



CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Transport of organic solutes

The transports of organic solutes into silica-packed columns were investigated by flowing the organic solutes; styrene or ethylcyclohexane at concentrations 300 mg/L and 80 mg/L, respectively through the column with a constant electrolyte concentration of 0.01 M NaCl and at temperature of 25°C. Styrene or ethylcyclohexane breakthrough curves are plotted by the relative pore volume (elute volume/pore volume) against the relative styrene or ethylcyclohexane concentration (C/C_0) (which were determined experimentally from Figure 4.1). According to Knox et al. (1993), the pore volume was determined by the centroid of tracer breakthrough curve. For the columns of styrene and ethylcyclohexane in single PADD system, values of pore volume were 11.88 mL and 11.70 mL, respectively. The columns of styrene and ethylcyclohexane in mixed SDS/PADD system, the pore volume were 12.06 mL and 11.88 mL, correspondingly (Appendix B).

Retardation factors of styrene in silica-packed columns were 1.67 and 1.68, respectively, (Figure 4.1a, 4.1b). The retardation factors of ethylcyclohexane in silica-packed columns were 1.30 and 1.29 (Figure 4.1c, 4.1d). These retardation factors showed the transport of organic solutes in the column without any surfactants in the system.

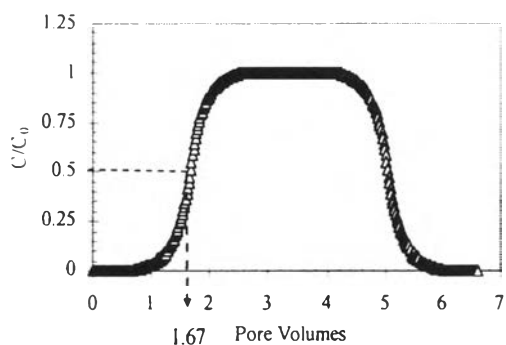


Figure 4.1a Transport of styrene 300 mg/L into silica-packed column at electrolyte concentration of 0.01 M NaCl, temperature 25°C (for single PADD system).

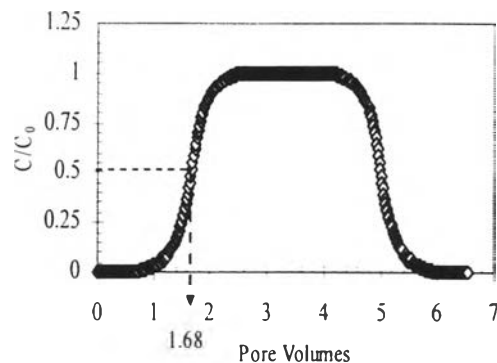


Figure 4.1b Transport of styrene 300 mg/L into silica-packed column at electrolyte concentration of 0.01 M NaCl, temperature 25°C (for mixed SDS/PADD system).

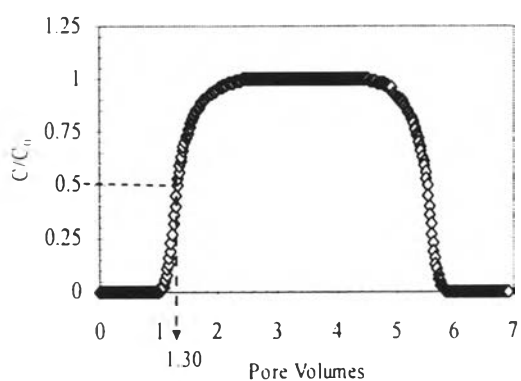


Figure 4.1c Transport of ethylcyclohexane 80 mg/L into silica-packed column at electrolyte concentration of 0.01 M NaCl, temperature 25°C (for single PADD system).

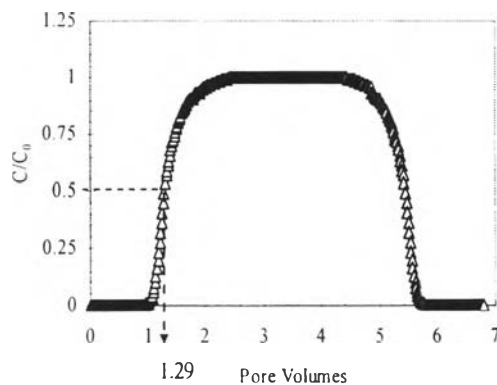


Figure 4.1d Transport of ethylcyclohexane 80 mg/L into silica-packed column at electrolyte concentration of 0.01 M NaCl, temperature 25°C (for mixed SDS/PADD system).

Figure 4.1 Transports of organic solutes into silica-packed column at electrolyte concentration of 0.01 M NaCl, temperature 25°C.

4.2 Adsorption study

The adsorption of single component and mole fraction of the mixed SDS and PADD onto negatively charged silica were conducted by using an electrolyte concentration of 0.01 M NaCl in column studies. The surfactant adsorption breakthrough curves were plotted by the relative pore volume against the relative surfactant concentrations. The adsorption was calculated as surfactant molecules/surface area, with the specific area of silica $142.6 \text{ m}^2/\text{g}$.

4.2.1 Adsorption of single PADD onto silica

The adsorption breakthrough curve of single component of cationic surfactant, PADD onto negatively charged silica was determined with electrolyte concentration of 0.01 M NaCl and room temperature of 25°C . The total adsorption of PADD (Figure 4.2), $2.30 \times 10^{-4} \text{ mole/g}$ ($0.98 \text{ molecules/nm}^2$) was obtained from mass balance and equation 2.2 (see details of calculation in Appendix C). Figure 4.2 indicated that PADD was adsorbed onto silica surface due to the electrostatic attraction between positively charged PADD (twin head cationic surfactant which contains two-positively charge head group) and negatively charged silica.

4.2.2 Adsorption of Mixed SDS/PADD onto Silica

The mixed SDS/PADD mole fraction of 1:3 was used to investigate the effect of mixed anionic and cationic surfactants adsorption onto negatively charged silica (with electrolyte concentration of 0.01 M NaCl and room temperature of 25°C).

The total adsorption of mixed SDS/PADD onto silica surface (Figure 4.3) was obtained from mass balance and equation 2.2 (Appendix C) which is 4.92×10^{-4} mole/g (2.08 molecules/ nm^2). The adsorption of individual anionic and cationic surfactants in the mixed surfactants system were 1.24×10^{-4} mole/g (0.52 molecules/ nm^2) and 3.68×10^{-4} mole/g (1.55 molecules/ nm^2), respectively (Appendix B).

In comparison, it is found obviously that the mixed SDS/PADD needs longer time for coalescing and arranging the molecule of each monomer but finally provided higher total adsorption as illustrated in Figure 4.4. Thus, it can be concluded that the mixed SDS and PADD at the ratio 1:3 performed strong synergism by evidences of higher surfactant molecules adsorbed onto the silica surface and lower concentrations of the surfactants. This phenomenon can also be explained that affected by the counter ions (0.01 M NaCl was used in this study) added to the system to reduce the electrostatic repulsion between positively charge cationic surfactants and negatively charged anionic surfactants.

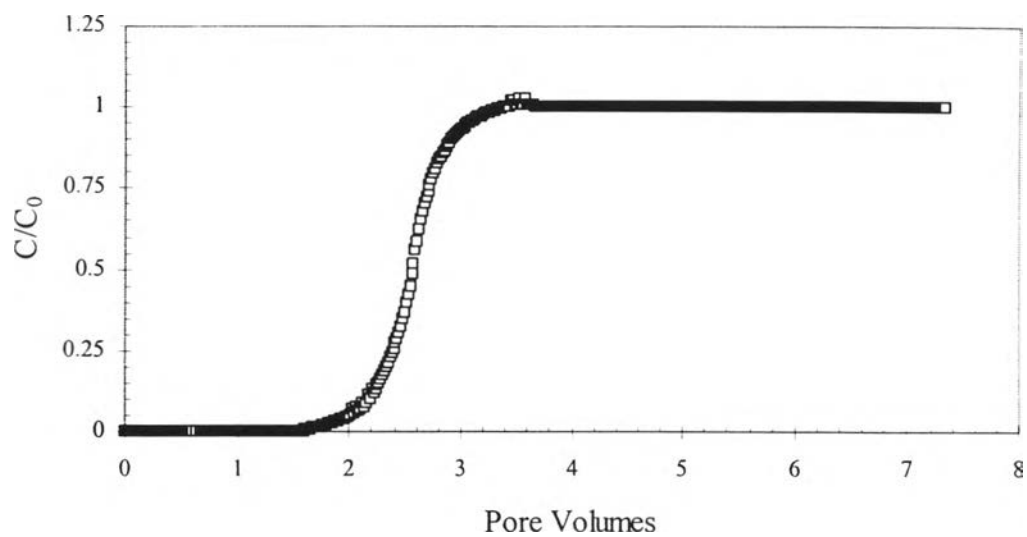


Figure 4.2 The single PADD 20 mM adsorbed onto silica surface at electrolyte concentration of 0.01 M NaCl and temperature of 25 °C.

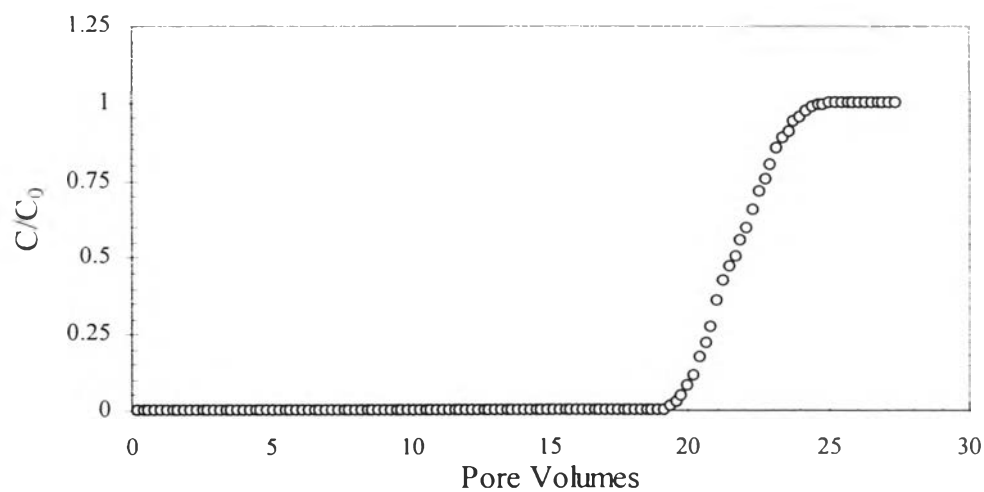


Figure 4.3 The mixed (1:3) SDS/PADD 4 mM adsorbed onto silica surface at electrolyte concentration of 0.01 M NaCl and temperature 25 °C.

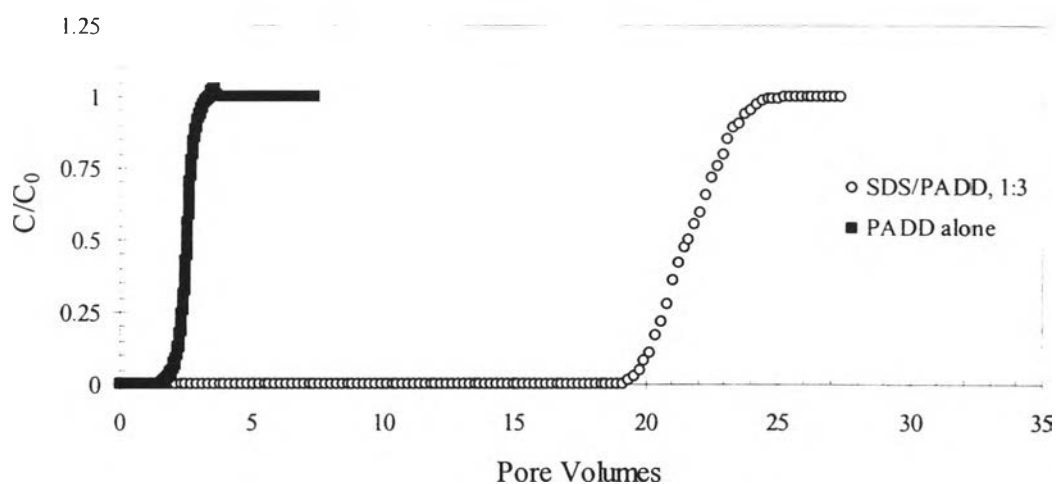


Figure 4.4 Comparison of single PADD 20 mM with the mixed (1:3) SDS/PADD 4 mM adsorbed onto silica surface at electrolyte concentration of 0.01 M NaCl and temperature 25 °C.

4.3 Adsolubilization Study

The adsolubilization isotherms of styrene and ethylcyclohexane in single PADD and the mixture of 1:3 SDS and PADD onto silica are shown in Figure 4.5 to 4.16 at electrolyte concentration of 0.01 M NaCl and room temperature 25 °C. The organic solutes adsolubilized breakthrough curves were plotted by the relative pore volume against the relative organic solutes concentrations. The adsolubilization was calculated as organic solutes molecules/surface area, with the specific area of silica 142.6 m²/g.

4.3.1 Styrene Adsolubilization

The adsolubilization of styrene by single PADD and SDS/PADD (1:3) mixture are shown in Figure 4.5 to 4.9. From the breakthrough curve of

styrene in Figure 4.5, adsolubilized by PADD admicelle was found to be 0.25 molecules/ nm². As expected, the styrene that flowed through the silica-packed column that contained adsorbed PADD admicelle on its surface has a higher retardation factor ($r_f = 4.00$) than the silica-packed column without PADD admicelle adsorption ($r_f = 1.67$) as shown in Figure 4.6.

The adsolubilized styrene with mixed anionic and cationic surfactants system was obtained from a calculation of an integration of the area under the curve (Figure 4.7), which equaled to 0.89 molecules/ nm². The retardation factors of styrene adsolubilization in both of single PADD and mixed SDS/PADD are compared as shown in Figure 4.8. The graph shows that, the retardation factors of styrene without surfactant are 1.68 and 12.80 in mixed anionic and cationic surfactants, respectively. The result of retardation factor values indicates significantly different between the columns of single and mixed surfactants which was influenced by admicelle and adsolubilization. This finding out supports the study of Chen et al. (2002) who find that mixed anionic and cationic surfactants exhibit the largest synergistic effect between surfactants and surface tension relative to single component systems. The experimental data for adsolubilization of styrene from this present study also confirm this synergism behavior of mixed cationic and anionic surfactants as shown by breakthrough curves in Figure 4.9 for the comparison plot between the two systems; single PADD and mixed SDS/PADD. The higher retardation factor indicated the higher adsolubilization of the system.

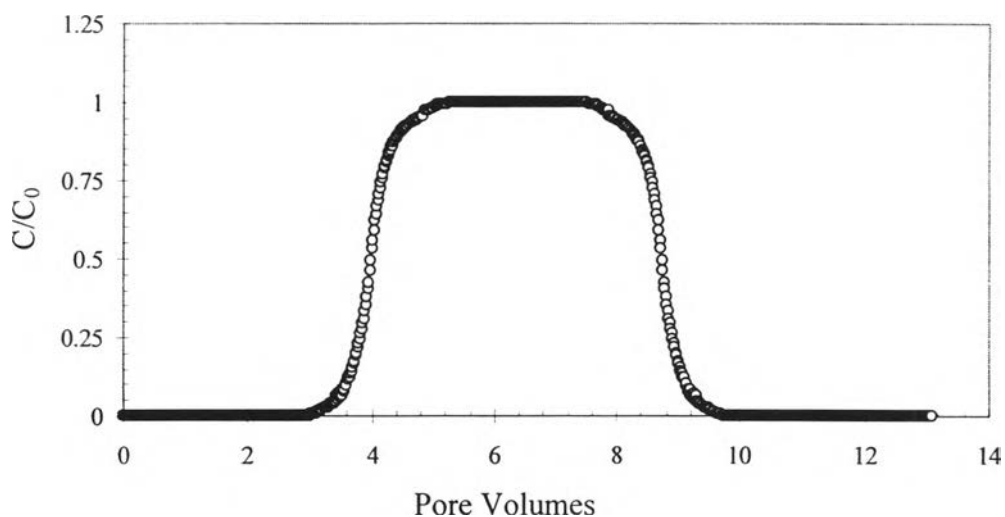


Figure 4.5 Adsolubilization of styrene into PADD admicelle at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

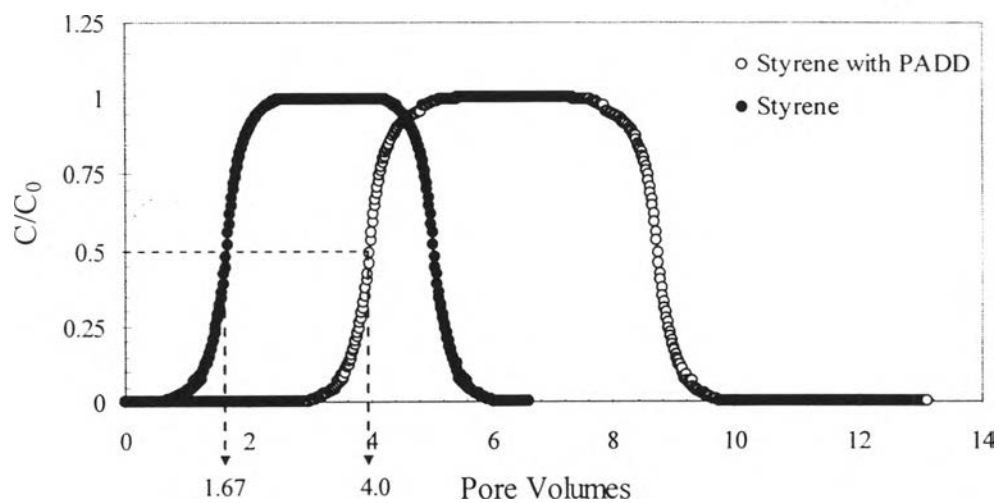


Figure 4.6 Adsolubilization of styrene into PADD admicelle and styrene without any surfactant admicelle formation at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

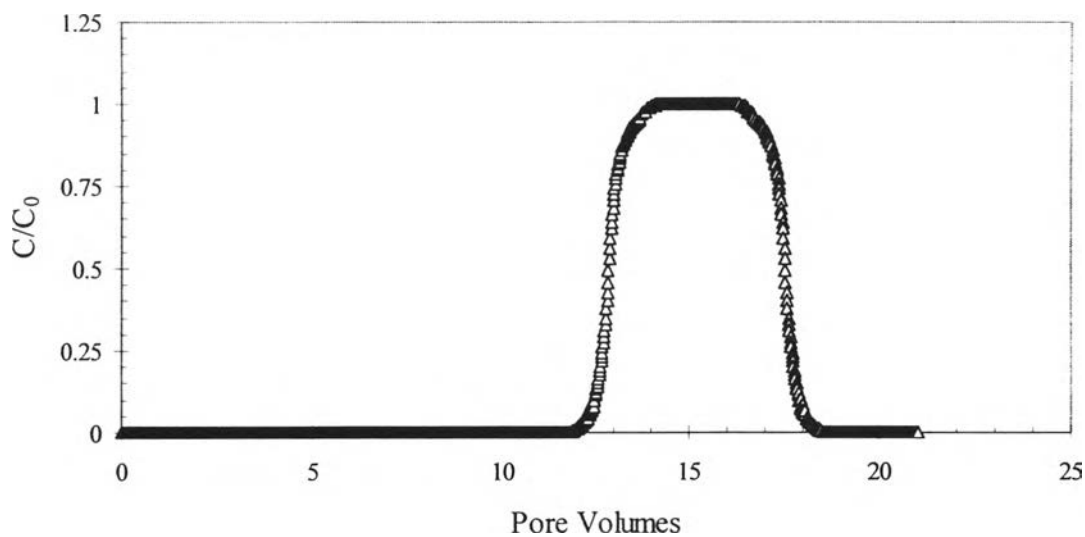


Figure 4.7 Adsolubilization of styrene into mixed SDS/PADD (1:3) admicelle at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

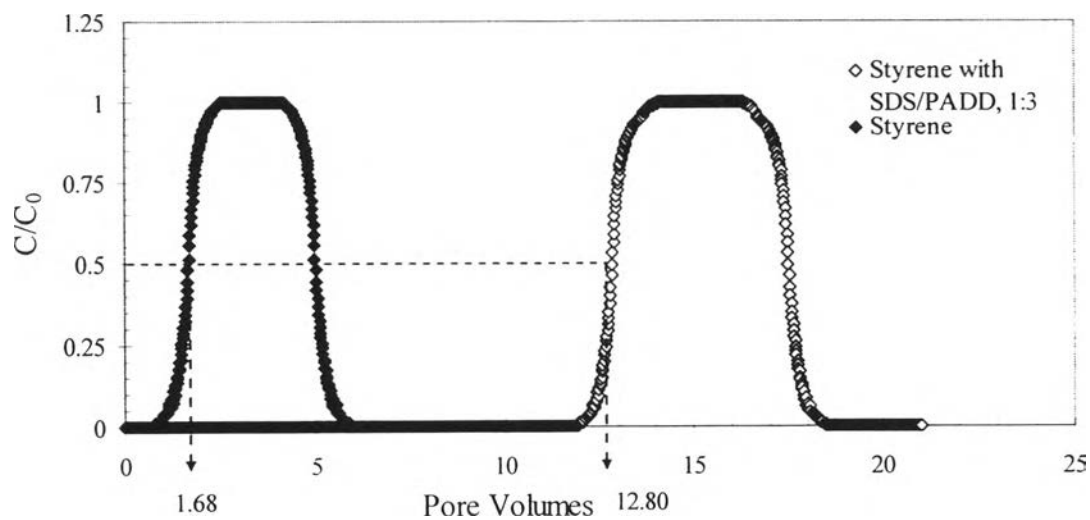


Figure 4.8 Adsolubilization of styrene by mixed SDS/PADD (1:3) admicelle and styrene without any surfactant admicelle formation at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

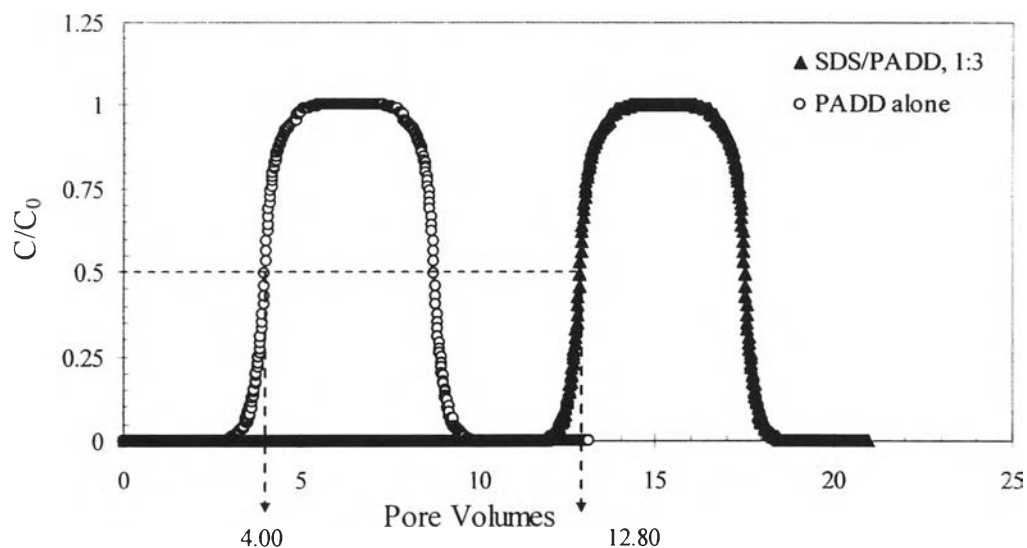


Figure 4.9 Adsolubilization of styrene into PADD admicelle and adsolubilization of styrene SDS/PADD (1:3) admicelle formation at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

4.3.2 Ethylcyclohexane Adsolubilization

The adsolubilization of ethylcyclohexane by single PADD and SDS/PADD mixtures are shown in Figure 4.10 to 4.13. The adsolubilized ethylcyclohexane by PADD admicelle was obtained from the calculation of the breakthrough curve in Figure 4.10 which equaled to 0.56 molecules/ nm². To study the transport of ethylcyclohexane in the column with and without PADD admicelle, the solvent was flowed through the column at the same flow rate. The results show their retardation factor at 32.10 and 1.30 for with and without PADD admicelle in the column, respectively (see Figure 4.11).

Figure 4.12 also shows the adsolubilized ethylcyclohexane by mixed SDS/PADD surfactants system were calculated from the breakthrough curve

in Figure 4.12 and obtained the value for ethylcyclohexane adsolubilized in mixed 1:3 SDS/PADD admicelle for 1.08 molecules/ nm^2 . The retardation factors of ethylcyclohexane are 60.95 and 1.29 for mixed SDS/PADD system and without surfactant, respectively as shown in Figure 4.13. The comparison of the breakthrough curves of adsolubilized ethylcyclohexane by mixed SDS/PADD surfactants system and single PADD system are shown in Figure 4.14. Similarly to styrene, ethylcyclohexane was found to be adsolubilized by mixed anionic and cationic surfactants much more than the single cationic surfactant. Moreover the ethylcyclohexane was trapped in the column by mixed SDS/PADD admicelle much longer than in a single surfactant admicelle. This indicated by the higher value of retardation factor.

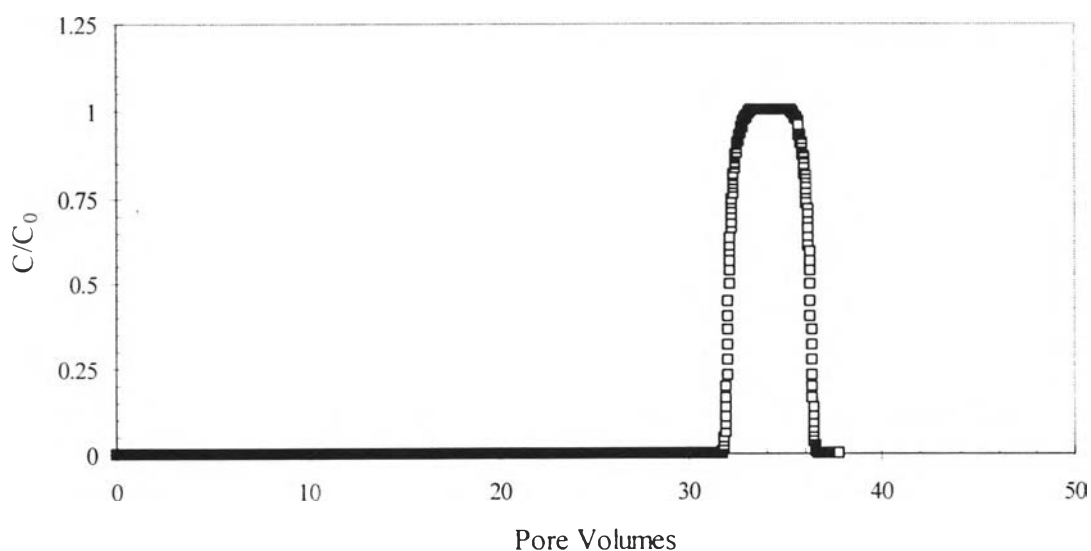


Figure 4.10 Adsolubilization of ethylcyclohexane by PADD admicelle at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

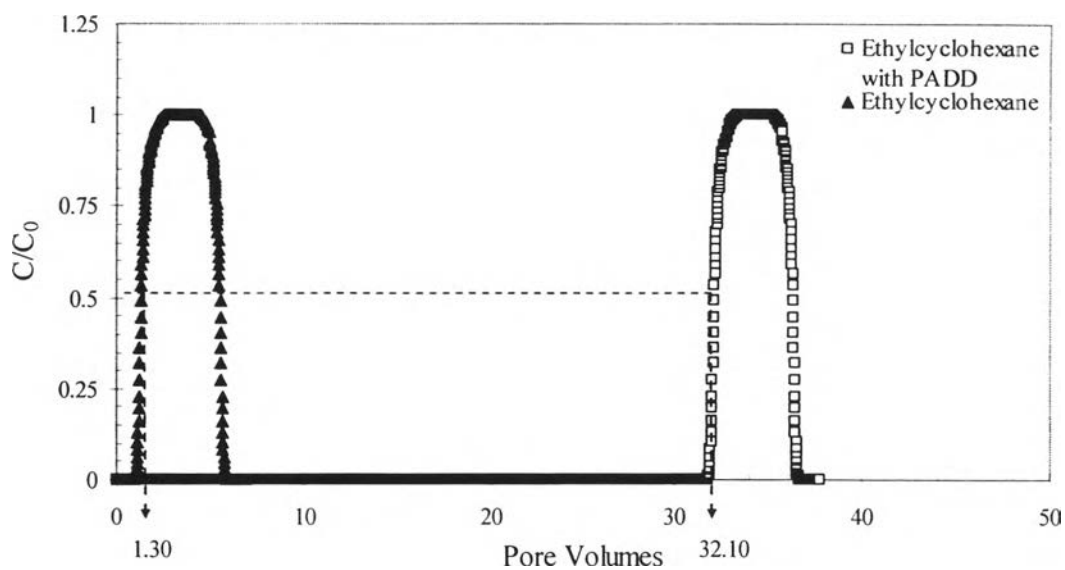


Figure 4.11 Adsolubilization of ethylcyclohexane by PADD admicelle and ethylcyclohexane without any surfactant admicelle formation at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

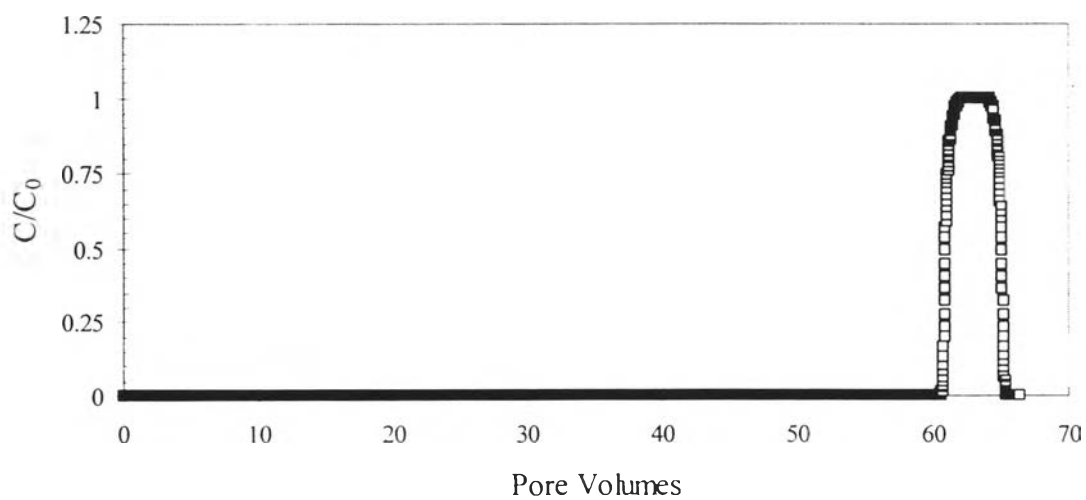


Figure 4.12 Adsolubilization of ethylcyclohexane by mixed SDS/PADD (1:3) admicelle at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

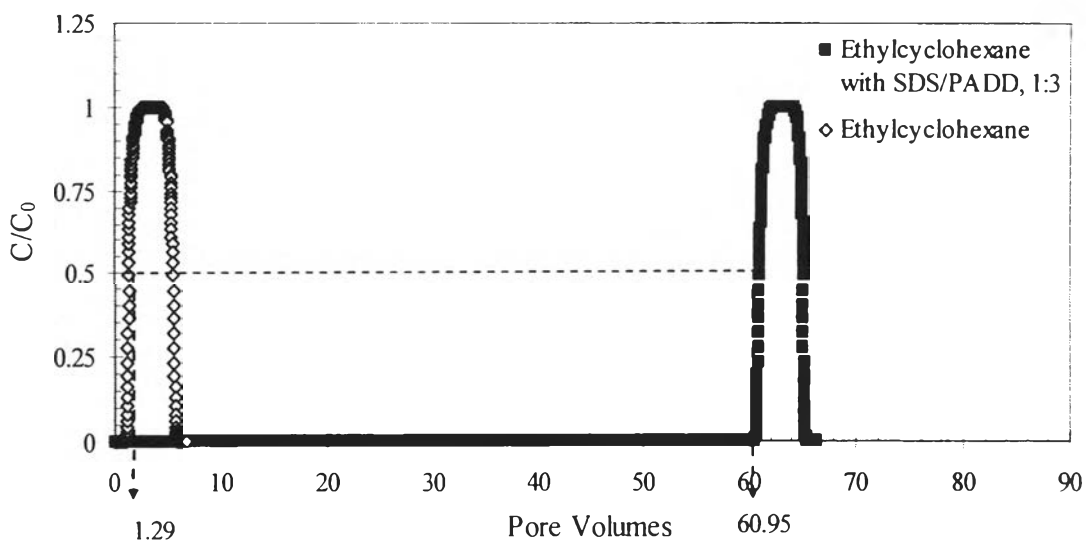


Figure 4.13 Adsolubilization of ethylcyclohexane by mixed SDS/PADD (1:3) admicelle and ethylcyclohexane without any surfactant admicelle formation at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

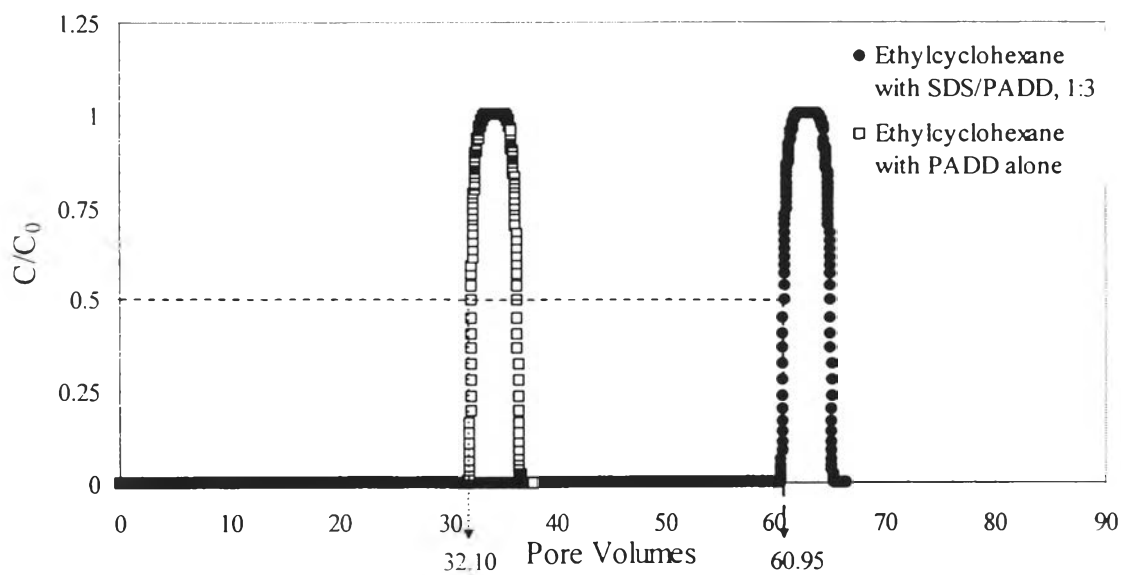


Figure 4.14 Adsolubilization of ethylcyclohexane by PADD admicelle and adsolubilization of ethylcyclohexane by SDS/PADD (1:3) admicelle formation at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

To compare between different nature of organic solute; styrene as polar solute and ethylcyclohexane as non-polar solute, the breakthrough curves of the two solutes were conducted for the column study contained single PADD system and mixed SDS/PADD system are shown in Figures 4.15 and 4.16, respectively. The adsolubilization values calculated from the plots show that styrene was adsolubilized much less than ethylcyclohexane both in single PADD system (0.25 and 0.56 molecules/nm², respectively) and in the mixed SDS/PADD system (0.89 and 1.08 molecules/nm², respectively). As previously mentioned by Lee et al. (1990) that adsolubilization of polar organic solutes is likely to be at palisade region of the admicelle. This work was supported by the following research of Nayyar, et al. (1994) who indicated that organic solutes tended to partition into the region of the admicelle that possessed similar polarity to the solute. To consider our system, a non-polar solute - ethylcyclohexane is expected to primarily partition within the core region while a polar solute - styrene is expected to preferentially adsolubilize in the palisade layer. This is because the mixed anionic and cationic surfactants system, especially, PADD which has two-positively charged cationic surfactant head groups can adsorb onto negatively charged silica with facing hydrophobic tail group to the aqueous phase and leading to anionic and cationic surfactants bilayers. As anionic surfactant molecule increases, the hydrophobic group in the core regions increases which in turn promotes the adsolubilization of non polar ethylcyclohexane in admicelle. When the anionic surfactants present in the system, they decrease charge of surface, thereby making the core more hydrophobic and promotes the

formation denser of aggregate, both which would increase hydrophobic adsolubilization surfactant into admicelles.

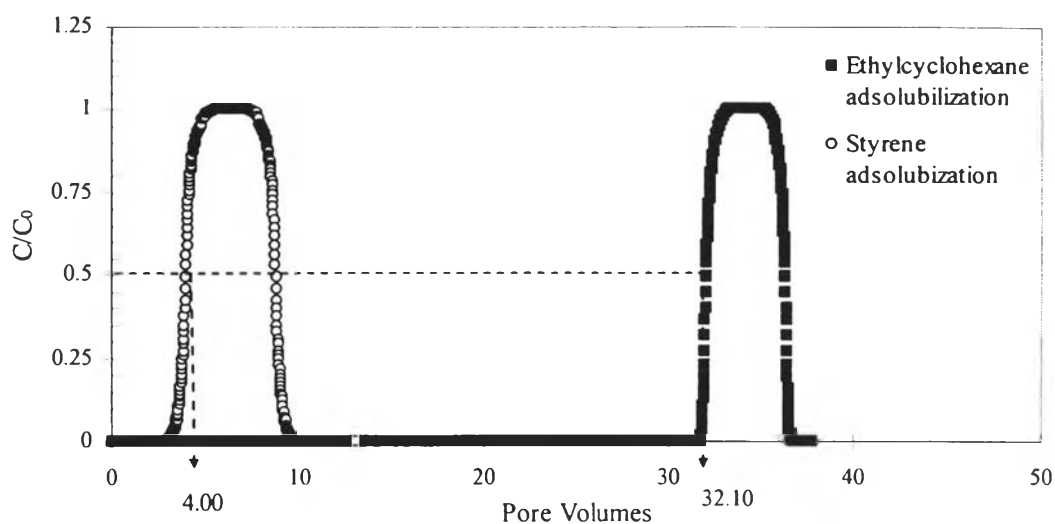


Figure 4.15 Adsolubilization of styrene and ethylcyclohexane by PADD admicelle at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.

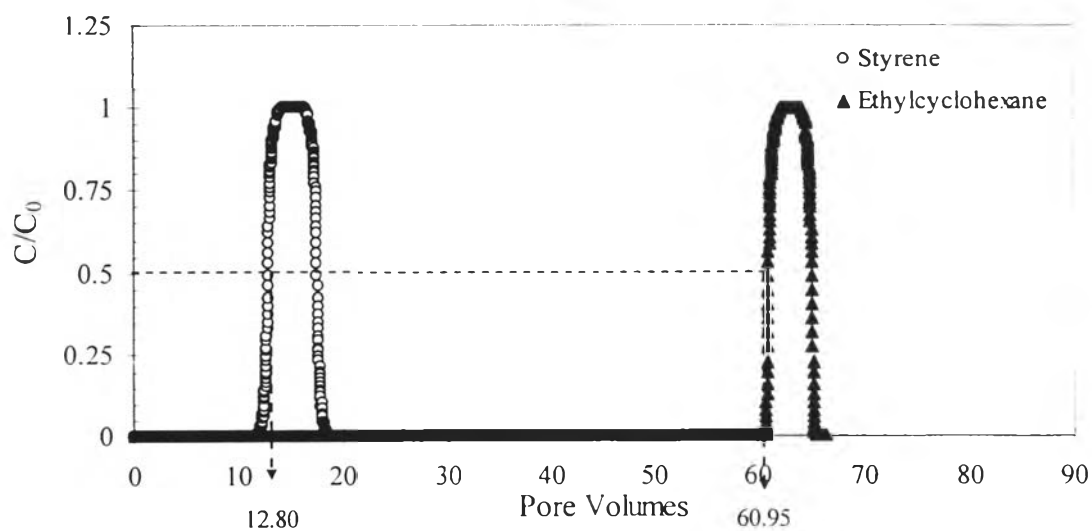


Figure 4.16 Adsolubilization of styrene and ethylcyclohexane by SDS/PADD (1:3) admicelle at electrolyte concentration 0.01 M NaCl and room temperature 25 °C.