Volume 65, Issue 7, 2021

Journal of Scientific Research

of

The Banaras Hindu University

Thermo Acoustic Studies of Mixed Surfactants (Brij-97 + DTAB) System in Presence of Various Additives

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Abstract: **Thermo-acoustic parameters of mixed surfactant system (Brij-97 +DTAB) in presence of inorganic electrolytes NaCl, $CaCl_2$ and $AlCl_3$ and non-electrolytes, sucrose and dextrose at various concentrations. Cloud point (CP) of nonionic surfactant Brij-97 was observed to increase with the increase in concentration DTAB in binary mixed surfactant system. In the ternary system (Brij-97+DTAB + additives) CP of the mixed surfactant system was observe to increases at 10 Mm concentration but slowly decreases with an increase in the concentration of additives. CP of mixed surfactant system was strongly influence by the structure and ions-ionic interaction of additives with micelle in aqueous solution. The clouding components release their solvated water and separate-out from the solution. Therefore, the CP of an amphiphile can be considered as the limit of its solubility. Considering the cloud point as threshold temperature of the solubility, the thermodynamic parameters of the clouding process (ΔG^o_{Cl}, ΔH^o_{Cl} and ΔS^o_{Cl}) was evaluated using the "Phase Separation Model". The phase separation results from micelle-micelle interaction. It was found that the overall clouding process was exothermic and $\Delta S^o_{Cl} > \Delta H^o_{Cl}$, indicating that the process of clouding was guided by both enthalpy and entropy-driven.**

Index Terms: **Surfactants, Thermodynamic parameters, Cloud point, Brij-97, DTAB.**

I. INTRODUCTION

The amphiphiles are molecules which contain two parts: one is the oil preferring, referred to as lipophilic or hydrophobic and the other one is the water preferring part, hydrophilic. In aqueous environment, these molecules can form a kind of self-organized molecular assembly above their critical micelle concentrations, CMC, which can be called as micelles (Alam, M. S., et al.,). The self- assembly and self-organization is natural and spontaneous) processes occurring mainly through non-covalent interactions, such as, Vander Waals, hydrogen bonding, hydrophobic, hydrophilic and electrostatic interactions (Alam, M.S., et al., 2015). Clouding is a well-known phenomenon and observed in non-ionic) surfactants; upon raising the temperature, the system becomes cloudy and phase-separates at a well-defined temperature called as cloud point (CP). Aqueous solution of a water-soluble surfactant becomes turbid. Knowing the cloud point is an important for determining storage stability (Khan F., et al.,2012; Lee., B.H.,2017). In pharmaceutical drugs penetrating power enhancement and various formulations needs knowledge of cloud point. Generally, nonionic surfactant shows optimal effectiveness when use near or below their cloud point. Low-foam surfactants should be use at temperatures slightly above their cloud point. Cloud points are typically measured using various concentration range of aqueous surfactant solution, it can be measured Cloud point range for 0º to 100ºC (32 to 212ºF), limited by freezing and boiling point of water. Cloud point is characteristic properties helps to calculating thermodynamic parameters of nonionic surfactants (Borse M.S., 2004).

Cationic surfactants are more water-soluble than that of nonionic surfactant and hence it will significantly improve the cloud point of non-ionic surfactant. Increased interest in these mixed systems can be attributed to the ease with which desired physicochemical properties can be obtained by just varying the cationic surfactant concentration in solution systems (Azum N., et al.,2014, Akbar J., et al 2012, Kakuste A.,2015).

Non-ionic surfactant are non-toxic and non-pollutant compounds that why studies get utilized in various fields interactions with cationic surfactant also gives remarkable interactions mostly those combinations used commercially and industrially applied as a detergent, emulsifying agent, wettability enhance to agrochemicals formulations cloud point is a extensive properties. These kind of surfactant mixed systems have a number of unique aggregations, critical micelles concentrations much greater efficiency to reduced surface tension due to performance and tunable geometry of surfactant solutions system containing molecules interaction (Munoz S.Z., et al.,2015). The physicochemical property of mixed surfactant system shows synergistic effects which will be more beneficiary for their various technological applications, domestic used products formulations such as soaps and detergents (Alam M.S.., et al 2010, Mandal, et al 1988, Lakshmi T. S., et al., 1978, Sulthana, S. B., et al.,1997). Hence in this paper we have undertaken a systemic study of nonionic (Brij-97) + cationic (DTAB) mixed surfactants (binary system) and in presence various additives (ternary system) may influence their physicochemical properties, which provide a better combination of solutions having number of important applications.

II. MMATERIALS AND METHOD

A. Materials

Surfactants: Nonionic surfactants; Polyoxylene-10-oleyl-ether (Brij-97) and cationic surfactant; Dodecyltrimethyl ammonium bromide (DTAB), are procure from Sigma Aldrich (U.K.). Additive's electrolytes; sodium chloride (NaCl), and Calcium chloride ($CaCl_2$,), Aluminum Chloride ($AlCl_3$) and non-electrolytes; sucrose, dextrose are procured from S D Fine-Chem Limited, India were used without any purification. All the solutions were prepared in Milli-Q water.

B. Methods

Fig:1 (a)Before clouding Fig:1(b)After clouding

Cloud point for all solutions of surfactant and different additives mixture were determined by heating method using controlled heating plate with magnetic stirrer. The turbid solution was then allowed to cool slowly while being stirred and the temperature for the disappearance of turbidity was considered as the cloud point of the solution. Heating and cooling were regulated to about 1^0C per minute around the CP. The reproducibility of the measurement was found to be within ± 0.2^0C. As the CP value are not small, the observed values have been rounded off to the nearest degree and are results are given in Table 1. (a), (b), and (c). The following images help to understanding clouding phenomenon (Lainez, A., et al., 2004, Ghosh, S., et al.,2016, Alam Md. S., et al 2012)

III. GRESULT AND DISSCUSSION

A. Effect of Concentration of DTAB on CP

Effect of concentration of cationic surfactant DTAB on clouding phenomenon of nonionic surfactant Brij-97 is evaluated and data are compiled in Table 1. CP of Brij-97 increases from 52.1^0Cto 87.2^0C with increase in concentration of cationic surfactant DTAB from 0.25 to 5 mM as shown in Table 1 and Figure 1. The increase in CP of Brij-97 with addition DTAB, DTAB molecules are participated in to the formation of highly stable mixed micelles system, which provides additional thermal stability to the micelles system and hence CP will increase with increases in the concentration of DTAB. At higher concentration (>5mM) CP will be higher than 100^0C, practically it is not possible to determine the exact value of CP, due to the vaporization of water at above 100^0C.

B. Effect of Concentration of Sugars onCP

Effect of concentration of simple sugar molecules dextrose and sucrose on clouding phenomenon of mixed surfactant system and clouding data are compiled in Table 2. As we see the CP values of mixed surfactant system was observed to increases initially in presence of dextrose and sucrose at 10mM, but further increases in concentration sugars CP values will observed to decrease (Figure 2). This decrease in CP value with sugar molecules is due to the increase in dehydration and decrease the stability of micelle solution.

C. Effect of Concentration of Inorganic Electrolytes on CP

Effect of concentration of inorganic electrolytes such as NaCl, $CaCl_2$, $AlCl_3$ on clouding phenomenon of mixed surfactant system and clouding data are compiled in Table 3. CP value of mixed surfactant system was observed to increase at 10 mM concentration but at higher concentration of electrolytes CP value was observed to decreases. The presence of electrolytes ions will provide additional stability at moderate concentration but at higher concentration of electrolytes the stability will disturb due to ion-ionic interaction and hence CP value decreases. As we compared effect of different inorganic electrolytes the trend in CP values were observe in order of $AlCl_3$>$CaCl_2$>NaCl (Figure 3). This may be due to the increase in number of counter-ions (Cl^-)which will provide additional stability to the micelle solutions and hence CP value. The counter-ion associations will play very important role in the stability of micelle solutions (Sharma K., et al., 2003, Sachin K. M., et al., 2018).

Table I: Effect of concentration of DTAB on clouding behavior of non-ionic surfactant Brij-97 at 80mM.

DTAB (Wt%)	Molarities (x 10^{-3}M)	Mole fractions (10^{-4})	-lnXs	Cloud point (CP^0C)
0.008	0.25	0.4499	10.01	52.1
0.015	0.50	0.8999	9.32	54.4
0.023	0.75	1.3498	8.91	56.5
0.038	1.25	2.2494	8.40	59.0
0.046	1.50	2.6993	8.22	62.5
0.062	2.00	3.5987	7.93	66.0
0.077	2.50	4.4980	7.71	74.4
0.154	5.00	8.9919	7.02	87.2

Table II: Effect of concentration of sucrose and dextrose sugar on cloud point (CP)of binary Brij-97 + DTAB mixed system at (80 + 0.25 mM).

(Conc. mM) Sugars	0.00	10mM	20mM	30mM	40mM	50mM
Sucrose	52.1	61.5	60.0	59.7	59.1	59.0
Dextrose	52.1	63.7	63.2	63.0	62.5	61.6

Table III: Effect of concentration of Inorganic electrolytes on cloud point (CP) of binary Brij-97 + DTAB mixed system at (80 + 0.25 mM).

Conc.(mM) Inorganic Additives	0.00	10 mM	20 mM	30 mM	40 mM	50 mM
Nacl	52.1	58.5	58.0	57.7	57.2	57.0
$Cacl_2$	52.1	59.0	58.5	58.0	57.4	57.2
$AlCl_3$	52.1	60.0	59.8	59.3	59.0	58.6

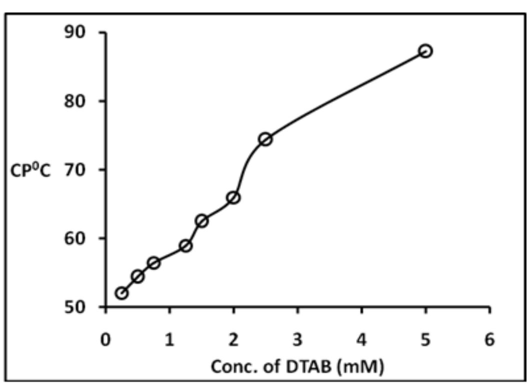

Fig.2: Effect of concentration DTAB on cloud point (CP) of Brij-97 at 80 mM.

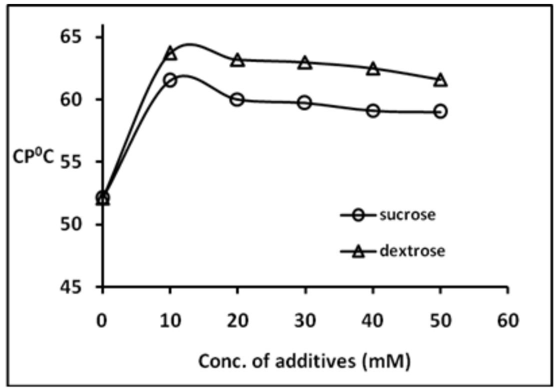

Fig.3: Effect of concentration of sucrose and dextrose sugar on cloud point (CP) of binary Brij-97 + DTAB mixed system at 80 + 0.25 mM.

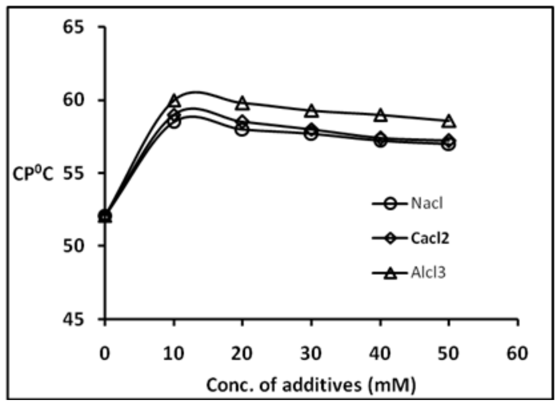

Fig.4: Effect of concentration of Inorganic electrolytes on cloud point (CP) of binary Brij-97 + DTAB mixed system at 80 + 0.25 mM.

D. Thermodynamics of clouding

All physicochemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. CP is the characteristics of non-ionic surfactants. Thermodynamic of Brij-97+DTAB mixed surfactant system were studied in presence of non-electrolyte sugars and Inorganic electrolytes. The CP of an amphiphile can be considered as the limit of its solubility as its phase separates at temperatures above CP. The clouding components release their solvated water and separate out from the solutions. Therefore, the standard change in Gibb's energy of clouding ΔG^0_{Cl} of the mixed surfactant solution can be evaluated from the relation (Akbar J., etal.l.,2012, Ghosh, S., et al., 2016).

$$\Delta G^0_{Cl} = -RT \ln X_s \quad (1)$$

Where Xs is the mole fraction concentration of additives at CP, R is a gas constant and T is the clouding temperature in Kelvin scale.

The standard enthalpy ΔH^0_{Cl} for the clouding process is calculated from the slope linear plot of lnXs vs. 1/T.

$$d\ln X_s / dT = \Delta H^0_{Cl} / RT^2 \quad (2)$$

The standard entropy change of clouding process ΔS^0_{Cl} have been calculated from the following relationship

$$\Delta S^0_{Cl} = (\Delta H^0_{Cl} - \Delta G^0_{Cl})/ T \qquad (3)$$

The thermodynamic parameters for mixed surfactants in presence of non-electrolytes sucrose and dextrose and in presence electrolytes NaCl, CaCl2 and AlCl3 are compiled in Table 4 and 5. The value of ΔH^0_s indicating that overall clouding process is exothermic and also $\Delta H^0_s > \Delta S^0_s$ indicate that the process of clouding is guided by both enthalpy and entropy (Sachin K. M., et al., 2018). The present work would be supportive evidence regarding the probable interaction between nonionic-cationic mixed surfactant system and macromolecules, leading to the phase separation at the CP. The effect of Inorganic salts on cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. However, ΔH^0_{Cl} is negative or positive depending upon the selection of surfactant types, concentrations, and nature of additives.

Table IV: Thermodynamic parameter of Brij-97+DTAB (80+0.25mM) mixed surfactant in presence of sugars

(Brij-97+DTAB)+ Sucrose (mM)	ΔG^0_s $kJmol^{-1}$	$-\Delta H^0_s$ $kJmol^{-1}$	ΔS^0_s $Jmol^{-1}K^{-1}$
10mM	27.10		126.65
20mM	26.74		125.13
30mM	26.49	14.94	124.52
40mM	26.24		123.99
50mM	26.05		123.43
Dextrose (mM)			
10mM	27.06		177.67
20mM	26.61	32.77	176.60
30mM	26.24		175.59
40mM	25.88		174.79
50mM	25.53		174.21

Table V: Thermodynamic parameter of Brij-97+DTAB (80+0.25mM) mixed surfactant in presence of inorganic electrolytes

Brij-97+DTAB+ NaCl (mM)	ΔG^0_s $kJmol^{-1}$	$-\Delta H^0_s$ $kJmol^{-1}$	ΔS^0_s $Jmol^{-1}K^{-1}$
10mM	25.86		289.88
20mM	24.95		287.61
30mM	24.28	70.24	285.85
40mM	23.72		284.62
50mM	23.27		283.32
$CaCl_2$ (mM)			
10mM	26.42		206.04
20mM	25.80	41.99	204.48
30mM	25.29		203.24
40mM	24.84		202.24
50mM	24.47		201.24
$AlCl_3$ (mM)			
10mM	26.61		233.30
20mM	26.09	51.08	223.44
30mM	25.62		230.80
40mM	25.22		229.82
50mM	24.87		229.02

CONCLUSION

The presence studies evaluated on the basis of evidence of cloud point and thermodynamic parameters. We have performing CP measurements to investigate the effect of additives e.g. electrolytes and non-electrolytes on the CP of mixed surfactant Brij-97+ DTAB(80+0.25mM)system with various additives in aqueous solutions. CP of non-ionic surfactant depending upon nature of additives and concentration and types mixed surfactants system. CP of mixed surfactant system was strongly influence by the structure and ions-ionic interaction of additives with micelle in aqueous solution. The clouding components release their solvated water and separate-out from the solution. Therefore, the CP of an amphiphile can be considered as the limit of its solubility. Thermodynamic of clouding parameters ΔG^o_{Cl}, ΔS^o_{Cl} , ΔH^o_{Cl} indicates that the process of clouding was guided by both enthalpy and entropy-driven.

ACKNOWLEDGEMENT

The authors are grateful to Principal of Kisan Arts, Commerce and Science College, Parola, Jalgaon, Maharashtra, India, for providing laboratory facility for this research works.

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