MOLECULAR INTERACTION STUDIES OF SURFACTANTS IN NEEM OIL USING ULTRASONIC TECHNIQUE

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Abstract : Pesticides are substances or a mixture of substances, of chemical or biological origin, used by human society. Neem oil is a bio pesticide used by farmers to prevent the formation of pests in plants. It is hydrophobic in nature, for application purposes, it must be formulated with appropriate surfactants. In the present study neem oil is mixed with surfactants viz., sodium dodecyl sulphate (SDS) and cetyl-trimethyl ammonium bromide (CTAB). The density (ρ), viscosity (η) and ultrasonic velocity (U) have been measured for SDS and CTAB in neem oil at 303K. The experimental data have been used to estimate the adiabatic compressibility (β), molar hydration number (n_h), molal hydration number ($n_{h'}$), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their constants (S_k, S_v) and viscosity co-efficients A and B of Jones-Dole equation are found. The variation of these parameters with concentration of surfactant solutions have been discussed in terms of ion-ion, ion-solvent interactions.

***Keywords* - Ultrasonic velocity, adiabatic compressibility, hydration number, apparent molal compressibility, apparent molal volume.**

I. INTRODUCTION

In recent years, ultrasonic method has become a powerful tool in providing information regarding the physico-chemical properties of the liquid system [1, 2]. A large number of studies have been made on the intermolecular interaction in liquid system by various methods like Ultraviolet, dielectric constant, Infrared, Raman effect, Nuclear magnetic resonance and ultrasonic method. Few research workers have investigated the molecular interactions in soaps, oils and detergents [3]. Pesticides are substances meant for attracting, seducing and then destroying or mitigating any pest [4]. Bio pesticides are commonly target specific and affect only the target pest and closely related organisms. Neem oil is vegetable oil pressed from the fruits and seeds of neem [5-7].

In this research work, deliberate analyses were done with different surfactants in neem oil at 303K. The ultrasonic velocity data alone will not provide sufficient information about nature and types of interactions present in the solution. Hence their derived parameters such as adiabatic compressibility (β), molar hydration number (n_h), molal hydration number ($n_{h'}$), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their constants (S_k, S_v) and viscosity B co-efficient have been found to know about the various types of interactions between solute and solvent.

II. EXPERIMENTAL TECHNIQUE

The chemicals used in the present study are of AR grade (99% of purify) and hence used without further purification. Deionised water was used for the preparation of solutions. Solutions of surfactants at different concentrations were prepared by molarity scale using a Denver digital electrical balance with a precision of accuracy of ± 0.01 kg m^{-3}. A 10ml Ostwald's viscometer was used for the viscosity measurement. The ultrasonic velocity of solution has been measured using an ultrasonic interferometer

(Mittal Enterprises, New Delhi, Model F81) working at a fixed frequency of 2MHz. A digital electrically operated constant temperature bath (Raaga Industries, Chennai) was used to maintain the desired temperature. The accuracy of the measurement of temperature was $\pm$ 0.1° C. Using the measured values of density, viscosity and velocity of surfactants solutions, the compressibility, hydration parameters have been calculated using the standard relations,

1. Adiabatic compressibility $\beta = \frac{1}{U^2\rho}$

2. Molar hydration number $n_h = (\frac{1}{n_2})(n_1 - \frac{\beta N}{\beta_0})$

3. Molal hydration number $n_{h'} = \frac{n_1}{n_2}\,(1 - \frac{\beta}{\beta_0})$

4. Apparent molal compressibility $\phi_k = \frac{1000}{m\rho_0}\,(\rho_0\beta - \beta_0\rho) - (\frac{\beta_0 M}{\rho_0})$

where, β and β_0 are adiabatic compressibilities of solution and solvent. N denotes the number of solvent molecules. n_1 and n_2 are the number of moles of solvent and solute. ρ and ρ_0 are density of solution and solvent. M is the molecular weight of solute.

The apparent molal compressibility ϕ_k is the function of m as obtained by Gucker [8] from Debye Huckel theory [9] and is given by

$$\phi_k = \phi_k^0 + S_k\sqrt{m}$$

where ϕ_k^0 is the limiting apparent molal compressibility at infinite dilution and S_k is a constant.

5. Apparent molal volume $\phi_v = \frac{1000}{m\rho_0}\,(\rho_0 - \rho) + \frac{M}{\rho_0}$

The apparent molal volume ϕ_v has been found to differ with concentration. According to Masson's [10] empirical relation as,

$$\phi_v = \phi_v^0 + S_v\sqrt{m}$$

where ϕ_v^0 is the limiting apparent molal volume at infinite dilution and S_v is constant.

6. A and B coefficient (η)

The importance of viscometric study of electrolytic solution in mixed solvent is well established by M S. Chauhan et.al., in the year 2002 [11]. The entire viscosity data have been analysed in the light of Jones-Dole semi-emprical equation [12].

$$\frac{\eta}{\eta_0} = 1 + Am^{\frac{1}{2}} + Bm$$

where η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute-solvent system. A and B are constants which are distinct for a solute-solvent system. A - Falkenhagen coefficient which characterises the solute interaction and B is the Jones-Dole or viscosity B-coefficient which depends on the size of the solute and nature of solute-solvent interactions[13,14].

III. RESULTS AND DISCUSSION

The experimentally measured values of density (ρ), viscosity (η) and ultrasonic velocity (U) for different concentrations of aqueous surfactants viz, SDS and CTAB in neem oil are given in table 1. The values of adiabatic compressibility (β), molar hydration number (n_h), molal hydration number ($n_{h'}$) apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v) of surfactant solutions are presented in table 2. The limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their constants, A and B co-efficient of Jones-Dole equations are shown in table 3.

In the two systems, the density and ultrasonic velocity of the solutions increases with the addition of surfactants is noted except at (CMC) critical micelle concentration. This suggests that molecular interaction exists between surfactant and solvent molecules. The values of ultrasonic velocities are smaller in CTAB than SDS solutions. This may be due to weak molecular association between CTAB and neem oil. The increase in ultrasonic velocity values of SDS and CTAB in neem oil solution may be attributed to the overall increase of cohesion brought about by solute-solvent interaction in solutions. The hydrophilic end of surfactants interacts with water whereas hydrophobic end interact with neem oil. The addition of surfactant in neem oil will increase the cohesion between neem oil and hydrophobic part of surfactants. The cohesion increases with the increase of surfactant concentration in the solutions. The addition of surfactants will enhance the effectiveness of neem oil. It also increases in the order: CTAB < SDS.

From table 2, it was observed that the values of adiabatic compressibility (β) decreases with increase of surfactants to neem oil. The decrease in adiabatic compressibility is due to the increase in electrostriction compression of solvent around the surfactant molecules, which results in a large decrease in the compressibility of solution [15]. The sudden increase in β is noted at CMC of each surfactant. This may be due to the formation of the micelle in the solution. The increasing compressibility implies weak molecular association in the systems.

The process of attraction and association of water molecules with solute molecules is termed as hydration. The molar hydration number (n_h) is positive in SDS (0.01mM) and negative in CTAB (0.011mM). The positive values of increases the appreciable solvation of solutes [16]. This is also suggesting that the compressibility of the solution will be less than that of the solvent. Sudden fall in hydration number is observed at CMC. This may be due to micelle formation which will reduce the cohesion between solute and solvent. It is observed from the values of n_h of solutions that molecular association is greater in SDS than CTAB. The increasing behaviour of n_h predicts the strong interaction between solute and solvent molecules [17]. This indicates the hydrophobic- hydrophobic interactions occurring between hydrophobic part of surfactant and neem oil. The decreasing values of n_h forecasts that micelle aggregates are formed at that concentration called CMC. The increase in concentration of surfactants increases the number of micelles and also the free molecules of surfactants. The free molecules are responsible for the increase in n_h values after CMC.

The observation of ϕ_k and ϕ_v of surfactant solutions are noted as follows:

i. The value of ϕ_k for SDS solution is negative whereas for CTAB solution it is positive at 0.01mM and 0.011mM.

ii. The ϕ_k values are decreases with increasing concentration of surfactants. There is a steep increase in ϕ_k is found at CMC of surfactants. The negative value of ϕ_k in SDS and CTAB indicates ionic and hydrophobic interaction occurring in the systems [18]. The same behaviour was studies by pandey et.al, in the year 1987.

iii. The values of ϕ_v are positive for the entire range of molarities observed in the two systems. ϕ_v values are decreases with the addition of SDS and CTAB. There is a rise in ϕ_v value is observed at 0.011mM afterwards it decreases with concentration. This indicates the existence of strong ion-ion interactions.

iv. From the values of ϕ_v, it can be conclude that, strong molecular association is found in SDS solution than CTAB.

The limiting apparent molal compressibility ϕ_k^0 and related constant S_k have been computed for different surfactant solutions, using least square method. The ϕ_k^0 value is positive for SDS and negative value for CTAB. The value of ϕ_k^0 is maximum in SDS indicate the existance of solute-solvent interaction. The negative values of ϕ_k^0 shows the existence of strong ion-solvent interaction in CTAB. The magnitude follows the order SDS > CTAB. The values of S_k show negative in SDS and positive in CTAB indicate the existance of weak and strong ion-ion interaction in the solution. The limiting apparent molal volume ϕ_v^0 at infinite dilution, reflects the effects of solute-solvent interaction. The values of ϕ_v^0 were positive in the two systems. The negative values of S_v are found in both the solutions. From the magnitude of S_v values it is found that strong ion-ion interaction is found in SDS.

The modification of structure and molecular association occurring in the solution is very well understood by viscosity parameter. The structural changes in solution affect the viscosity to a greater extent. From the table 1, it is observed that the values of (η) increases with concentration in all the systems. This behaviour indicates the existance of molecular interaction in these systems. In order to understand more about this A and B coefficient of Jones-Dole equation have been obtained. It is observed from the table 3, that A values are positive and B coefficients are negative in two systems. Since A is measure the ionic interaction, it is found that there is a strong ion-ion interaction in the surfactant solutions. From the value of A it is clear that ionic interaction between SDS and neem oil is greater than between CTAB and neem oil. The measurement of B co-efficient will give information about solute-solvent interaction and used for measure of order or disorder introduced by the solute in the solvent.

The negative values of B indicates the structure breaking capacities of surfactants in neem oil. The magnitude of B is greater in SDS than CTAB.

Table 1: Values of ultrasonic velocity (U), density (ρ) and viscosity (η) of surfactants-neem oil solutions at 303K.

Molarity (M)	U (m/s)	ρ (kg/m^3)	η (Nsm^{-2})
System 1: Neem oil with aqueous SDS			
0.007	1526	996.3893	0.8135
0.008	1532	996.5728	0.8285
0.009	1544	997.6541	0.8366
0.010	1562	997.9518	0.8457
0.011	1532	996.6366	0.8259
0.012	1540	997.2374	0.8477
0.013	1550	998.5250	0.8679
System 2: Neem oil with aqueous CTAB			
0.007	1528	997.3304	0.8313
0.008	1536	998.2707	0.8712
0.009	1540	998.5973	0.8843
0.010	1516	999.2265	0.8913
0.011	1520	998.9282	0.8693
0.012	1529	999.6323	0.8819
0.013	1536	1001.226	0.8907

Table 2: Values of adiabatic compressibility (β), molar hydration number (n_h), molal hydration number (n_h'), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v) of surfactants-neem oil solutions at 303K.

Molarity (M)	β (10^{-10} Kg^{-1} ms^{-2})	n_h	n_h'	ϕ_k (10^{-8} m^{2}N^{-1})	ϕ_v (m^{3}mol^{-1})
System 1: Neem oil with aqueous SDS					
0.007	4.3098	-15.9277	-0.08544	12.5561	289.7723
0.008	4.2753	40.0168	54.4816	-31.5461	266.7083
0.009	4.2046	140.138	148.067	-110.474	148.6531
0.010	4.1070	249.948	256.870	-197.039	132.8525
0.011	4.2751	25.4216	39.9057	-20.0404	267.0826
0.012	4.2282	74.2569	85.9870	-58.5381	218.6966
0.013	4.1685	131.079	137.675	-103.332	124.7326
System 2: Neem oil with aqueous CTAB					
0.007	4.2945	-20.0611	-0.02926	15.7176	364.5061
0.008	4.2458	63.9736	77.3918	-50.1229	288.3925
0.009	4.2225	89.8324	101.921	-70.3831	221.6895
0.010	4.3545	-86.1823	-76.4376	67.5231	217.7173
0.011	4.3328	-56.6023	-44.4466	44.3475	433.2192
0.012	4.2790	6.97177	16.4259	-5.46234	396.7139

0.013	4.2334	56.4645	59.9747	-44.2396	313.1780

Table 3: Values of limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their constants S_k and S_ν and A & B coefficients of Jones-Dole equation of solutions at 303K.

Solutions	ϕ_k^0 ($10^{-8}m^2 N^{-1}$)	S_k ($10^{-8}m^{-1} N^{-1}mol^{-1}$)	ϕ_v^0 ($m^{-1}N^{-1}mol^{-1}$)	S_ν ($m^{-1}N^{-1}mol^{-1}$)	Viscosity (η)	
					A	B
Neem oil + aqueous SDS	160.205	-2340.4	5.451	-33.99	13.647	-1.070
Neem oil + aqueous CTAB	-27.820	218.44	9.5020	-74.48	12.340	-0.726

IV. CONCLUSION

The density (ρ), viscosity **(η)** and ultrasonic velocity (U) have been measured for different surfactants in neem oil at 303K which have been used as biological pesticides. The values are used to calculate the adiabatic compressibility, hydration parameters. The evaluated parameters clearly suggest that SDS is strong structure breaker in neem oil. The hydrophobic parts of surfactants molecules shed light on solute-solvent interaction in neem oil. There is much scope for further studies in these systems by varying the concentration of neem oil in surfactants and temperature which may reveal more about hydrogen bonding as well as other interactions such as ion-solvent, ion-ion, hydrophobic-solvent etc., exiting between surfactant and neem oil molecules.

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