



# Treatment of Waste Water Streams by Surfactant Micelles Using Semi-Equilibrium Dialysis (SED) Technique

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## Abstract

separate molecular and ionic impurities from aqueous streams. In the recent communication, semi-equilibrium dialysis (SED) technique is used to separate 1-, 2- Naphthols (1-, 2- Naph.OH), 1-, 2- Naphthoic acids (1-, 2- Naph.A) and 1-, 2- Naphthyl acetic acid (1-, 2- Naph.A.A) from aqueous streams by aqueous surfactant solution (Cetyl pyridinium chloride CPC). The solubilisation equilibrium constant  $K$  in case of polar solutes are related to the mole fraction of organic in micelles ( $X_{org}$ ) by the relation:  $K = K_o (1 - bX_{org})^2$ ,  $K_o$  is the value of the solubilisation constant as  $X_{org}$  approach zero.

From the obtained results of the solubilisation constants  $K$  for the recent organic pollutants, one can concludes that inserting a phenyl ring as well as other groups to the parent compound (benzene) accompanied by increasing the solubilisation constant  $K$ . The activity coefficients of both organic pollutant and surfactant were also calculated.

**Keywords:** SED, surfactant micelles, organic solute, aqueous stream and solubilisation equilibrium constant  $K$ .

## Introduction

Industrial waste water frequently contains high concentration of toxic compounds, water – soluble organics and multivalent heavy metal cations, which are often present, associated with coal, petroleum refiners, textiles and dyes and metal plating. Solubilisation phenomenon plays a very important role in industrial and biological processes. Also, the phenomenon can be used to remove many of soluble, slightly soluble and even normally insoluble organic molecules from aqueous streams<sup>1</sup>. Surfactant molecules have the ability to form micelles in a solution of concentration above the Critical Micelle Concentration of the surfactant (CMC). These micelles have been used to solubilize the organic pollutants present in the waste water<sup>2</sup>.

The Semi-equilibrium Dialysis technique (SED), one of the very effective techniques used for studying the solubilisation process. It has been used to study the removal of neutral, ionic organic pollutants and heavy metals from industrial wastes<sup>3-8</sup>. In a particular application of the solubilisation process, the Micellar Enhanced Ultra Filtration technique (MEUF) is used also to remove the pollutants from aqueous stream<sup>9-11</sup>. A surfactant is added to the aqueous stream to obtain a final concentration well above its CMC, the resulting solution is passed through the ultra filtration cell which prevents the passage of the micelles with the solubilised pollutants.

In the present paper, removal of 1- and 2- Naphthol (1-, 2- Naph.OH), 1- and 2- Naphthoic acid (1-, 2- Naph.A) and 1- and 2- Naphthyl Acetic acid (1-, 2- Naph.A.A) from waste water by Cetyl Pyridinium Chloride (CPC) has been studied using SED

technique at 25° C. The solubilisation equilibrium constants  $K$  for all the organic solutes, as well as the activity coefficient of the organic and surfactant are calculated. Also, comparisons can be made between the results obtained for these compounds with other that obtained previously for many organic solutes.

## Material and Methods

Cetyl Pridinium Chloride CPC obtained from Hexal Corporation was used as received. The organic solutes 1-, 2- Naphthoic acids (1-, 2- Naph.A), 1-, 2- Naphthyl Acetic acid (1-, 2- Naph.A.A) and 1-, 2- Naphthol (1-, 2- Naph.OH) are obtained from Aldrich Chemical Company. Stock solutions were prepared with redistilled deionised water. Ordinary equilibrium dialysis cells (Fisher Scientific) were used with regenerated cellulose membrane (6000 n molecular weight cut-off).

SED experiments were performed as described previously<sup>6-8, 11, 12</sup>. An aqueous solution containing known concentration of organic solute and CPC is placed on one side of the membrane (retentate compartment) and the other side is filled with pure water (permeate compartment). After 18-24 hours at 25°C for attainment of equilibrium with respect to the solubilized organic. The organic solute is assumed to be found at the same concentration on both sides of the membrane. The concentration of the surfactant will however, continue to be somewhat greater in the retentate than permeate. The concentration of the organic solute and CPC in the permeate solution has been determined simultaneously from U.V. spectral measurements at several wavelengths. Concentrations of the surfactant and organic solute

in the retentate side were inferred from the initial concentration and the known amount of these solutes that transferred into the permeate side.

**Data Analysis:** It is possible to relate the monomeric and micellar organic concentrations to the solubilisation equilibrium constant  $K^{13}$ . But when  $K$  depends strongly on the intramolecular composition, we can define the equilibrium constant by:

$$K = X_{org} / C_o \quad (1)$$

where,  $X_{org}$  represents the mole fraction of organic solute in micelles. Micellar solution is one in which the monomers and micelles of the surfactant are assumed to form separate pseudo phases which resemble co-existing liquid and vapour phases. So, the micellar phase treated as liquid phase and the monomer as the vapour phase. For sparingly soluble compounds, the activity of the solute in the micellar phase is usually equated to  $C_o / C$ , where  $C$  is the saturation concentration of the organic solute in water. The concentration of the organic in the bulk aqueous phase, give an indication about the escaping tendency of the organic form the micellar phase. If the solution obeys Raoult's law, one can say that  $C_o / C$  would be equal to  $X_{org}$ .

So,  $\gamma_{org}$  is given by the equation:

$$\gamma_{org} = a_{solute} / X_{org} = (C_o / C) / X_{org} \quad (2)$$

By combining the two equations 1, 2 on can obtain on:

$$\gamma_{org} = (C_o / C) / KC_o = 1/(KC) \quad (3)$$

Equation (3) correlates activity coefficient of the organic to the solubilisation equilibrium constant and the solubility of the solute in water. The concentration of CPC and organic solute in both side of membrane can be represented by the equations 4:

There are three unknowns value in equations 6,  $C_{org}$ ,  $X_{org}$  and  $\gamma_{CPC}$  can be obtained as discussed before in<sup>5,7,13</sup>. Gibbs-Duerm equation used to relate  $\gamma_{CPC}$  and  $\gamma_{org}$  within micelle<sup>2,14,15</sup>. At low values of  $X_{org}$ , the activity coefficients of the surfactant in the micelles close to unity, so  $\gamma_{CPC}$ , simply ignore in equation 6.

It was found that for the solubilisation of polar organic solutes in surfactant micelles, the equilibrium constant can be related to the mole fraction  $X_{org}$  by the equation:  $K = K_o(1 - bX_{org})^2$  is quite represents the dependence of  $K$  on  $X_{org}$ . From the equation at limiting value as  $X_{org}$  goes to zero,  $K$  approaches  $K_o$ . The parameter (b) in the last equation can be related to constants of Langmuir equation.

$$\begin{aligned} [CPC]_{per} &= [CPC]_{mon} + [CPC]_{mic} = \gamma_{CPC} (1 - X_{org}) CMC_{per} + [CPC]_{mic \cdot per} \\ [CPC]_{ret} &= [CPC]_{mon} + [CPC]_{mic} = \gamma_{CPC} (1 - X_{org}) CMC_{ret} + [CPC]_{mic \cdot ret} \end{aligned} \quad (4)$$

$$\begin{aligned} [Org]_{per} &= C_{org} + \frac{X_{org}}{(1 - X_{org})} [CPC]_{mic \cdot per} \\ [Org]_{ret} &= C_{org} + \frac{X_{org}}{(1 - X_{org})} [CPC]_{mic \cdot ret} \end{aligned} \quad (5)$$

Substituting the values of  $[CPC]_{per}$  and  $[CPC]_{ret}$  from the equations 4 in equations 5, one can obtain on equations 6:

$$\begin{aligned} [Org]_{per} &= C_{org} + \left( \frac{X_{org}}{1 - X_{org}} \right) \{ [CPC]_{per} - \gamma_{CPC} (1 - X_{org}) CMC_{per} \} \\ [Org]_{ret} &= C_{org} + \left( \frac{X_{org}}{1 - X_{org}} \right) \{ [CPC]_{ret} - \gamma_{CPC} (1 - X_{org}) CMC_{ret} \} \end{aligned} \quad (6)$$

## Results and Discussion

Table-1:4 includes the experimental SED results and the calculated values of the organic solute concentrations in the permeate solution for 1-, 2- Naph.OH systems. Data for the other systems will be provided on request. The final column in Tables-1 and 3 list values  $[Org]_{per}^{pred}$  predicted concentration of the organic solute. Tables-2 and 4 lists the values of mole fraction of organic  $X_{org}$ , activity coefficient for the organic solute  $\gamma_{org}$  calculated using eq. 3, and activity coefficient of the surfactant  $\gamma_{CPC}$  and the final column lists the solubilisation equilibrium constant  $K$  ( $M^{-1}$ ).

Figures 1:12 show the dependence of both the solubilisation equilibrium constant  $K$  and the activity coefficient of the organic solute  $\gamma_{org}$  on the mole fraction of organic in micelles  $X_{org}$ .

To explain the results obtained for the different systems, one should remember the factors affecting the solubilisation of organic solutes by surfactant micelles and summarized in the following points: i. Bulk solution effect which occurs in the ordinary solution<sup>16</sup>, ii. Laplace pressure effect<sup>17</sup>, iii. Interaction between the electrical potential of ionic micellar surface and polar solute that solubilized within the micelles<sup>18</sup>.

Previous publications, have discussed these factors in detail, supporting the view that ionic micelles have a hydrocarbon-like core where the aliphatic hydrocarbon group and non-polar organics tends to reside in the micellar interior. The aromatic hydrocarbons are also able to solubilize in the core region and these solutes appear to be attracted by the positive head group of the cationic surfactant surface<sup>5,7,12</sup>. Metal cations and polar compounds are solubilized only on the micellar surface due to the electrostatic attraction between the polar solutes and head groups of the cationic surfactant<sup>9,11</sup>.

In the present communication, studies the effect of inserting phenyl group as well as other chemical groups to the benzene which considered as a parent compound. Generally, comparing the values of solubilisation constant of the three kinds of solutes, it could be shown that they differ from each other. The higher values of  $K_o$  obtained for the acids (Naph.A. and Naph.A.A.) comparing with Naph.OH are attributed to the stronger interaction between COOH group with cationic head groups of the micellar surface than OH group. This reflects that the carboxylic is more intensely charged and better able to form hydrogen bonds with the surrounding water molecules in the medium than the hydroxyl group.

**1-, 2- Naphthols:** In case of 1-, 2-Naph.OH, one can see from Figures 2, 4 that  $\gamma_{org}$  increase with increasing mole fraction of organic in micelles. This relation indicates that both solutes

solubilized on the micellar surface. Reduction in the number of sites available for solubilisation with increasing  $X_{org}$  leads to raise the values of  $\gamma_{org}$ . On the other hand the initial values of  $\gamma_{CPC}$  is nearly unity and decrease with increasing  $X_{org}$ . This is due to that as more solute solubilized the micelles become larger, resulting an increase the radius of curvature which reduces the Laplace pressure within the micelles.

From figures 1, 3 one can show the linear dependence of  $K$  on  $X_{org}$ , also  $K$  decrease with increasing  $X_{org}$ , which is due to the fact that distortion of the spherical shape of micelles structure reduce Laplace pressure. This proves that the solubilisation occurs on the micellar surface due to the interaction between the ionic charge of the micellar surface and the OH group. This attraction enhanced by the possible hydrogen bonding formed between OH group and surrounded water molecules.

The limiting value of the solubilisation constant  $K_o$  for 2-Naph.OH ( $\approx 255 M^{-1}$ ) is lower than that obtained for 1-Naph.OH ( $\approx 400 M^{-1}$ ). This may be attributed to intermolecular hydrogen bond that formed within the molecule which leads to the formation of five membered rings out of plane. This makes the molecule less bulky, and more molecules solubilized within the surface in case of 1-Naph.OH. Comparing values obtained for  $K$  with those obtained previously<sup>8</sup>, for phenol ( $\approx 60 M^{-1}$ ) one can say that introducing a phenyl group increase the solubilisation of the solute.

**1-, 2- Naphthoic acids:** Figures 5,7 shows that the value of  $K_o$  obtained in case of 1-, 2- Naph. A. and that obtained previously<sup>6</sup> for benzoic acid ( $\approx 72 M^{-1}$ ), could be attributed to the presence of fused phenyl ring for parent benzoic acid. The presence of that ring increases the polarity of the carboxylic group which cause stronger interaction between the COOH group and micellar surface. It can be seen that the initial values of  $\gamma_{org}$  in case of 1-Naph.A. is less than that of 2-Naph.A. (figures 6, 8), and  $\gamma_{org}$  increase with increasing mole fraction of organic in micelles. This is due to that on increasing the organic concentration i.e. increasing of  $X_{org}$  accompanied by decrease the charge density on the micellar surface, hence reducing the tendency of the acid to solubilize. Accordingly, the initial value of  $\gamma_{org}$  in case of 1-Naph.A. ( $\approx 2.5$ ), is higher than that of 2-Naph.A. ( $\approx 1.5$ ) which means that 1-Naph.A. is more solubilized than 2-Naph.A. This may be attributed to the structure of the two acids and the possible formed intermolecular hydrogen bond. In case of 1-Naph.A. and according to the formed hydrogen bond, a six membered ring may be formed, while five membered ring in case of 2-Naph.A.

Hence, the acid solubilized on the surface by the attraction between the carboxylic group and the charge on the micellar surface, the rest of the molecule is oriented inside the plaside layer<sup>7</sup>. The geometrical structure of 2-Naph.A. comparing with that of 1-Naph.A. leads to a steric effect, so obtained on lower value of  $K_o$  in case of 2-Naph.A.

**1-, 2- Phenh.A.A.:** Figures 9, 11 show the relation between the  $K$  values and  $X_{org}$ . It is shown from the figures that  $K_o$  for 2-Naph.A.A. is higher than that of 1-Naph.A.A.. It may be due formation of intermolecular hydrogen bond, leads to formation of a third six membered ring in case of both acids, the third ring produce a linear molecule in case of 2-Naph.A.A. while a non-linear one in case of 1-Naph.A.A. Moreover, the geometrical structure of the side chain in case of 1- position makes it larger molecule comparing with that of the linear 2- position molecule, which leads to solubilise the 2-position acid on the surface between the COOH and charged micellar surface hanging the rest of the linear molecule inside the core of the micelles. So,  $K_o$  is higher in case of 2-position acid. Also, the relation between the activity coefficient of both 1-, 2- Phenh.A.A. and mole fraction of organic in micelles  $X_{org}$  are shown in figures 10, 12 which show the same behaviour as discussed before for the other systems.

As a final conclusion, one can say that inserting a phenyl group increase the limiting value of  $K_o$  compared the parent molecule. Also, inserting  $CH_2$  group to the phenyl ring not effect on the value of  $K$ , this is may be attributed to the compensation effect occurs as discussed previously<sup>6</sup>.

## Conclusion

Semi-equilibrium dialysis (SED) and Micellar Enhanced Ultra Filtration technique (MEUF) are used to determine the solubilisation of organic compounds in surfactant micelles. Removal of organic pollutants from the water streams (waste water) is one of the most important applications of ESD and MEUF. Depending on the kind of organic pollutants, one can chose the suitable surfactant used for the solubilisation process. The polar organic compounds are solubilized on the surface of the surfactant micelles due to the electrostatic attraction between charge of the organic solutes and the polar head groups of the surfactant micellar. Comparison occur between the obtained results in this paper and pervious works indicates that, the geometrical structure of the side chain of the organics used effect on the solubilisation equilibrium constant. In the present organic used, it was shown that inserting a phenyl ring to the phenol molecule leads to increase the solubilisation extend of the organic pollutants. Also, the position of the side (1- or 2-position) chain effect on the solubilisation extends.

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