12.043	43.83	0.113
4.2	0.0366	12.642	36.69	0.108
5.4	0.470	13.137	38.19	0.910

Table (1- d) , 3M of MgCl₂ . 6H₂O

Conc. g/dl.	ϕ	$[\eta_c]$	G_w / G_s	$K \times 10^{-9}$
2.4	0.0209	15.685	45.58	0.294
3.0	0.0261	15.412	44.81	0.227
3.6	0.0314	15.050	43.78	0.181
4.2	0.0366	14.824	43.14	0.150
4.8	0.0418	42.79	42.72	0.129

The stability of a non - ionic surfactant micelles in water arises from hydration that required to separate the micelles and prevent their aggregation . It is evident from Table (1a-d) and Figures (1, 2) that , the micelle size and K values decreases with increasing temperature and concentration of the electrolytes , KNO₃ , K₂SO₄, NaNO₃ . This trend is not unusual behaviour for micelle consist of non - ionic surfactant containing about 40 EO units .

Addition of an electrolyte tend to " Salt out" the amphiphile as well as the oil [14]. That is the hydrophilicity of the amphiphile seems to decrease and the system becomes sensitive to temperature.

The effect of increasing electrolyte concentration

and temperature are similar in this non-ionic surfactant system. Similar behaviour have been reported for the non-ionic surfactant Brij 35(C₁₂H₂₅(OCH₂CH₂)₂₃OH) in presence of NaCl [2].

The presence of salt in solution may cause a contraction of the hydrophilic part of the micelle and, as result, smaller micelles are formed . On other hand, a constant value K at all surfactant concentration implies that the treatment of cylindrical micelles as rigid rods agrees well with the two essential features of large micelles, namely, the dependence of the average micellar size on the square root of the concentration of micelles and the polydispersity of the micellar solution.

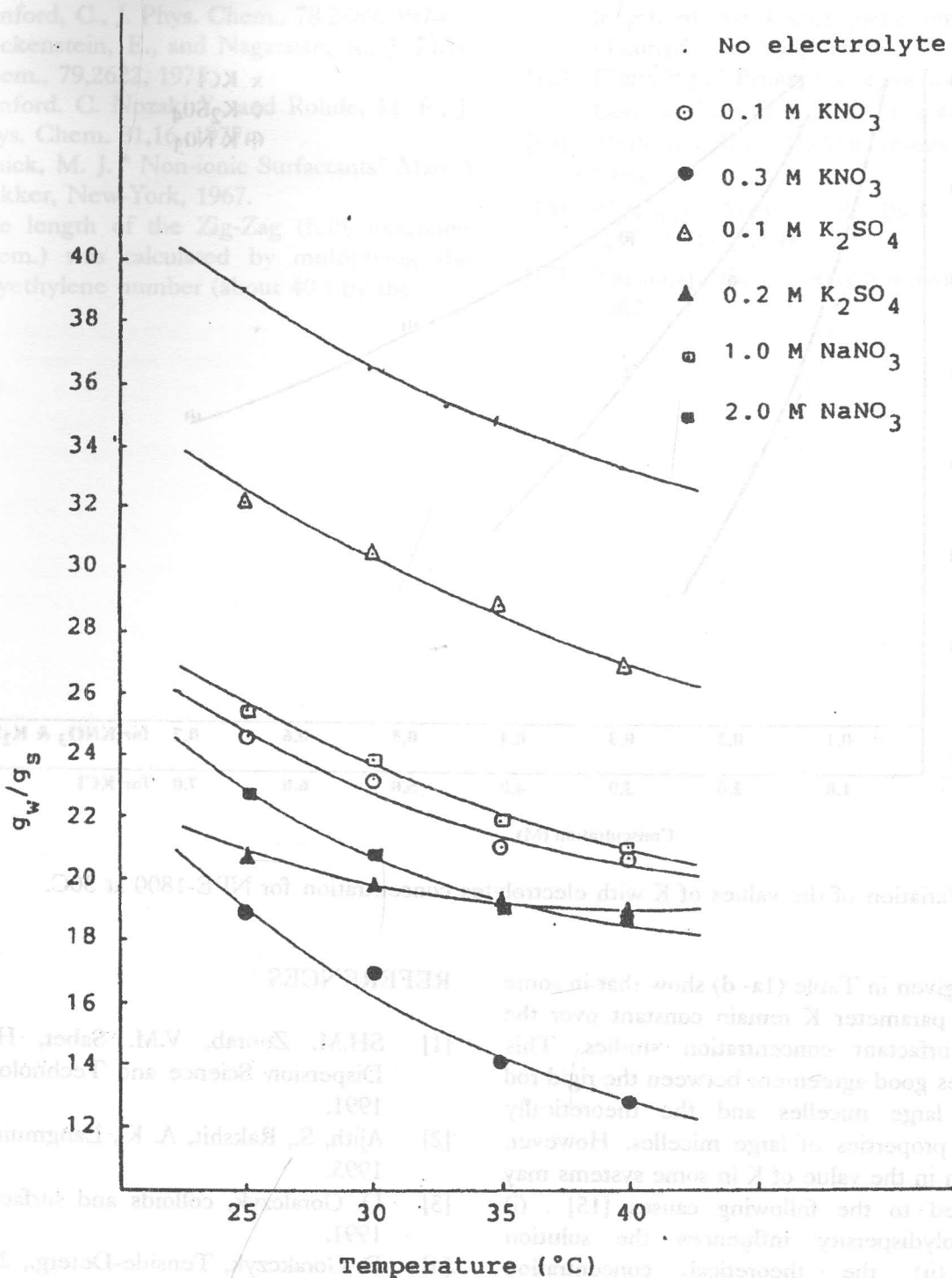


Figure 1. Variation of g_w/g_s with temperature for NPE-1800, in presence of different electrolytes.

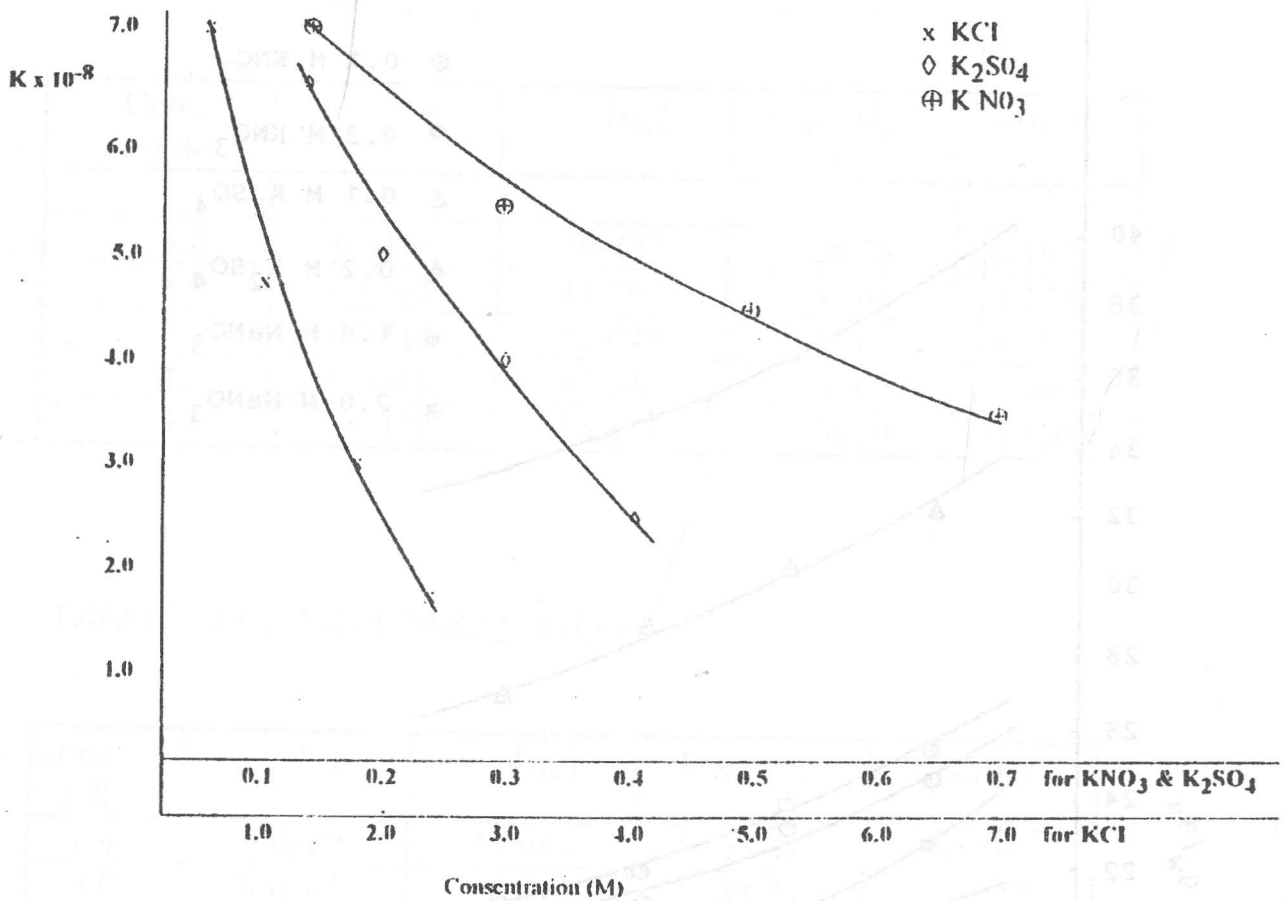


Figure 2. Variation of the values of K with electrolytes concentration for NPE-1800 at 30C.

The data given in Table (1a- d) show that in some system the parameter K remain constant over the range of surfactant concentration studies. This demonstrates good agreement between the rigid rod model for large micelles and the theoretically anticipated properties of large micelles. However, the variation in the value of K in some systems may be attributed to the following causes [15] . (i) micellar polydispersity influences the solution viscosity, (ii) the theoretical concentration dependence of the micellar size that given by equation [11] is altered to intermicellar interactions, and (iii) the large micelle are flexible and therefore the influence the solution viscosity differently compared to the rigid rods.

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The interval eigenvalue problem is considered for the interval matrix A and on the interval \mathbb{R} . The interval eigenvalue problem is also presented.

Keywords: Interval arithmetic, interval eigenvalue problem, interval matrix.

1. INTRODUCTION

When practical computational problems are solved, the answers should be "What is the error in the result". As already pointed out by Moore [34], the fundamental amount of the applied interval arithmetic is the interval arithmetic which can be used to bound the interval eigenvalue problem. The demands of the computer age are for more precise floating point arithmetic. Interval arithmetic is the result, supported by an interval arithmetic, which is used to bound the interval eigenvalue problem. The interval arithmetic is used to bound the interval eigenvalue problem.

Self-validating interval arithmetic methods are proposed as an approach, but also a guaranteed interval bound is used to bound the interval eigenvalue problem.

- i. An essentially error-free interval arithmetic accuracy, compared with an interval arithmetic competing algorithm, is an interval arithmetic newly developed algorithm.
- ii. The computed result has to satisfy some given accuracy requirements when it will be used in subsequent computations.

To obtain self-validating interval arithmetic methods, subject called *interval analysis* has emerged in the mid sixties (Moore [34]). This analysis uses interval numbers and interval arithmetics. Interval analysis is used in many areas of applied mathematics, such as solution of linear matrices.

Interval analysis is used to bound the interval eigenvalue problem.

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