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Micellar Properties of Tween – 80 in Aqueous Solutions of Poly (Ethylene) Glycols: An Ultra Sonic Study

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ABSTRACT

Densities (ρ) and sound velocities (U) of Polyoxyethylene (20) mono sorbitan oleate (Tween- 80) in aqueous solutions of four Poly (Ethylene) Glycols (PEGs) of different molecular weight 200, 400, 2000 and 4000 have been measured at 293 K using Pyknometer and Ultrasonic interferometer respectively. The experimental data of sound velocity have been used to calculate adiabatic compressibility (β) acoustic impedance (Z) and isentropic compressibility Φ_k respectively. The values of sound velocities in aqueous solutions of PEGs of different concentration have been utilized to explain the aggregation behavior of surfactant in terms of critical aggregation concentration (CAC) and polymer saturation concentration (PSP). A comperative study of these parameters for all the PEGs has been discussed in the light of polymer – saturation interactions.

Keywords: Polyoxyethylene (20) mono sorbitan oleate (Tween-80), Poly (Ethylene) Glycols, Adiabatic compressibility (β), Acoustic impedance (Z), Isentropic compressibility Φk

INTRODUCTION

Polyoxyethylene (20) mono sorbitan oleate (Tween 80) belong to the class of nonionic surfactant which is eco-friendly and biodegradable [1,2] having industrial and pharmaceutical applications. The aggregation and micellization is an important property of surfactants in any solutions [3]. The critical micelle concentration of surfactants is a measure of effectiveness in aqueous solutions and can be influenced by the presence of co-solute/solvents [4-6]. The presence of additives like polar, nonpolar, ionic or nonionic character, the solvent properties like density, dielectric constant and hydrogen bond formation capability influence the micellization in solution [7]. Water – glycol mixed solvents have been used to investigate the micellization behaviour of some surfactants [8-10].

Survey of literature reveals that many studies on the effect of an alcohol on micellization in solution have been carried out [11,12]. The organic solvents having properties resembling those of water like ethylene glycol and formamide have been widely used due to their strong polarity and miscibility with water [13]. These solvents share three physical characteristics high cohesive energy, high dielectric constant and hydrogen bond forming capability [14,15]. The ability to form hydrogen bonding is a necessary condition for the micellization process [16]. However, it has been shown that the unique structure of water, H – bonding is not necessary condition for aggregation process [17,18]. The micellization of surfactants sodium dodecyl sulphate, hexa decyl trimethyl ammonium bromide and poly oxyethylene (20) sorbitan mono oleate (Tween 80) have been studied in ethylene glycol water and formamide water mixed solvents using surface tension, viscosity and conductance measurement and results are compared with those reported in pure water [19]. Poly ethylene glycols (PEG) in aqueous solutions have been used as co – surfactant or plasticizers in the formulation industrial electrolyte, micro structural engineering [20], membrane selectivity [21], molecular selectivity [22] of protein and antibiotics [23]. PEG and PEG derivatives are used as humectants, solvents, binders, emulsion stabilizers and viscosity increasing agents [24]. In the last three decades the surfactant – polymer mixture have been the important compounds in many products like pharmaceuticals, cosmetics, detergents, emulsions etc. [25,26]. Surfactant in solutions in presence of polymer / additives have been extensively studied by viscometery [27], surface tension [28], conductivity [29], NMR spectroscopy [30], fluroscence spectroscopy [31], light scattering [32], neutron scattering [33] The participation of ethylene glycol in the micellar solvation layer has been indicated with its structure breaker nature [34].

In the present work the sound velocities in aqueous solutions of PEG 200, 400, 2000 and 4000 in different concentrations of Tween 80 have been experimentally measured. The ultrasonic study mainly aims at understanding the role of PEGs in the micellization of the surfactant.

EXPERIMENTAL SECTION

Materials

All the polyethylene glycols namely PEG 200, PEG 400, PEG 2000, and PEG 4000, were obtained from CDH India and used as received without further purification. The aqueous solutions were obtained by dissolving calculated amount by using average molecular weight in conductivity water. The Tween – 80 (LR) was obtained from S.d. fine chemicals ltd. India. The purity of the sample was checked by determining the cmc value from the surface tension measurement the solution of known concentration were always prepared fresh in conductivity water. The observed cmc values were in agreement with the reported cmc values of Tween 80 [35].

Measurements

A Pyknometer having U – Tube with a cylindrical bulb and two capillaries at two arms was used for the measurements of density. The volume of the Pyknometer was 5 ml. The weight of the Pyknometer was measured with the help of single pain electronic balance (C X 200 Citizen Scale. Co. Ltd. U.K.). The Pyknometer was filled with the experimental solution and weight was again measured with the help of single pain electronic balance. The densities of the solution were calculated from weight – volume ratio. The Ultrasonic interferometer model M – 81 S manufactured by Mittal Enterprises, New Delhi, having high frequency generator (1, 2, 3 and 4 MHz) with digital Vernier micrometer (LC 0.001 mm) controlled top assembly was used in the measurement of sound velocity. Sound velocity measurements are based on the measurement on wave length of wave in the medium. The ultrasonic waves of known frequency are produced by quartz plate at the bottom of the steal cell containing liquid. The wave reflected by a movable metallic plate kept parallel to the quartz plate. The acoustic resonance gives an electrical reaction on the generator and anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half of the wave lengths (λ/2) or multiple of it, anode current again becomes maximum. The sound velocities of the solution were calculated from the relation; Velocity (U, ms-1) = 2 × Wave length (λ) × Frequency (f).

RESULTS AND DISCUSSION

The velocities of sound in Tween 80 in aqueous solutions of PEGs (200, 400, 2000, and 4000) at different concentration have been summarized in Table 1. The values of sound velocities have been utilized to calculate the adiabatic compressibility (β) and acoustic impedance (Z) at different cmc of Tween 80 in aqueous PEGs solutions. The calculated values of acoustic parameters are also given in Table 1.

The variation of these parameters with concentration of Tween 80 has been utilized to obtain the critical aggregation concentration and polymer saturation point with the following facts:

The concentration at which decrease in sound velocity takes place, the solute – solvents interactions is strong which results the formation of micelles or aggregation. The concentration has been taken as critical aggregation concentration as CAC, in lower concentration region and PSP like cmc, in higher concentration region of Tween 80 [36]. The variations of sound velocity with concentration of the Tween 80 in aqueous solution of PEG (200, 400, 2000 and 4000) have been demonstrated in Figure 1. For all the PEGs the plots are nonlinear in nature which indicates the presence of dipole - induced dipole interactions are stronger than induced dipole - induced dipole attraction where linear plots are normally obtained [37].

Generally the interactions between water soluble polymers and surfactants takes place due to hydrophobic – hydrophilic interactions between the nonpolar / polar parts present in the molecules [38].

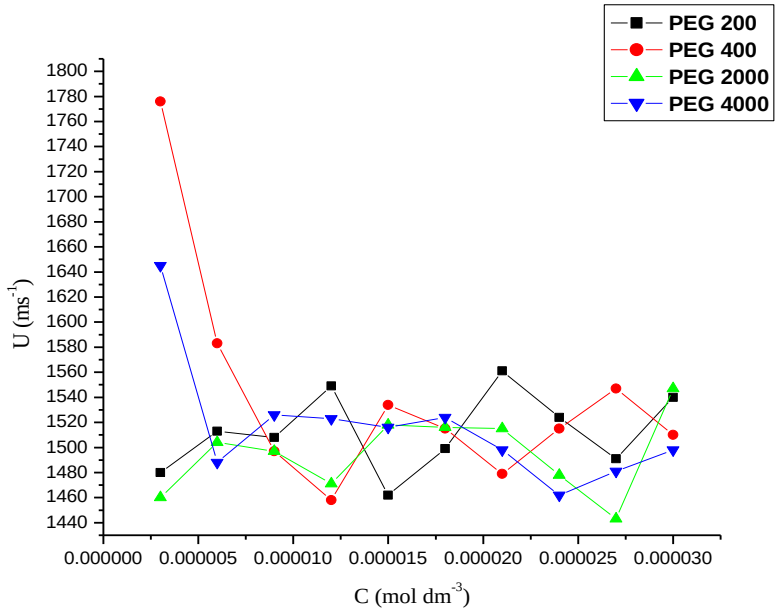

Figure 1: Plot of Sound velocity of Tween 80 verses concentration in aqueous PEG (200, 400, 2000, and 4000) at 293 K

The variation of acoustic impedance with concentration of Tween 80 is shown in Table 1. It also shows the same trend of association/micellization as observed from adiabatic compressibility data. The higher value of impedance at CAC and PSP further supports the micellization/aggregation at these concentrations of Tween 80.

It is recognized the adiabatic compressibility provide information about molecular interactions but the isentropic compressibility Φ_k also important for identification of interactions in solutions. The values of isentropic compressibility Φ_k were calculated for Tween 80 in aqueous solutions of PEGs by means of the Equation [39,40].

$$\phi_k = \frac{MK_s}{\rho} + \frac{1000(\rho_0 K_s - \rho K_{s0})}{C\rho_0}$$

Where, M is the molecular weight. ρ is density of a solution of is molarity C, of the solution and ρ_0 is density of pure solvent. The K_{s0} and K_s are the isentropic compressibility of the solvent and solution respectively. The vales of K_s is calculated from sound velocity data by using the relation $K_s=1000/\rho U^2$. The values of Φ_k are given in Table 1. The larger and negative value of Φ_k indicates the ionic nature of the compounds in water, positive for hydrophobic solute and intermediate, small and negative for uncharged hydrophilic solutes/nonionics solutes. These values shown in Table 1, confirms the micellization or aggregation obtained from the adiabatic compressibility, acoustic impedance and sound velocity. All the PEGs and Tween 80 are nonionic molecules hence the presence of electrostatic interactions is negligible. The PEGs molecule consist oxygen atoms having hydrophilic nature and CH_2-CH_2 groups having hydrophilic / lipophilic nature.

Table 1: ρ, U, β, and Z of different concentration of Tween – 80 with aqueous PEG 200 at 293 K

PEG	S. No.	CON. mol.dm^{-3}	(ρ) kg.m^{-3}	U ms^{-1}	Zx10^6 kgm^{-2}s^{-1}	β x 10^{-10} m^{2}N^{-1}	Φ_k Cm^3 mol^{-1}
200	1	0	1008.66	1544	1.557	4.16	-
0.2501 mol. dm^{-3}	2	0.000003	1010.58	1480	1.495	4.52	11.74
	3	0.000006	1012.00	1513	1.531	4.31	2.27
	4	0.000009	1010.08	1508	1.523	4.35	2.04
	5	0.000012	1013.34	1549	1.569	4.11	-0.58
	6	0.000015	1010.84	1462	1.477	4.63	3.00
	7	0.000018	1009.82	1499	1.513	4.41	1.31
	8	0.000021	1012.30	1561	1.580	4.05	-0.59
	9	0.000024	1011.77	1524	1.542	4.25	0.322
	10	0.000027	1011.24	1491	1.507	4.45	15.45
	11	0.000030	1010.14	1540	1.555	4.17	0.013
400	1	0	1010.84	1480	1.496	4.51	-

0.128 mol. dm^{-3}	2	0.000003	1006.76	1776	1.788	3.14	-45.06
	3	0.000006	1011.88	1583	1.601	3.94	-9.58
	4	0.000009	1011.46	1497	1.514	4.41	-1.14
	5	0.000012	1010.86	1458	1.473	4.65	1.14
	6	0.000015	1008.54	1534	1.547	4.21	-1.93
	7	0.000018	1005.78	1515	1.523	4.33	-2.53
	8	0.000021	1011.78	1479	1.496	4.52	0.028
	9	0.000024	1011.94	1515	1.533	4.30	-0.895
	10	0.000027	101212	1547	1.565	4.13	-14.28
	11	0.000030	1007.70	1510	1.521	4.35	-0.49
2000	1	0	1008.66	1544	1.557	4.16	-
0.02524 mol. dm^{-3}	2	0.000003	1010.58	1480	1.495	4.52	11.74
	3	0.000006	1012.00	1513	1.531	4.31	2.27
	4	0.000009	1010.08	1508	1.523	4.35	2.04
	5	0.000012	1013.34	1549	1.569	4.11	-0.58
	6	0.000015	1010.84	1462	1.477	4.63	3.00
	7	0.000018	1009.82	1499	1.513	4.41	1.31
	8	0.000021	1012.30	1561	1.580	4.05	-0.59
	9	0.000024	1011.77	1524	1.542	4.25	0.322
	10	0.000027	1011.24	1491	1.507	4.45	15.45
	11	0.000030	1010.14	1540	1.555	4.17	0.013
4000	1	0	1010.84	1480	1.496	4.51	-

0.0127 mol. dm^{-3}	2	0.000003	1006.76	1776	1.788	3.14	-45.06
	3	0.000006	1011.88	1583	1.601	3.94	-9.58
	4	0.000009	1011.46	1497	1.514	4.41	-1.14
	5	0.000012	1010.86	1458	1.473	4.65	1.14
	6	0.000015	1008.54	1534	1.547	4.21	-1.93
	7	0.000018	1005.78	1515	1.523	4.33	-2.53
	8	0.000021	1011.78	1479	1.496	4.52	0.028
	9	0.000024	1011.94	1515	1.533	4.30	-0.895
	10	0.000027	101212	1547	1.565	4.13	-14.28
	11	0.000030	1007.70	1510	1.521	4.35	-0.49

For Tween 80 the CAC and PSP concentrations have been observed from the adiabatic compressibility data shown in Table 2. The lesser magnitude of compressibility vales suggest the aggregation / micellization obtained by the compactness of various groups [39].

Table 2: The values of CAC and PSP for Tween 80 – PEG – water systems at 293 K

PEG	[PEG]	CAC	PSP
	(mol dm^{-3})	Mmol dm^{-3}	mmol dm^{-3}
200	0.2501	0.012	0.021
400	0.128	0.018	0.027
2000	0.02524	0.006	0.015
4000	0.0127	0.009	0.012

The aggregates values of CAC and PSP have been utilized to access the binding capacity for each PEG with poly ethylene glycol. The binding capacities for all the PEGs are summarized in Table 3 indicate that the binding capacities increase with increase in molecular weight of PEG. It may be said from these results that the PEG having more number of ethylene oxide unit has greater binding capacity. The binding capacity of ethylene oxide monomer has been calculated for each PEG which is (0.0085 ± 0.0015). These values are also given in Table 3. The free energy of micellization ΔG^0_m and free energy of aggregation associated with the process of micellization and aggregation/saturation have been evaluated by the Equation $\Delta G^0_x = RT \ln X$, where X is the mole fraction of CAC or PSP depending upon the process. The values of free energies for both the process are given in Table 3. All these values are negative indicates the spontaneous nature of both the process. The values of ΔG^0_m are greater than that of ΔG^0_a for all the PEG – water – Tween 80 systems. The aggregation process is stronger than the micellization or saturation process. From this it may be concluded that aggregate formation is spontaneous compared to saturation of micelle formation. The poly ethylene head groups of Tween 80 has tendency to solublize and stabilize by hydrogen bond formation via dipolar interaction in water [41].

Table 3: Values of ΔG^0_m, ΔG^0_a and binding capacity of Tween 80 –PEG

S. No.	PEG	ΔG^0_m KJ/mol^{-1}	ΔG^0_a KJ/mol^{-1}	Binding capacity (mmol) Tween/(mol) PEG	Binding capacity (mmol) Tween/EO monomer
1.	200	-21.26	-19.31	0.44	0.009
2.	400	-20.36	-18.77	0.093	0.010
3.	2000	-21.26	-19.18	0.47	0.010
4.	4000	-21.00	-19.45	0.70	0.007

CONCLUSION

On the basis of the results obtained for all four systems for PEG –water – Tween 80 the following conclusion can be drawn**.** In aqueous ethylene glycol solution the aggregation of Tween 80 takes place with the PEG molecules at lower concentration below its cmc in pure water which is mainly due to a decrease in solubility of surfactant tails. The value of ΔG^0_a and $\Delta,\wedge\#_m$ in all the PEG systems are less negative in comparison to the values in pure water reported in literature. This indicates less spontaneity for micelle formation in presence of PEGs. The addition of PEG favours the aggregation of micelles in aqueous solutions. The PEGs acts as a co-surfactant and structure forming solute. The structure forming solutes are known to increase the hydrophobic effect which is driving force for micellization / aggregation. Structure maker in aqueous solutions may arrange the dissolved hydrophobic groups and results the aggregation/micellization at lower concentration. The formation of pre-aggregates before the cmc justifies the nature of PEGs. The micellization / aggregation have been accessed by evaluating the binding capacity of PEGs and binding capacity of surfactant per monomer of ethylene oxide. A clear correlation of micellization and molecular mass of PEGs has been investigated. The micellization depends upon the number of monomers of poly ethylene oxide. The dependence of micellization/aggregation on monomer units of poly ethylene glycol have same nature of ionic and nonionic surfactant with different strength / magnitude depending upon the electrostatic interactions followed by ion – dipole interactions in case of ionic surfactants. In case of nonionic interactions the Vander Waal interactions between hydrophobic groups and hydrogen bonding tendency among constituent surfactants molecules. For the first time the dependence of micellization / aggregation on monomer unit of polymer has been presented to access the surfactant polymer interactions. The findings of the study reveal that the understanding of the polymer surfactant interactions on number of monomer unit would be useful in solution chemistry particularly in the field of green solvents.

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