

Density, Viscosity and Ultrasonic Velocity of Brij-35 in Presence of Water-Soluble Polymers

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Abstract: Density, viscosity and ultrasonic velocity of aqueous solutions of Brij-35 in presence of water-soluble polymers such as polyacrylic acid (PAA) and polyacrylamide (PAM) at different concentrations and temperatures (298.15, 303.13, 308.15 and 313.15) K. Different interaction parameters have been calculated using the experimental values of density, viscosity and ultrasonic velocity of aqueous solutions of pure Brij-35 and Brij-35 + PAA Brij-35 + PAM mixed system. The viscosity of surfactant solution increases with increasing concentration of PAA and PAM. The viscosity of Bri-35 solution was observed to more in presence of PAM. The ultrasonic velocity increases from 298.15 K to 308.15 K, then again decreases for 313.15 K. As the temperature increases, density, adiabatic compressibility and intermolecular free length decrease and ultrasonic velocities, acoustic impedance, molar volumes and molar sound velocities was observed to increases. The ultrasonic velocities initially increase then decreases with increasing concentration of PAA. For 0.03% PAA it shows maximum ultrasonic velocities.

Index Terms: Surfactants, Non-ionic surfactant Brij-35, acoustic parameter, polymer, polyacrylic acid, polyacrylamide

I. INTRODUCTION

Surfactants are among the most versatile materials appearing in diverse products such as motor oils, pharmaceuticals, detergents and petroleum and as flotation agents for beneficiation of ores. The last decade has seen the extension of surfactants applications to high-technology areas. Nonionic surfactants represent a major component material for applications ranging from personal care to a wide range of industrial uses. Structurally, nonionic surfactants combine uncharged hydrophilic and hydrophobic

group that make them effective in wetting, spreading and as emulsifiers and foaming agents. Concurrently, they have minimal skin and eye irritation effects and exhibit a wide range of critical secondary performance properties.

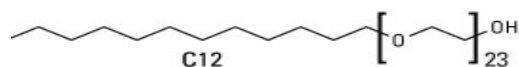
In the complex world of surfactants formulation today, the surfactant technologist needs to have worked knowledge of surfactant-additives mixing principles as per the application desired for. This includes an understanding of surfactant behaviors both in the end use domains as well as in the formulation domains.

Ultrasonic velocity technique is widely used to study the solution behavior of organic liquids, polymers, surfactants and their mixtures in aqueous and non-aqueous solutions. It plays an important role in understanding the physico-chemical behavior of liquids (Amrutia, R, et al.2006; Bhura, B.et al., 2011; Iqbal, M., et al.,2006). It is well known that surfactant molecules can organize themselves into aggregates when dissolved in water. The micelle formation takes place above CMC. The functions and properties of surfactant systems depend on their structure, concentrations, temperature, solvent and additives etc. The small addition of additives can improve the properties of surfactants (Patel, J., et al.,2004; Razavizadeh, B. M., et al.,2004). The non-ionic surfactant Brij-35 widely used in leather and textile industries, herbicides to increase the penetration power, oil dispersant, used in buffers for lysing cells and dissociating cell membrane without protein disruption. In this paper the effect of temperature and different concentration of additives on density, viscosity and ultrasonic velocity on Brij-35 has been studied.

II. MATERIAL AND METHODS

Non-Ionic Surfactants-Brij-35 was purchased from Loba Chemie, India. The Additives used are-Polymers-Water soluble polymer Polyacrylic acid (PAA) (Mol. Wt. 50,000) and Polyacrylamide (PAM) (Mol. Wt. 50, 00,000) was purchase from Otto Chemica India. Doubly distilled water was used for preparation of all solutions. Brij-35 solutions were prepared in 30% ethanol.

Brij-35



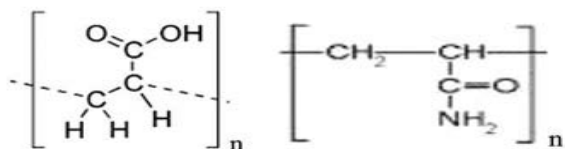
Polyoxyethylene (23) Lauryl Ether (Brij- 35)

Molecular Weight: 1199.57 g

Critical Micelle Concentration (CMC): 0.09 mM
(0.011 % W/V)

Cloud Point (CP): > 100°C

Additives- Polymers



Polyacrylic acid (PAA)

Polyacrylamide (PAM)

(Aver. Molecular Wt.50,000) (Aver. Molecular Wt.50, 00, 000)

III. EXPERIMENTAL METHODS

A. Ultrasonic velocity measurements

The interferometer cell was filled with the experimental solution and connected to output terminals of the high frequency generator through the shielded cable. Water was circulated around the measuring cell from a thermostat maintained at require temperature. When the solution in cell attains the temperature of bath, the micrometer screw was slowly moved till the anode current meter showed at maximum. The frequency 'F' of the crystal is accurately known. Here the frequency of the crystal is 2 MHz, the ultrasound velocity (U)was calculated by using following formula: $U = \lambda \times f$

The observed densities (ρ) and ultrasound velocity (U) were used to calculate the following thermodynamic properties (Xu, H., et al.,2005; Mehrotra, K. N., et al.,2002).

Adiabatic Compressibility	$(\beta_{ad}) = 1/\rho U^2$
Intermolecular free length	$(L_f) = K (\beta_{ad})^{1/2}$
Molar Sound Velocity	$(R_m) = (\bar{M}/\rho) U^{1/3}$
Specific Acoustic Impedance	$(Z) = (\rho U)$

$$\text{Molar Volume} \quad (V_m) = (\bar{M}/\rho)$$

$$\text{Surface Tension} \quad (\gamma) = (U^{3/2}) (6.3 \times 10^{-4}) \rho$$

Where U is the ultrasound velocity, ρ is the density; K is the Jacobson's temperature depended constant. M is the effective molecular weight and can be calculated using relation.

$$M = X_1 M_1 + X_2 M_2$$

Where M_1 and M_2 are molecular weights and X_1 and X_2 are the mole fractions of component-1 additive and component-2 surfactant solution as solvent.

IV. RESULT AND DISCUSSION

A. Density

The densities of Brij-35 (0.011%) were determined for different temperatures [Table 1]. It was observed that for a particular concentration solution, the density goes on decreasing with increasing temperature, because on increasing temperature, kinetic energy of particles, thermal agitation and volume of solution increases. The densities of Brij-35 (0.011%) in presence of PAA and PAM increases with increasing concentration of PAA and PAM. Increases in density with concentration indicate an increase in solvent-solvent and solute-solvent interactions and this may be due to shrinkage in volume owing to the presence of solute molecules.

B. Viscosity.

The viscosity of Brij-35 (0.0115%) in presence of different polymers carried out for various concentrations and temperatures [Table 2]. As the concentration of additives increases the viscosities of solution increases indicate stronger solute-solvent interaction due to alkyl side chain. The values of viscosities increase with concentration of additives and decreases with increasing temperature occur for all systems. According to "flickering cluster" model of water, there are large void spaces within the hydrogen bonded framework of the water structure, the molecules may have penetration into the void spaces and may have positive interaction with water. The increase in viscosity due to increase in ion size, orientation of polar molecules by the ionic field, since the freedom of movements of these molecules is restricted; this generally results in a stiffening of the solution (Bhattarai, A., et al.,2013; Chimankar, O. P., at al.,2010). Viscosity increases due to stronger hydrophilic and hydrophobic interactions in aqueous media the hydrophobic units of surfactant associate with each other forming hydrophobic domain, they play important role of intermolecular cross links which can lead to a significant increase in viscosity. The viscosity of surfactant solution increases with increasing concentration of PAA and PAM.

The viscosity of solution in presence of PAM is more than PAA due to its larger average molecular weight.

Table 1 Ultrasound velocities of pure Brij-35 (0.011 % w/v)

Temp. (K)	Density (ρ) Kg m^{-3}	Ultrasonic Velocity (U) ms $^{-1}$	Adiabatic Compressibility (β_{ad})x10 $^{-10}$ Kg $^{-1}$ ms 2	Intermolecular Free length (L_f) A $^\circ$	Acoustic Impedance (Z)x10 6 Kg m $^{-2}$ s $^{-1}$	Molar Vol. (V_m)x10 $^{-3}$ L.mol $^{-1}$	Molar Sound Velocity (R_M) x 10 $^{-4}$ mmol $^{-1}$ (N/m $^{1/2}$) $^{-1/3}$	Surface Tension (γ)x10 4 Nm $^{-1}$
298.15	997.9481	2248.00	1.9829	0.2769	2.2434	190.12812	2490.64	6.701
303.15	997.5540	2592.00	1.4921	0.2425	2.5857	190.20324	2612.74	8.293
308.15	997.1602	2720.00	1.3555	0.2333	2.7123	190.27835	2656.11	8.912
313.15	996.3736	2144.00	2.1834	0.2988	2.1362	190.42857	2455.50	6.232

Table 2 Viscosity of Brij-35 (0.011 % w/v) in presence of PAA/ PAM at various temperatures and concentrations

Conc. % W/v)	PAA				PAM			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.005	0.9806	0.8446	0.6584	0.6418	1.0670	1.0410	1.0233	0.9937
0.01	0.9698	0.8365	0.6553	0.6389	1.0786	1.0503	1.0287	1.0031
0.02	0.9636	0.8312	0.6530	0.6365	1.2451	1.0850	1.0639	1.0170
0.03	0.9542	0.8238	0.6461	0.6330	1.2558	1.0946	1.0738	1.0271
0.04	0.9492	0.8165	0.6431	0.6300	1.2601	1.1024	1.0859	1.0313
0.05	0.9420	0.8029	0.6403	0.6186	1.2693	1.2517	1.1106	1.0986

Table 3. Ultrasonic velocity of Brij-35 (0.011 % w/v) in presence of PAA at various temperatures and concentrations at 298.15 K

[PAA] %w/v	Density (ρ) Kg m^{-3}	Ultrasonic Velocity (U) ms $^{-1}$	Adiabatic Compressibility (β_{ad})x10 $^{-10}$ Kg $^{-1}$ ms 2	Intermolecular Free length (L_f) A $^\circ$	Acoustic Impedance (Z)x10 6 Kg m $^{-2}$ s $^{-1}$	Molar Volume (V_m)x10 $^{-3}$ L.mol $^{-1}$	Molar Sound Velocity (R_M) x 10 $^{-4}$ mmol $^{-1}$ (N/m $^{1/2}$) $^{-1/3}$
0.005	997.2609	1984.00	2.5475	0.3138	1.9786	128.71055	1617.32
0.01	997.7284	2036.00	2.4179	0.3057	2.0314	159.41012	2020.42
0.02	998.8302	2060.00	2.3592	0.3020	2.0576	189.96022	2417.05
0.03	999.5757	2444.00	1.6749	0.2545	2.4430	251.22459	3383.99
0.04	1000.1529	2132.00	2.1997	0.2916	2.1323	312.45023	4021.39
0.05	1000.9142	2096.00	2.2742	0.2965	2.0979	373.53651	4780.39

C. Ultrasonic measurement of Brij-35 (0.011%)

The ultrasonic velocities of Brij-35 (0.11%) were carried out for density, adiabatic compressibility and intermolecular free length decrease hence ultrasonic velocities, acoustic impedance, molar volumes and molar sound velocities increases.

different temperatures (Table1). The ultrasonic velocity increases density, adiabatic compressibility and intermolecular free length decrease hence ultrasonic velocities, acoustic impedance, molar volumes and molar sound velocities increases.

D. Ultrasonic measurement of Brij-35 (0.0115) in presence of PAA

For ultrasonic velocity measurement of Brij-35 + PAA mixed system the concentration of Brij-35 corresponding to its CMC is kept constant and varying the concentration of PAA at 298.15. The data presented in the Table No. 3. The ultrasonic velocities initially increase then decreases with increasing concentration of PAA. For 0.03% PAA it shows maximum ultrasonic velocities may be due to structural rearrangement as a result of hydration, it may be also due to the changes in geometry of the micelles. At higher ultrasonic velocities, the surfactant molecule aggregated to form large molecular cluster together by cohesive forces. The decrease in ultrasonic velocities with further increase in concentration of polymers due to the formation of strong hydrogen bonds which generally increases the inter proton distance between adjacent hydrogen bonds. At maximum value of ultrasonic velocity an aggregation of monomers to form micelles. The decrease in ultrasonic velocity may be due to the change in geometry of micelles. This interesting aspect closely linked to the well-known inter polymeric association reactions which occur between polyethylene oxide and poly carboxylic acids.

As the concentration of surfactant increases adiabatic compressibility (β_{ad}) decreases also support the solute and solvent interaction i.e., when ultrasonic velocity increases L_f and β_{ad} decreases and vice-versa showing inverse behavior according to Eyring and Kincaid model (Dixit, A., et al., 2014; Muraliji, D., et al., 2002). The decreases of L_f and β_{ad} values with increases in ultrasonic velocity reveals that, there is a significant interaction between PAA and surfactant affect structural arrangement in solution mixture suggest strong solute-solvent interaction with less close packing molecules. Since variation of β_{ad} elucidated as, the minimum compressibility leads to enhancement of bond strength while maximum compressibility indicates weaker bond strength of molecules and β_{ad} values increases due to removal of solvent molecules around ions supporting weak interaction. β_{ad} values decreases with increase in concentration of PAA.

The acoustic impedance increases with increase in

concentration of PAA can be attributed to effect of solute-solvent interaction (Mehra, R., 2005).

E. Ultrasonic measurement of Brij-35 (0.0115) in presence of PAM

For ultrasonic velocity measurement of Brij-35 and PAM mixed system the concentration of Brij-35 corresponding to its CMC is kept constant and varying the concentration of PAM and at 298.15. The data presented in the Table No. 4 for non-ionic surfactant + PAM mixed system shows that the ultrasonic velocities initially increase then decreases with increasing concentration of PAM. For 0.03% PAM it shows maximum ultrasonic velocities. The ultrasonic velocity of Brij-35 solution was more in presence of PAM than PAA. This may be due to higher average molecular weight of PAM and structural rearrangement as a result of hydration, it may be also due changes in free energy and the shape of the micelles changes from rod to spherical. At higher ultrasonic velocities, the surfactant molecule aggregated to form large molecular cluster together by cohesive forces. The decrease in ultrasonic velocities with further increase in concentration of polymers due to the formation of strong hydrogen bonds which generally increases the inter proton distance between adjacent hydrogen bonds. At maximum value of ultrasonic velocity an aggregation of monomers to form micelles. The decrease in ultrasonic velocity may be due the shape of the micelle's changes from rod to spherical. This interesting aspect closely linked to the well-known inter polymeric association reactions which occur between polyethylene oxide and poly carboxylic acids.

CONCLUSION

The density of Brij- 35 (0.011 % w/v) decreases with increase in temperatures, The density of surfactant solution increases with increase in concentration of water-soluble polymers. The density of solution in presence of PAM is more than density of solution in presence of PAA. Viscosity of Brij-35 (0.0115%) in presence of water-soluble polymers, such as PAA and PAM were studied at different concentrations. The values of viscosities increase with concentration of PAM and decreases with increasing concentration of PAA and with increasing temperature. The viscosity of solution in presence of PAM is more than PAA due to its larger average molecular weight. For Brij-35 (0.011%), as the temperature increases, density, adiabatic compressibility and intermolecular free length decrease hence and ultrasonic velocities, acoustic impedance, molar volumes and molar sound velocities increase. For 0.03% PAA and PAM it shows maximum ultrasonic velocities may be due to Structural rearrangement as a result of hydration,

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