Journal of Research in Chemistry 2025; 6(1): 245-248

Journal of Research in Chemistry

E-ISSN: 2709-9423
P-ISSN: 2709-9415
Impact Factor (RJIF): 5.29
JRC 2025; 6(1): 245-248

www.chemistryjournal.net
Received: 02-01-2025
Accepted: 25-01-2025

VB Jadhav
Department of Chemistry,
JET's Z. B. Patil College,
Deopur, Dhule, Maharashtra,
India

RS Dhivare
Department of Chemistry,
BSSPM's Arts, Commerce and
Science College, Songir, Dhule,
Maharashtra, India

Clouding behaviour and thermodynamics investigation of non-ionic surfactant Tween 80 in presence of Polymethacrylic acid (PMA)

VB Jadhav and RS Dhivare

DOI: https://www.doi.org/10.22271/reschem.2025.v6.i1c.241

Abstract
The introduction of foreign materials to non-surfactants alters the temperature at which clouding happens. In this research, we explored how the non-ionic surfactant Tween 80 interacts with the additive PMA in water, focusing on measuring the cloud points (CP) of both pure Tween-80 and its mixture with PMA. Our findings revealed that as the concentration of Tween-80 rises, the CP of pure Tween-80 actually drops. On the other hand, when Tween-80 is mixed with PMA, the CP rises with a higher concentration of PMA. This suggests that PMA influences the cloud point of Tween-80, indicating that the clouding effect is related to the merging of different micelles. Overall, this study sheds light on how PMA affects the Cloud Point (CP) of Tween-80 at various concentrations. Taking CP as the key temperature for solubility, the researchers have looked into the thermodynamic factors tied to the clouding process (ΔG°_{cl}, ΔH°_{cl}, and ΔS°_{cl}) using the *Phase Separation Model*. This phase separation happens because of interactions between micelles. Our findings show that the clouding process is exothermic, with ΔH°_{cl} being greater than $T\Delta S^\circ_{cl}$, indicating that both enthalpy and entropy play a role in this process. This research highlights that clouding is more than just the growth of micelles; it is a significant phenomenon in its own right. The results suggest that there is likely some interaction between polymers and surfactants in water.

Keywords: Non-ionic surfactant, Micellization, cloud point (CP), tween 80 (Tw-80), PMA, phase Separation

Introduction

Nonionic surfactants are incredibly versatile and find use in a variety of fields, including the separation of organic compounds and metal ions. This innovative separation technique [1-3] is advantageous as it does not adversely affect proteins and functions as a biocatalyst [4]. Ionic surfactants usually don't show clouding properties, while non-ionic surfactants struggle to stay stable at higher temperatures, which leads to a noticeable effect called "clouding". The temperature at which this happens is known as the Cloud Point [5]. This effect is tied to phase separation that can occur when the temperature changes in the micellar solution of non-ionic surfactants, often referred to as CP [6-7]. The cloud point (CP) is an important feature of non-ionic surfactants. Below this point, you have a single phase of molecular or micellar solution; above it, the surfactant's solubility in water decreases, causing a cloudy mixture due to the formation of large molecular aggregates in a different phase [8]. The key phenomena in micellar solutions and micro-emulsions are becoming increasingly important and are being explored in depth by many researchers [9-10].

Understanding the cloud point as a critical threshold reveals that as we approach this point, micelles start to cluster together, and once we cross it, they break apart into a separate phase. This cloud point behavior can be affected by several factors, including the concentration of surfactants, ionic strength, pressure, and the addition of other substances [11-12]. There are various mechanisms that help explain processes like micelle formation, solubilization, and the creation of complexes [13]. Measuring the cloud point is essential for evaluating the quality and characteristics of surfactants, whether they are used on their own or in combinations, especially before applying them in areas like pharmaceutical formulations, biomedical applications, and oil recovery, particularly under high-temperature conditions [14].

The relationship between polymers and surfactants has been studied through various methods [15-17]. Understanding how surfactants interact with polymers in water is really

Correspondence
VB Jadhav
Department of Chemistry,
JET's Z. B. Patil College,
Deopur, Dhule, Maharashtra,
India

important for many industries [18-20]. These interactions can be grouped into three types: solute-solute, solute-solvent, and solvent-solvent. The differences in the critical micelle concentration (CP) values of surfactants [21] are mainly influenced by the additives used. Many researchers have laid a solid foundation for investigating Polymer-Surfactant interactions by measuring the CP of both ionic and nonionic surfactants, as well as polymers on their own and in combinations [22-26].

This paper shares the results of our research into how pure Tween 80 behaves when mixed with PMA at various concentrations. We believe these findings could have a meaningful impact on understanding the interactions between medicinal products, agrochemicals, detergents, and more. By considering the cloud point as the key temperature for solubility, we've evaluated the thermodynamic parameters of the clouding process ($\Delta G°_{cl}$, $\Delta H°_{cl}$, and $\Delta S°_{cl}$) using the “Phase Separation Model”.

Materials and Methods

The non-ionic surfactant Tween 80 (with a molecular weight of 1310) is produced by SIGMA-ALDRICH in the USA. The water-soluble polymer, a 15% sodium salt solution of polymethacrylic acid (MW 8415337), is sourced from National Chemicals Baroda in India. Both of these products were used as they were received. To prepare all solutions with different concentrations, we utilized doubly distilled water that has a specific conductance of 2-4 $\mu S\ cm^{-1}$ at a temperature of 303.15 K.

The cloud point (CP) was determined using a controlled heating method with a sample solution placed in a Pyrex glass tube. The solution was gently heated while being stirred continuously in the heating apparatus [27]. The heating rate was kept below 1°C per minute. The measurements showed a reproducibility within ±0.2°C. Since the CP values aren't minimal, the recorded figures have been rounded to the nearest degree and are presented in the tables.

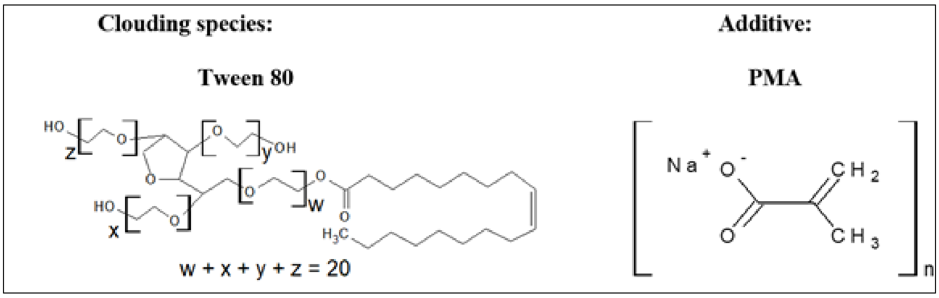

Fig 1: Molecular structures of clouding species and additive

Results and Discussion

Cloud Points of Pure Tween - 80

The cloud points of the pure surfactant Tween-80 at various concentrations, shown in weight percent, are detailed in Table-1 (A). It was found that as the concentration of Tween-80 increases, the cloud point (CP) of the surfactant actually decreases. This trend can be linked to the increase in micelle concentration, which leads to phase separation due to micelle-micelle interactions. Interestingly, at concentrations below 0.5 wt%, there’s a slight dip in the cloud point. This is mainly because there is not enough surfactant molecules present to create visible micelle clusters. Additionally, only minor changes in CP have been observed for some non-ionic surfactants like Triton X-100, Tween 20, Brij-35, and Brij-56 [28].

Mixed system of Tween-80 and PMA

The impact of PMA on the cloud point (CP) of Tween-80 at different concentrations of [PMA] is detailed in Table-2 (A). As the concentration of the water-soluble polymer PMA increases, the cloud point of the non-ionic surfactant Tween-80 rises significantly. This suggests that, when the surfactant concentration remains constant, a higher polymer concentration typically results in a higher CP [29], which can be attributed to the increase in micellar charge density. It appears that the charge density of the mixed micelle plays a crucial role in determining the cloud point; in simpler terms, a greater charge density is linked to a higher cloud point. Moreover, the polymer-surfactant complex shows improved strength due to interactions between the solute and solvent. In this scenario, some water molecules stay connected to the polymer-surfactant complex, which means a higher temperature is needed to break apart this strong complex system. Additionally, adding the polyelectrolyte PMA into non-ionic micelles creates electrostatic repulsion among the micelles, which makes it harder for phases to form and raises the cloud point, as shown in Table-2 (A).

Table 1: A] CP of pure TW-80 at different concentration in wt% and B] Thermodynamic parameters of solubilization of Tw- 80

A] CP of pure TW-80				**B] Thermodynamic parameter of solubilization of Tw- 80**			
[Tw-80] Wt%	**Molarity x 10^{-3}**	**Mole Fraction x 10^{-4}**	**CP /^{0}C**	**[Tw-80] Wt%**	**$-\Delta G^0_{cl}$ KJmole^{-1}**	**$-\Delta H^0_{cl}$ KJmole^{-1}**	**$-\Delta S^0_{cl}$ J mole^{-1}K^{-1}**
0.5	3.8168	0.6870	91.8	0.5	29.07	207.3	648.0
1	7.6336	1.3739	91.4	1	26.94		642.8
2	15.2672	2.7474	90.2	2	24.76		638.9
3	22.9008	4.1205	89.1	3	23.46		637.3
4	30.5344	5.4932	87.8	4	22.52		637.0
5	38.1679	6.8656	86.4	5	21.76		637.4

Table 2: A] Influence of PMA on CP of TW-80 and B] Thermodynamic parameters of Tw- 80 in presence of PMA

A] Influence of PMA on CP of TW-80						**B] Thermodynamic parameter of Tw-80 in presence of PMA**			
[Tw-80] Wt%	**Wt % of PMA**					**[PMA] Wt%**	**$-\Delta G^0_{cl}$ KJmole^{-1}**	**$-\Delta H^0_{cl}$ KJmole^{-1}**	**$-\Delta S^0_{cl}$ J mole^{-1}K^{-1}**
	0.001	**0.002**	**0.003**	**0.004**	**0.005**				
0.5	93.1	94.6	96.4	98.1	98.8	0.001	74.78	152.4	620.6
1	92.4	93.8	95.3	97.0	98.0	0.002	72.53	159.3	634.3
2	91.6	93.2	94.9	95.4	96.7	0.003	71.14	166.4	651.4
3	90.5	91.8	92.3	93.4	95.2	0.004	70.06	171.0	663.1
4	88.9	90.3	91.9	92.7	93.8	0.005	69.08	88.3	435.0
5	86.5	88.2	90.2	91.9	92.1				

The dependence of CP on [PMA] is depicted in Fig. 3

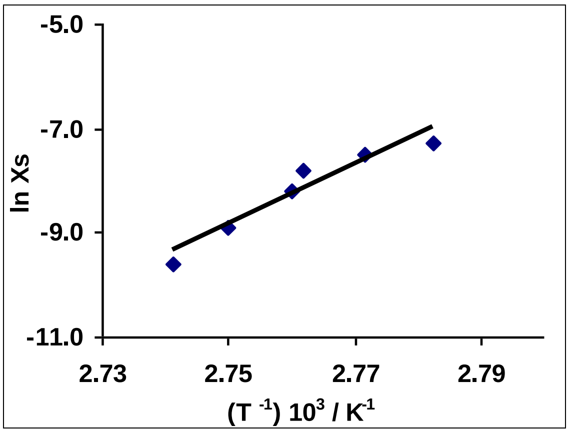

Fig 2: CP of Tw- 80 at different concentrations

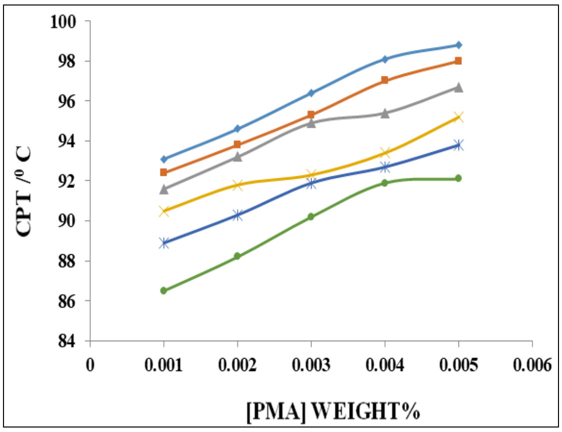

Fig 3: Influence of PMA on CP of Tw-80

Thermodynamics of Clouding

All physical and chemical processes are influenced by energy factors. For instance, the spontaneous formation of micelles is significantly affected by thermodynamic principles. Understanding the energetics behind these processes is crucial for formulation, application, and a fundamental grasp of the concepts involved. By finding the thermodynamic parameters for pure Tween-80 in Table-1 (B), while Table-2 (B) outlines the parameters for the Tween-80/PMA mixed system. When it comes to non-ionic surfactants, the de-solvation of the hydrophilic groups leads to cloudiness or turbidity in the surfactant solution at elevated temperatures. The appearance of the cloud point is mainly driven by entropy, and at this point, water molecules are released from the micelles.

Taking the cloud point as the phase separation point, we've figured out the thermodynamic parameters for the clouding process, including standard free energy ($\Delta G°_{cl}$), enthalpy ($\Delta H°_{cl}$), and entropy ($\Delta S°_{cl}$), all using the Phase Separation Model [30].

$$\Delta G^{\circ}_{c\,l} = -\,RT \ln Xs \;\ldots\ldots\ldots\ldots ❶$$

Where “cl” stands for clouding process and ln Xs is the mole fractional solubility of the solute. The Standard enthalpy ($\Delta H°_{cl}$) for the clouding process have been calculated from the slope of the linear plot of ln Xs Vs 1/T in Fig.2 for pure nonionic surfactants Tw-80.

$$d \ln Xs / dT = \Delta H^{\circ}_{c\,l} / RT^2 \;\ldots\ldots\ldots\ldots ❷$$

The Standard free energy ($\Delta S°_{cl}$) of the clouding process have been calculated from the following relationship

$$\Delta S^{\circ}_{c\,l} = (\Delta H^{\circ}_{c\,l} - \Delta G^{\circ}_{c\,l}) / T \;\ldots\ldots\ldots\ldots\ldots ❸$$

$\Delta H°_{cl} < \Delta G°_{cl}$ indicating that overall clouding process is exothermic and also $\Delta H°_{cl} > T\Delta S°_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy [31].

The current study offers compelling evidence for the interaction between non-ionic surfactants and polyions, leading to phase separation at the cloud point. The effect of PMA on the cloud point clearly shows that this clouding phenomenon is tied to the merging of different micelles. This paper strengthens the idea that the cloud point is a significant phenomenon.

Acknowledgement

The author also thankful to Hon’ble Chairman, Mr. V. P. Patil, JET’s Z.B.Patil College, Dhule, Hon’ble Chairman CDC, JET’s Z.B.Patil College, Dhule Mr. V. G. Borse, Hon’ble Principal, Dr. P. H. Pawar, JET’s Z.B.Patil College, Dhule and Vice Principals, also Head, Department of Chemistry and all colleagues of Chemistry Department, JET’s Z.B.Patil College, Dhule.

References

1. Akita S, Takeuchi H. Separation Science and Technology. 1995;30:833–840.
2. Okada T. Analytical Chemistry. 1992;64(18):2138–2143.
3. Tani H, Kamidate T, Watanabe H. Analytical Sciences. 1998;14(5):875–880.
4. Wang Z, Zhao W, Hao L, Chen DW. Journal of Molecular Catalysis B: Enzymatic. 2004;27(4–6):147–153.
5. Shinoda K, Nakagawa T, Tamamushi B, Isemura T. Colloidal surfactant: Some physicochemical properties.

New York: Academic Press; 1963.
6. Schott H. Colloids and Surfaces. 1984;11(1):51–58.
7. Myers D. Surfactant science and technology. 2nd ed. Weinheim, New York: VCH; 1992.
8. Myers D. Surfactant science and technology. 2nd ed. New York: VCH; 1992.
9. Kjellander R, Florin E. Journal of the Chemical Society, Faraday Transactions I. 1981;77:2053–2077.
10. Rupert LAM. Journal of Colloid and Interface Science. 1992;153:92–99.
11. Yu ZJ, Xu G. Journal of Physical Chemistry. 1989;93:7441–7446.
12. Buhai L, Meng M. Talanta. 1990;37(9):885–890.
13. Schott H, Royce AE. Journal of Pharmaceutical Sciences. 1984;73:793–798.
14. Ghosh S, Moulik SP. Indian Journal of Chemistry. 1999;38A:207–213.
15. Goddard ED. Colloids and Surfaces. 1986;19:255–266.
16. Cabane B, Duplessix R. Journal de Physique (Paris). 1987;48:651–660.
17. Chari K, Antalek B, Lin MY, Sinha SK. Journal of Chemical Physics. 1994;100:7–15.
18. Fishman ML, Erich FR. Journal of Physical Chemistry. 1975;79:2740–2746.
19. Bloor DM, Jones WE. Journal of the Chemical Society, Faraday Transactions II. 1982;78:657–665.
20. Tonder C. Journal of Physical Chemistry. 1985;89:5110–5115.
21. Schubert KV, Strey R, Kahlweit M. Journal of Colloid and Interface Science. 1991;141:21–29.
22. Moulik SP, Ghosh S. Journal of Molecular Liquids. 1997;72:145–152.
23. Wang Y, Olofsson G. Journal of Physical Chemistry. 1995;99:5588–5595.
24. Fishman ML, Erich FR. Journal of Physical Chemistry. 1971;75:3135–3141.
25. Bailey FE Jr, Koleske JV. Poly(ethylene oxide). New York: Academic Press; 1976.
26. Molyneux P. Water-soluble synthetic polymers: Properties and behaviour. Vol II, Chapter 2. Boca Raton (FL): CRC Press; 1984.
27. Bhadane BS, Patil TJ. Oriental Journal of Chemistry. 2008;24:3–8.
28. Ghosh S, Moulik SP. Indian Journal of Chemistry. 1999;38A:201–206.
29. Koshy L, Saiyad AH, Rakshit AK. Colloid and Polymer Science. 1996;274:582–589.
30. Attwood D, Florence AT. Surfactant systems. London: Chapman and Hall; 1983. p. 9.
31. Patil TJ, Patil HA. International Journal of Chemical Sciences. 2005;3:507–514.