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RESEARCH ARTICLE

Tuning of Coacervate Phase Behavior of Polyoxymethylene (4) Lauryl Ether in Aqueous Alcoholic Solution: Investigation of Thermodynamics

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ABSTRACT

In case of non-ionic surfactant, the phase partition behavior (CP) of micellar solution was vary under the influence of various additive mixed systems. The non-ionic surfactant in an aqueous medium shows phase separation above the critical micelle concentration (CMC), There is a change in micellar interactions at cloud point (CP) with increase in temperature. The insertion of foreign material to surfactant solution alters the clouding temperature. In this paper we report how cloud point varies with addition of alcohol as additives. For non-ionic surfactant Polyoxyethylene (4) lauryl ether (Brij-30) the CP temperature was investigated at variable concentrations of surfactant in pure and additive mixed systems. The results we obtained shows that cloud point of pure Brij-30 surfactant decreases with enhancement in surfactant concentration from 1% to 10% (w/v) in a 22% aqueous ethanolic medium. Similarly, the cloud point values of Brij-30 in presence of n-alcohols shows increasing trend in case of propanol and butanol, specifying that their solubilization helps to form swollen water structures, thus favoring micelle hydration, while the presence of alcohols like pentanol, hexanol and heptanol shows a decreasing trend with increasing micelle size. The change in cloud points of Brij-30 in participation of various n-alcohols plays an important role in demonstrating the effect of the nature of additives on the stability of micelle. The foam ability and foam stability data discusses the stability of micelle aggregation. The important information about the thermodynamic entities were calculated using "Phase Separation Model".

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1. Introduction

Presently surfactant chemistry is attracting new researchers due to its unique characteristics and properties in different applications [1], [2]. Surfactants are mostly used in the field of petroleum, pharmaceuticals, food processing, laundry processes, biological, medical, and safety field. They are moreover importantly utilized within the field of analytical chemistry for solubilization of organic molecules, micellar catalysis and to alter the spectral features of reaction products [3]–[6].

Surfactants are amphiphilic molecules and accumulate in an aqueous solution [7], comprising both hydrophilic head and hydrophobic tail parts in a single molecule. The nonionic surfactants are a combination of water-insoluble alkyl phenol and ethylene oxide and form an oil-dissoluble group linked to a water-dissoluble polyoxyethylene chain, which shows more dissolving ability due to hydrogen bonding between the oxygen of ether and solvent. This hydrogen bonding depends on temperature, the temperature at which the degree of hydration of the hydrophilic group is insufficient to dissolve the remaining hydrocarbon chain called a cloud point [8]. Clouding is consider to be the most important property of a non-ionic surfactant, which can be observed by changing the temperature of the solution. CP is a temperature at which a transparent single layer solution becomes hazy on heating [9]–[14]. CP is characteristic of surfactant molecular architecture. The CP phenomenon is having equal importance in both practical and theoretical fields [15]. Bellow the cloud point temperature a single phase appears and phase partition is observed above the cloud point. Most surfactant port goes to a smaller phase while the bulky watery phase contains surfactant concentration close to CMC [16]–[19]. The CP phenomenon is used in the extraction technique based on phase separation, which is a simple convenient method with minimal use of solvent and requires a, discrete amount of non-volatile, non-flammable surfactant material, which is non-hazards and eco-friendly and minimizes the risk toward mankind and environment as compared to volatile organic solvents [20]. The nonionic surfactant along with its clouding properties has impressively been utilized in the extraction and pre-concentration of species like metal ions, organic molecules, amino acids, proteins, and byproducts from fermentation [21], [22], also used as detergents, solubilizers, and emulsifiers [1], [17]. The mechanism of clouding is yet not clear still it is a point of controversy, the dehydration of the hydrophilic portion is the main necessity for the clouding process [23], [24].

The dielectric constant is get altered by the elimination of water from the hydrophilic head group [25], [26], which plays a significant role in the clouding process. The Concentration of surfactant and the presence of foreign materials like additives significantly change the CP [27], [28].

The additives consisting electrolytes, macromolecules, and ionic surfactants, tuned the CP of nonionic surfactants which have been reported by a number of researchers [29]–[34]. The bulky structured organic and inorganic species also affect the phase behavior of nonionic surfactants was well explained by many researchers [35]–[39]. The results of alcohol additives on the CP of polyoxyethylene (7.5) nonyphenyl ether nonionic surfactant indicates that the introduction of small-chain aliphatic alcohols enhances the CP while the introduction of long-chain alcohols lowers the cloud point of polyoxyethylene (7.5) nonyphenyl ethe [40]. The acceptance of the CP variation phenomenon with additives is rely on the temperature dependence of inter micellar interactions that are repulsive at minimal temperature and associative at higher temperatures with the loss of water from the hydrophilic group [41]. The clouding phenomenon is also well explained on the basis of micellar gathering which is favorable with rising temperatures [42]. As aggregation number increases, micellar size increases which causes a reduction in the hydration zone and decreases the cloud point. In this way, the CP of nonionic surfactants is transformed by additives that modify the size and shape of the micelle. This CP approach also affects the thermodynamic parameters [43].

Alcohols are widely used as additives, in emulsion formation. On the basis of the water-loving nature of alcohol, they can locate on the micellar layer of the hydrophobic core. This alcohol dissolution point in the micellar zone is an important aspect to investigate its action on the micelle system as well as on the phase partition behavior of the surfactant system. In this way alcohols can act as a co-surfactant depending upon their carbon chain, hence combining the n-alcohol with a surfactant system provides various technological applications.

Brij-30 is the most important nonionic surfactant used as an emulsifier, solubilizer, and wetting agent also used in drug formulation [44], used as a corrosion inhibitor [45], due to its high purity, nontoxicity, low cost, low cloud temperature also promotes phase separation.

Hence in this paper, we report the effect of a series of n-alcohols as additives on the coacervate phase behavior of Brij-30 surfactant.

2. Materials and Methods

The nonionic surfactant Brij-30 [Polyoxyethylene (4) lauryl ether] having CAS No. 9002-92-0 with 99% purity was purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai, India, and was used without further purification. The Analytical reagent grade n-alcohols we used for this work were purchased from Merck (Germany) with a purity of >99%. All the solutions used during experimental measurements are prepared in double distilled water, the glassware we used was washed at first with 50:50 ethanol and dried with the help of a drier.

The structure of Brij-30 is shown in Fig. 1.

The CP of Brij-30 is a very low point (70 °C). Hence it is difficult to prepare its clear aqueous solution at room temperature, so all the solutions which are under study were prepared in 22% ethanol solvent in an aqueous medium. The CP temperature was assessed by the method experimentally proved by Carvalho and Briganti. The CP was determined by placing a glass tube containing nearly 10 ml of the pure aqueous alcoholic Brij-30 solution or Brij-30 along with an additive mixed system into temperature-controlled apparatus with continuous shaking, the temperature was raised at the rate of 10 c/min. The temperature at which the turbidity in solution appears on heating was noted. Discontinue the heating, and cool the solution until it becomes clear note this temperature as cloud point temperature.

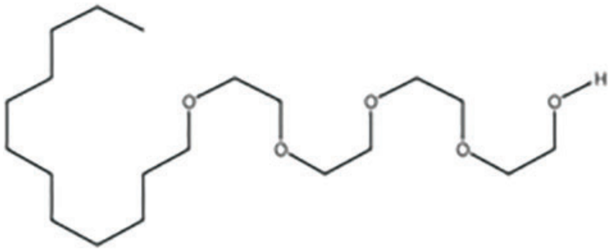

Fig. 1. Brij-30.

In this way, CP can be calculated in both the heating and cooling methods. The observed results are reproducible within ±0.10 °C. At first, turbidity occurs at the interface of the glass and the solution, after that some little amount of heating causes a cloudy appearance to the solution.

Here, CP was taken as the average value of temperatures for the appearance and disappearance of clouding.

To assure the accuracy of the result the experimental method was repeated thrice. For a clear view of temperature at cloud point a colored lamp was placed near the glass tube.

2.1. Measurement of Foamability and Foam Stability

The stability of micelle aggregation was measured by using foam ability and foam stability values which show a relation with CP temperature. Foamability and foam stability give us a piece of information about surface tension and viscosity [46]. The foaming ability and foam stability data were collected according the method well demonstrated by Myers [47]. A measuring glass cylinder of 100 cm^3 volume was used for foam ability and foam stability measurements. Twenty cubic centimeters of pure surfactant solution or surfactant with additives mixed solution was taken into the measuring cylinder. Then the solution undergoes ten uniform jerks within the span of 10 seconds. The height of the foam generated represents the foaming ability and the time taken by the foam to collapse half of its initial height represents foam stability. The same procedure was repeated thrice for each solution to get an accurate value.

3. Results and Discussion

3.1. Cloud Point Values Of Pure Brij-30

CP of Brij-30 is having numerous applications in various fields. CP values of pure nonionic surfactant Brij-30 were measured in aqueous ethanolic solution as a function of concentration and the observations are noted in Table I. CP of aqueous alcoholic Brij-30 solution shows variation with concentration. CP value for Brij-30 in 22% aqueous ethanolic solution was observed to decrease as the concentration of surfactant increased. As the surfactant solution concentration increases, there is an increase in micellar molecular weight, which results in an increasing aggregation number of the micelle, and increases hydrophobicity. When the solutions are heated to a particular temperature, the polyoxyethylene chain loses water molecules resulting decrease in surfactant solubility remarkably thus decreasing CP. As shown in Table I. This decrease in CP is also supported by foamability and foam stability data. The observed increase in foam ability and decrease in foam stability with an increasing concentration of surfactant is an indication of the formation of a less stable micelles system. These lesser stable micelles have a higher rate of diffusion towards the newly formed interface during the

TABLE I: Cloud Point of 1% to 10% Aqueous Ethanolic Solution of Pure Brij-30 Surfactant

% of Brij-30 (w/v)	CP temperature (°C)	Foamability (cm^3)	Foam stability (sec.)
1	71.2	7.6	170
2	68.2	8.0	111
3	64.2	9.0	105
4	61.6	9.8	95
5	60.2	10.8	90
6	57.1	11.8	84
7	55.2	12.8	78
8	52.8	14.8	62
9	50.6	15.2	58
10	49.8	16.00	50

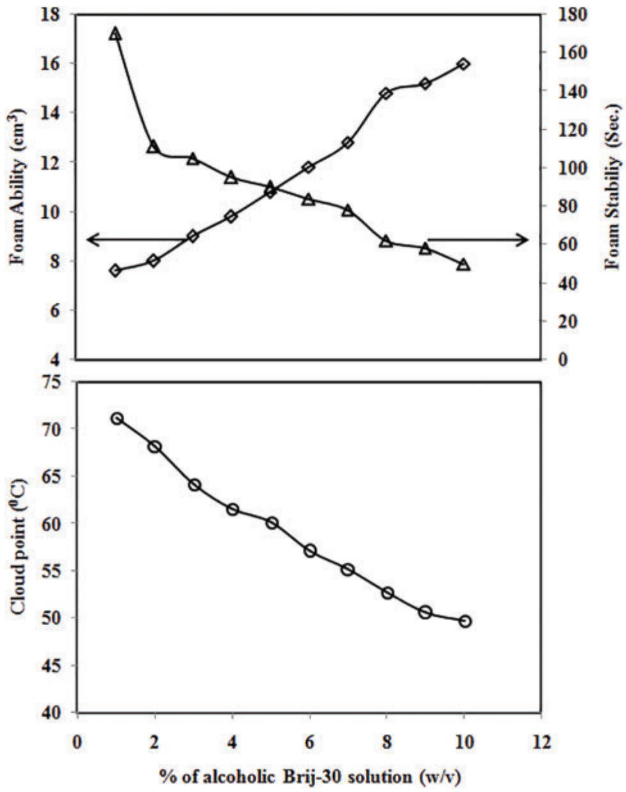

Fig. 2. Showing variation of cloud point, foamability, and foam stability with concentration of Brij-30 surfactant in an alcoholic aqueous medium.

foam formation and hence increasing foaming ability with an increase in the surfactant concentration as shown in Fig. 2.

3.2. Cloud Point of Brij-30-N Alcohol Systems

Considering n-alcohols as additives in a 10% aqueous-ethanolic Brij-30 surfactant solution, the result of chain length of n-alcohols on the CP was studied for Brij-30. The results we obtained shows that small chain alcohols like n-propanol, and n-butanol, elevates the cloud point at different concentration range as shown in Table II. The increase in CP in presence of lower alcohols is due to an increase in micelle stability. The lower alcohols associated with the surface of the micelles help to provide expanded water structure (more hydration) along micelles help to improve micelle stability which results in increased CP value in presence of C_3OH and C_4OH.

While long-chain n-alcohols like C_5OH, C_6OH, and C_7OH lower the cloud point of Brij-30, with an increase in concentration as shown in Table II. Similar trends for the series of n-alcohols with Triton-x-100 were well explained by Allaudin and Co-workers, and Parekh and Co-workers [48], [49]. It is found that lower weight alcohols shows significant increases in CP at higher concentration values but the observed CP value for higher alcohol is less than zero as shown in Fig. 3.

The decrease of CP for long-chain alcohols shows that the solubilization of long-chain alcohols occurs by a excessive decrease in the hydration of Brij-30 micelles. This shows that heavy alcohols are solubilized by surface assimilation at the interface of the micelle-water area containing the hydrocarbon

TABLE II: CP of 10% Aqueous Ethanolic Solution of Brij-30 Along with N-Alcohols at Variable Concentrations

CP of 10% aqueous ethanolic solution of Brij-30 with n-alcohol					
Conc. of alcohols (mol kg^{-1}) $\times 10^2$	Cloud Point (°C)				
	Propanol	n-Butanol	n-Pentanol	n-Hexanol	n-Heptanol
0.05	64.6	62.4	60.8	58.2	46.4
0.1	67.2	64.2	59.8	48.8	30.4
0.25	72.8	68.6	56.6	24.2	16.4
0.35	74.8	71.8	50.8	<0	<0
0.50	80.6	74.8	38.4	<0	<0
1.0	84.6	83.8	14.6	<0	<0

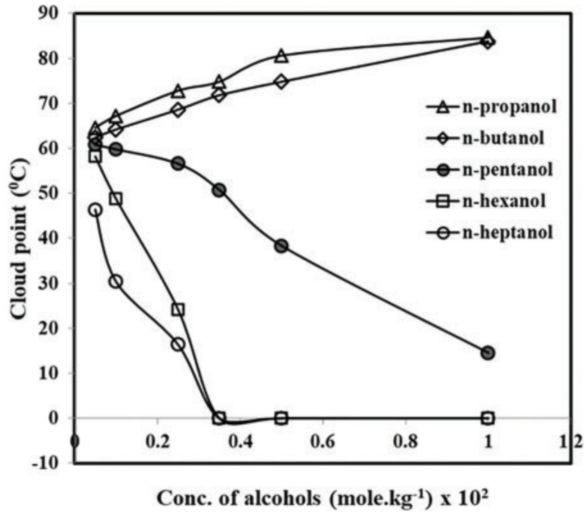

Fig. 3. Showing variation of cloud point of Brij-30 surfactant at different concentrations of n-alcohols in an alcoholic aqueous medium.

part in the outer zone of the hydrated POE chain. The dissolution of the long-chain alcohols near to micellar zone lowers hydration of Brij-30 micelle, which promotes micellar interaction resulting in phase separation and hence decreases in cloud point. Hence heavier alcohol molecule behaves as co-surfactant and penetrates in the micelle layer, causing weakness in the polyethylene-water interactions favoring dehydration resulting in phase separation showing a lowering of CP [40]. The water dissolving capacity of Brij-30 decreases as long-chain alcohols get readily dissolved in the oily phase which decreases the CP, while the water dissolving capacity of surfactant increases by increasing hydrophilic surface area as the small-chain alcohols can be located or partitioned on the micelle surface hence increases CP values.

3.3. Thermodynamic Parameters at CP

The physical properties have interrelated with changes in the energy of a system. The variation of thermodynamic properties of the non-ionic solution surfactant solution in the presence of additives was reported by Batıgöç and Akbas [50]. The micelles interaction is associated with thermodynamic principles. Clouding is the most applicable property of non-ionic surfactants. The aqueous ethanolic solution of Brij-30 with a series of n-alcohols mixed systems gives the clouding at a certain temperature. The dissociation of the hydrophilic group in the case of non-ionic surfactant is predominant. The water is separated from the micelles at the cloud temperature. The CP values and Gibbs free energy change varies according to the chain length of alcohols as shown in Fig. 4.

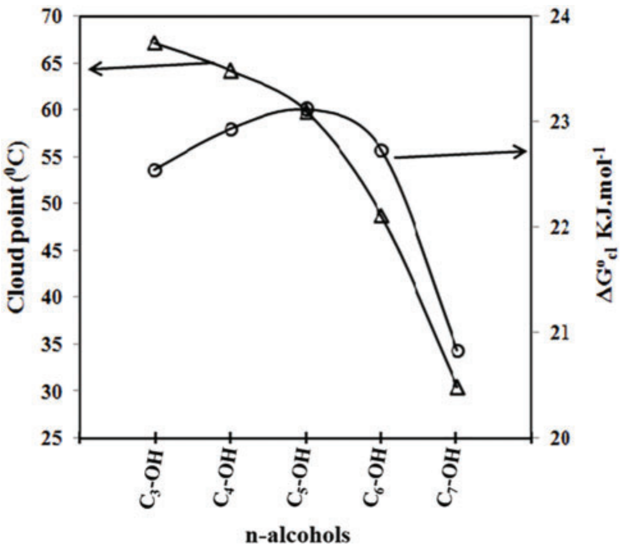

Fig. 4. Variation of chain length of n-alcohol on cloud point and ΔG^{o}_{cl} of Brij-30 surfactant alcoholic aqueous medium.

At clouding the thermodynamic properties like change in Gibbs free energy ($\Delta G^0{}_{cl}$) change in enthalpy ($\Delta H^0{}_{cl}$) and change in entropy ($\Delta S^0{}_{cl}$) at CP are calculated using the phase separation model [51]. The equations for free energy change, standard enthalpy change, and entropy change are given as:

$$(\Delta G^0_{cl}) = -RTlnXs \quad (1)$$

$$dlnXs/dT = (\Delta H^0_{cl})/RT^2 \quad (2)$$

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

where 'cl' represents the clouding process, Xs - solutes mole fraction, T- CP, temperature in Kelvin.

The change in standard enthalpy ($\Delta H^0{}_{cl}$) of clouding temperature is calculated by using the slope of the plot ln Xs vs. 1/T.

The thermodynamic parameters for pure surfactant system and additive mixed system are compiled in Tables III–VIII.

The thermodynamic processes are related to energy change. The formations of micelles are guided by thermodynamic properties. The $\Delta H^0{}_{cl}$ of pure Brij-30 was −41.39 kJ mol^{-1} while the values of

TABLE III: Thermodynamic Parameters of Pure Brij-30 Surfactant

Brij-30 (w/v) in %	$\Delta G^0{}_{cl}$ kJmol^{-1}	$-\Delta H^0{}_{cl}$ kJmol^{-1}	$-\Delta S^0{}_{cl}$ Jmol^{-1}k^{-1}
1	21.35	41.39	182.27
2	19.20		179.16
3	17.84		175.65
4	16.90		174.20
5	16.16		172.71
6	15.57		172.55
7	15.06		171.99
8	14.59		171.82
9	14.17		171.69
10	13.86		171.15

TABLE IV: Thermodynamic Parameters of Brij-30 in Presence of N-Propanol

Brij-30 (w/v) + n-propanol (moles)	$\Delta G^0{}_{cl}$ kJmol^{-1}	$-\Delta H^0{}_{cl}$ kJmol^{-1}	$-\Delta S^0{}_{cl}$ Jmol^{-1}k^{-1}
0.05	24.322	33.30	170.68
0.1	22.549		164.17
0.25	20.288		154.97
0.35	19.433		151.62
0.50	18.756		147.22
1.0	16.866		140.29

TABLE V: Thermodynamic Parameters of Brij-30 in Presence of N-Butanol

Brij-30 (w/v) + n-butanol (moles)	$\Delta G^0{}_{cl}$ kJmol^{-1}	$-\Delta H^0{}_{cl}$ kJmol^{-1}	$-\Delta S^0{}_{cl}$ Jmol^{-1}k^{-1}
0.05	24.747	32.67	171.20
0.1	22.939		164.91
0.25	20.637		156.05
0.35	19.866		152.37
0.50	19.010		148.59
1.0	17.449		140.47

TABLE VI: Thermodynamic Parameters of Brij-30 in Presence of N-Pentanol

Brij-30 (w/v) + n-pentanol (moles)	$\Delta G^0{}_{cl}$ kJmol^{-1}	$-\Delta H^0{}_{cl}$ kJmol^{-1}	$-\Delta S^0{}_{cl}$ Jmol^{-1}k^{-1}
0.05	25.112	34.12	177.45
0.1	23.120		172.00
0.25	20.399		165.31
0.35	19.123		164.43
0.50	17.468		165.67
1.0	14.478		163.98

TABLE VII: Thermodynamic Parameters of Brij-30 in Presence of N-Hexanol

Brij-30 (w/v) + hexanol (moles)	ΔG^0_{cl} kJmol^{-1}	$-\Delta H^0_{cl}$ kJmol^{-1}	$-\Delta S^0_{cl}$ Jmol^{-1}k^{-1}
0.05	25.322	30.93	169.76
0.1	22.749		166.72
0.25	18.747		167.05
0.35	–		–
0.50	–		–
1.0	–		–

TABLE VIII: Thermodynamic Parameters of Brij-30 in Presence of N-Heptanol

Brij-30 (w/v) + heptanol (moles)	ΔG^0_{cl} kJmol^{-1}	$-\Delta H^0_{cl}$ kJmol^{-1}	$-\Delta S^0_{cl}$ Jmol^{-1}k^{-1}
0.05	22.507	31.71	176.73
0.1	20.841		176.35
0.25	18.631		173.79
0.35	–		–
0.50	–		–
1.0	–		–

ΔG^0_{cl} and ΔS^0_{cl} show a decreasing trend with increasing surfactant concentration, similarly, with the addition of alcohol additives, the values of ΔG^0_{cl} and ΔS^0_{cl} also shows a decreasing trend. The positive values of ΔG^0_{cl} show that the clouding process is non-spontaneous also the values of $\Delta H^0_{cl} < \Delta G^0_{cl}$ indicate the phase change phenomenon is exothermic and the process forwarded spontaneously with the increase of alcohols concentration.

4. Conclusion

The effect of additives on the cloud point of Brij-30 is explained on the basis of their solubility in water. The water-miscible additives like small-chain alcohols transform the water structure into collapsed or expanded structures. This affects the solvation equilibrium of surfactants and changes the cloud point. The addition of small chain alcohol elevates the cloud point of the Brij-30 surfactant. In the case of long-chain alcohols which are considered water immiscible compounds which can solubilize inside the micellar core and their effect depends on the site of solubilization so there is a direct loss of water molecule from hydrophilic groups with a change in micelle packing properties and shows a decrease in CP with the addition of long-chain alcohols. This work is exploring the effect of n-alcohols on the cloud point of Brij-30 surfactant. The CP temperature was transformed by changing the nature, and concentration of alcohols. The ΔG^0_{cl} values for pure and alcohol mixed systems are positive shows a non-spontaneous system while ΔH^0_{cl} and ΔS^0_{cl} values are negative shows the system is exothermic and the formation of bulky aggregation. With increasing concentration of alcohol, the positive ΔG^0_{cl} value and negative ΔS^0_{cl} were observed to decrease in all the cases, indicating that the process moves toward spontaneity with the increase of alcohol concentration. The Gibbs free energy is controlled by enthalpy and entropy. The change in entropy is dominant during the clouding process. Both enthalpy and entropies are negative, indicating that the hydrogen bonding and dipole-dipole interaction exist in between the components of the solution [35]. The stabilized solution is formed by the formation of heavy aggregates of surfactant and is governed by negative entropy. The negative enthalpy shows the exothermic clouding phenomena.

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Conflict of Interest

Authors declare that they do not have any conflict of interest.

References

[1] Myers D. *Surfactant Science and Technology*. 2nd ed. New York: VCH; 1992. doi: 10.1002/bbpc.19920961246.

[2] Kakuste AD, Borse MS, Sonawane GH. Polyacrylic acid and polyacrylamide as cloud point modifier for Brij-30 in alcoholic aqueous solution. *J Dispersion Sci and Technology*. 2016;38(3):334–8. doi: 10.1080/01932691.2016.1165115.

[3] Perez-Bendito D, Rubio S, Merino FJ. Mixed aggregate-based acid-and induced cloud-point extractionion-trap liquid chromatography-mass spectrometry for the determination of cationic surfactants in sewage sludge. *Chromatography A*. 2003;998(1–2):143–54. doi: 10.1016/S0021-9673(03)00565-X.

[4] Williams RR, Paradkar RP. Micellar colorimetric determination of dithizone metal chelates. *Anal Chem*. 1994;66(17):2752–6. doi: 10.1021/ac00089a024.

[5] Hinze WL, Pramauro E. *Crit Rev Anal Chem*. 1993;24:133–77. doi: 10.1080/10408349308048821.

[6] Schamehorn JF, Tylor RW, Christian SD, Tucker EF, Dharmawardhana UR. A surface tension method for determining binding constants for cyclodextrin inclusion complexes of ionic surfactants. *Langmuir*. 1993;9:2258–63. doi: 10.1021/la00033a003.

[7] Gubont WM, Ben-Shaul A. The "New" science of "Complex Fluids". *J Phys Chem*. 1996;100:13169–89. doi: 10.1021/jp9606570.

[8] Schott H, Royce AE. Effect of inorganic additives on solutions of non-ionic surfactants VI: further cloud point relations. *J Pharm Sci*. 1984;73(6):793–9. doi: 10.1002/jps.2600730622.

[9] Hasanpour F, Taei M, Alimirzaei M, Karimi H, Samimi R. Cloud point extraction and surfactants, colloids and surfaces a: physicochemical and engineering aspects, spectrophotometric determination of cadmium in some vegetables. *Iran J Anal Chem*. 2014;1:44–9. http://ijac.journals.pnu.ac.ir.

[10] Bai D, Li J, Chen SB, Chen BH. A novel cloud point extraction process for pre-concentrating selected polycyclic aromatic hydrocarbons in aqueous solution. *Environ Sci Technol*. 2001;35(19):3936–40. doi: 10.1021/es010833.

[11] Mahajan RK, Vohra KK, Kaur N, Aswal VK. Organic additives and electrolytes as cloud point modifiers in octylphenolethoxylate solutions. *J Surfactant and Deterg*. 2008;11:243–50. doi: 10.1007/s11743-008-1074-6.

[12] Sharma KS, Patil SR, Rakshit AK. Study of cloud point of C12En nonionic surfactants effect of additives. *Colloids Surf A: Physicochem Eng Asp*. 2003;219:67–74. doi: 10.1016/S0927-7757(03)00012-8.

[13] Moulik SP. Micelles: self-organized surfactant assemblies. *Current Science Association*. 2003;71(5):368–76. https://www.jstor.org/stable/24099613.

[14] Paul BK, Moulik SP. Uses and applications of micro emulsions. *Current Science Association*. 2001;80(8):990–1008. https://www.jstor.org/stable/24105809.

[15] Pandit NK, Kanjia J, Patel K, Pontikes DG. Phase behavior of non-ionic surfactant–polyethylene glycol mixtures. *Int J Pharma*. 1995;122:27–33. doi: 10.1016/0378-5173%2895%2900032-E.

[16] Wanka G, Hoffmann H, Ulbritch W. Phase diagrams and aggregation behavior of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) triblock copolymers in aqueous solutions. *Macromolecules*. 1994;27:4145–5159. doi: 10.1021/ma00093a016.

[17] Gu T, Galera-Gomez PA. Clouding of Triton X-114: the effect of added electrolytes on the cloud point of Triton X-114 in the presence of ionic. *Colloids and Surfaces*. 1995;104:307–12. doi: 10.1016/0927-7757(95)03217-1.

[18] Garcia Pinto C, Perez Pavon JL, Moreno Coredero B. Cloud point pre-concentration and high-performance liquid chromatographic determination of organophosphorus pesticides with dual electrochemical detection. *Anal Chem*. 1995;67(15):2606–12. doi: 10.1021/ac00111a018.

[19] Akita S, Takeuchi H. Cloud-point extraction of organic compounds from aqueous solutions with nonionic surfactant. *Sep Sci and Technol*. 1995;30:833–46. doi: 10.1080/01496399508013895.

[20] Fernandes–Laespada ME, Perez-Povan JL, Moreno–Cordero B. Continuous membrane extraction co-unpled with chromatographic analysis for the determination of phenols in fuels. *Journal Chromatography*. 1999;823(2):537–48. doi: 10.1016/S0021-9673(98)00297-0.

[21] Revia RL, Makharadze GA. Cloud point preconcentration of fulvic and humic acids. *Talanta*. 1999;48:409–13. doi: 10.1016/S0039-9140(98)00262-8.

[22] Schott H. Lyotropic numbers of anions from cloud point changes of nonionic surfactants. *Colloids Surf*. 1984;11:51–4. doi: 10.1016/0166-6622(84)80234-6.

[23] Shigeta K, Olsson U, Kuneida H. Correlation between micellar structure and cloud point in long poly(oxyethylene)noleyl ether system. *Langmuir*. 2001;17:4717–23. doi: 10.1021/la001260x.

[24] Karlstroem G. A new model for upper and lower critical solution temperatures in poly(ethylene oxide) solutions. *J Phys Chem*. 1984;89:4962–4. doi: 10.1021/J100269A015.

[25] Tasaki K. Poly(oxyethylene)-water interactions: a molecular dynamic study. *J Am Chem Soc*. 1996;118(35):8459–64. doi: 10.1021/ja951005c.

[26] Rao IV, Ruckenstein E. Micellization behavior in the presence of alcohols. *J Colloid and Interface Sci*. 1986;113(2):375–87. doi: 10.1016/0021-9797(86)90173-6.

[27] Cerichelli G, La Mesa C, Luchetti L, Mancini G. Role of counter ions in the catalytic activity and phase equilibria of phosphonium salts in water. *Langmuir*. 2000;16:166–71. doi: 10.1021/la990893c.

[28] Johnson MD, Miller JR, Green NS, Closs GL. Distance dependence of intramolecular hole and electron transfer in organic radical ions. *Phys Chem*. 1989;93:1173–6. doi: 10.1021/j100341a001.

[29] Andleeb ZN, Al-Ahmadi MDA, Akram M, Din K. Study of clouding and dye solubilization in chlomipramine hydrochloride elyectrolyte system. *Chem Eng Comm*. 2012;199:461–71. doi: 10.1080/00986445.2011.591610.

[30] Deguchi K, Meguro K. The effects of inorganic salts and urea on the micellar structure of nonionic surfactant. *J Colloid Interface Sci*. 1975;50:223. doi: 10.1016/0021-9797(75)90224-6.

[31] Marszall L. Measurement of the effective HLB value of nonionic surfactants in the presence of electrolytes. *J Tenside Surf Det*. 1981;18:25. doi: 10.1515/tsd-1981-180109.

[32] Hans SK, Lee SM, Schott H, Kim M. Effect of protein denaturants on cloud point and Kraft point of nonionic surfactants. *Sci J Colloid Interface*. 1988;126:393. doi: 10.1016/0021-9797(89)90258-0.

[33] Schott H. Effect of electrolytes and protein denaturants on nonionic surfactants. *Tenside Surfactants Detergents*. 1996;33(6):457–63. doi: 10.1515/tsd-1996-330611.

[34] Sadaghiania AS, Khan A. Clouding of a nonionic surfactant: the effect of added surfactants on the cloud point. *J Colloid Interface Sci*. 1991;144:191. doi: 10.1016/0021-9797(91)90250-C.

[35] Li DN, Huang J, Ren ZH, Sheng R, Qian ZB, Li BB, Quan XF, Zhang YX, Wang JR, Tian H. Phase separation phenomena and thermodynamics of octylphenol Polyoxyethylene ether in micellar solutions: effect of high concentration of inorganic salts and linear correlation. *J Ind Eng Chem*. 2021;99:172–8. doi: 10.1016/j.jiec.2021.04.027.

[36] Khan MA, Ruhul Amin Md., Rahman M, Malik AR, Anamul Hoque Md., Khan Md., Abdullah M. Asiri. Influence of different additives on the clouding nature a thermodynamic behavior of tween 80 solution in the absence and presence of the amikacin sulfate drug. *J Chem Eng Data*. 2019;64(2):668–75. doi: 10.1021/acs.jced.8b00897.

[37] Rahman M, Anamul Hoque Md., Abdullah Khan Md., Abdul Rub M., Abdullah M.A.. Effect of different additives on the phase separation behavior and hermodynamics of p-tert-alkylphenoxy poly(oxyethylene) ether in absence and presence of drug. *Chin J Chem Eng*. 2018;26(5):1110–8. doi: 10.1016/j.cjche.2017.10.011.

[38] Ruhul Amin Md., Mahbub S, Molla MR, Masud Alam Md., Farhad Hossain Md., Rana S, Abdul Rub M, Anamul Hoque Md., Kumar D. Phase separation and thermodynamic behavior of Triton X-100 in the occurrence of Levofloxacin Hemihydrates: influence of additives. *J Chem Eng Data*. 2019;64(6):2750–8.

[39] Mahbub S, Abdul Rub M, Anamul Hoque Md. Clouding and thermodynamic characteristics of Triton X-100 in the presence of ciprofloxacin hydrochloride: influence of polyols. *J Chem Eng*. 2019;64(9):4181–8. doi: 10.1021/acs.jced.9b00579.

[40] Diaz-Fernandez Y, Rodriguez-Clavo S, Perez-Gramatges A. Inflence of organic additives on cloud point of PONPE-7.5. *Phys Chem*. 2004;4:5004–6. doi: 10.1039/B205341A.

[41] Koshy L, Saiyad AH, Rakshit AK. The effects of various foreign substances on the cloud point of Triton-X-100 and Triton-X-114. *Colloid and Polymer Science*. 1996;274:582–7. doi: 10.1007/BF00655234.

[42] Martinez RC, Gonzalo ER, Moreno CB, Perez-Povon JL, Pinto CG, Laespada EF. Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis. *J Chromatogr A*. 2000;902:251–65. doi: 10.1016/s0021-9673(00)00837-2.

[43] Mitchell DJ, Ninham BW. Micelles, vesicles and micro emulsions. *J Chem Soc Faraday Trans*. 1981;2(77):601–29. doi: 10.1039/F29817700601.

[44] Jing-Ling C, Jian-Hai M. Effect of various additives on the cloud point of dodecyl polyoxyethylene ether. *Journal of Colloid*. 2002;64:550–5. doi: 10.1023/A:1020601707802.

[45] Dubey AK, Singh G. Corrosion inhibition of mild steel using Brijj 30. *Portugaliae Electrochemical Acta*. 2007;25:205–19. doi: 10.4152/pea.200702205.

[46] Zhang W. The effects of frothers and particles on the characteristics of pulp and froth properties in flotation; a critical review. *J Miner Mater Charact Eng*. 2016;4:251–69. doi: 10.4236/jmmce.2016.44023.

[47] Shah DO. Significance of the 1:3 molecular ratio in mixed surfactant systems. *J Colloid Interface Sci*. 1971;37(4):744–52. doi: 10.1016/0021-9797(71)90353-5.

[48] Aladdin M, Parvin T, Begum T. Effect of organic additives on the cloud point of Triton X-100 micelles. *J Appl Sci*. 2009;9:2301–6. doi: 10.3923/JAS.2009.2301.2306.

[49] Bhadur P, Parekh P. Cloud point and thermodynamic parameters of a non-ionic surfactant heptaoxyethylene dodecyl ether (C12E7) in presence of various organic and inorganic additives. *Indian J Chem*. 2013;52A:1284–90. http://hdl.handle.net/123456789/21510.

[50] Batigoc C, Akbas H. Thermodynamic parameters of clouding phenomenon in nonionic surfactants: the effect of the electrolytes. *J Mol Liq*. 2017;231:509–13. doi: 10.1016/j.molliq.2017.02.024.

[51] Kakuste AD, Borse MS, Sonawane GH. Effect of ployacryalic acid and Polyacrylamide on clouding behavior of Triton X-100 in aqueous medium. *Tenside Surfactants Deterg*. 2015;52(1):62–6. doi: 10.3139/113.110349.