CHAPTER IV
RESULTS AND DISCUSSION

All the experimental data of both materials (MCM-41 and Hi-Sil 255) are shown in Appendix .

4.1 Octyltrimethylammonium Bromide Adsorption Isotherm

The equilibrium times required for octyltrimethylammonium bromide to be adsorbed on MCM-41 and Hi-Sil 255 are found to be approximately 5 days as shown in Figures 4.1 and 4.2, respectively. The adsorption isotherm of both solids illustrate clearly the characteristics of regions II, III and IV. The slope of the isotherm is greater than 1 from a concentration of octyltrimethylammonium bromide in the aqueous solution of 8 to 400 μM for MCM-41 and 12 to 350 μM for Hi-Sil 255 as shown in Figures 4.3 and 4.4, respectively. These very high slopes indicate the onset of octyltrimethylammonium bromide aggregation on the surfaces of both MCM-41 and Hi-Sil 255. From the plateau region data, the maximum adsorption of octyltrimethylammonium bromide on MCM-41 was around 8200 μmol/g and on Hi-Sil 255 was 820 μmol/g. The reported surface area of this MCM-41 from the University of Oklahoma is 1005 m^2/g. Based on monolayer coverage, it can be calculated that MCM-41 allows a coverage of 4.91 molecules/nm^2 or 20 $Å^2$/molecule. For Hi-Sil 255, the BET surface area is 170 m^2/g and gives a coverage of 2.90 molecule/nm^2 or 34 $Å^2$/ molecule. These can be assumed as a formation of hemimicelle and if the admicelles were successfully formed it should take areas of 40 $Å^2$ and 68 $Å^2$ respectively.

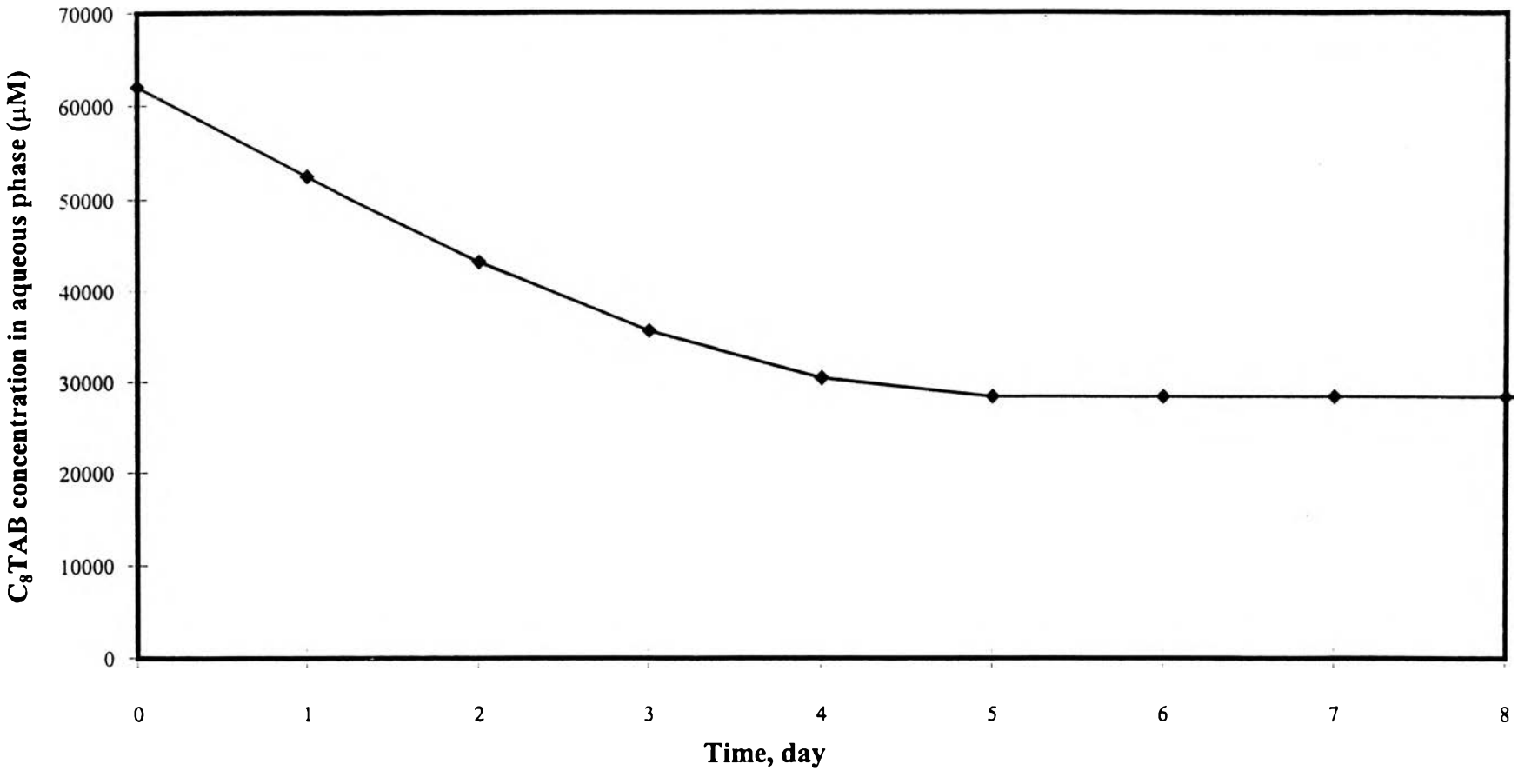

Figure 4.1 Dynamic adsorption of octyltrimethylammonium bromide (C_8TAB) on MCM-41

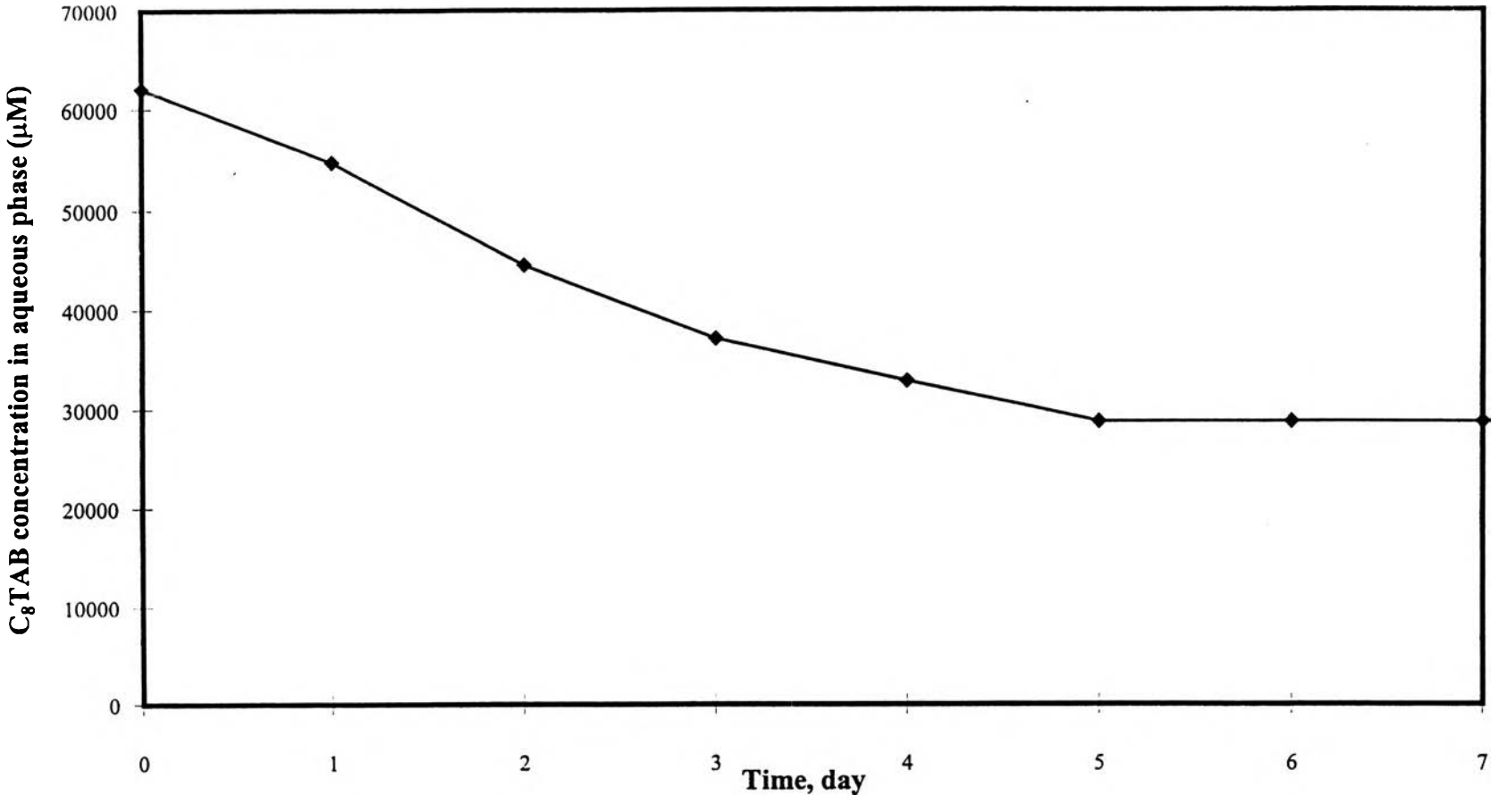

Figure 4.2 Dynamic adsorption of octyltrimethylammonium bromide (C_8TAB) on Hi-Sil 255

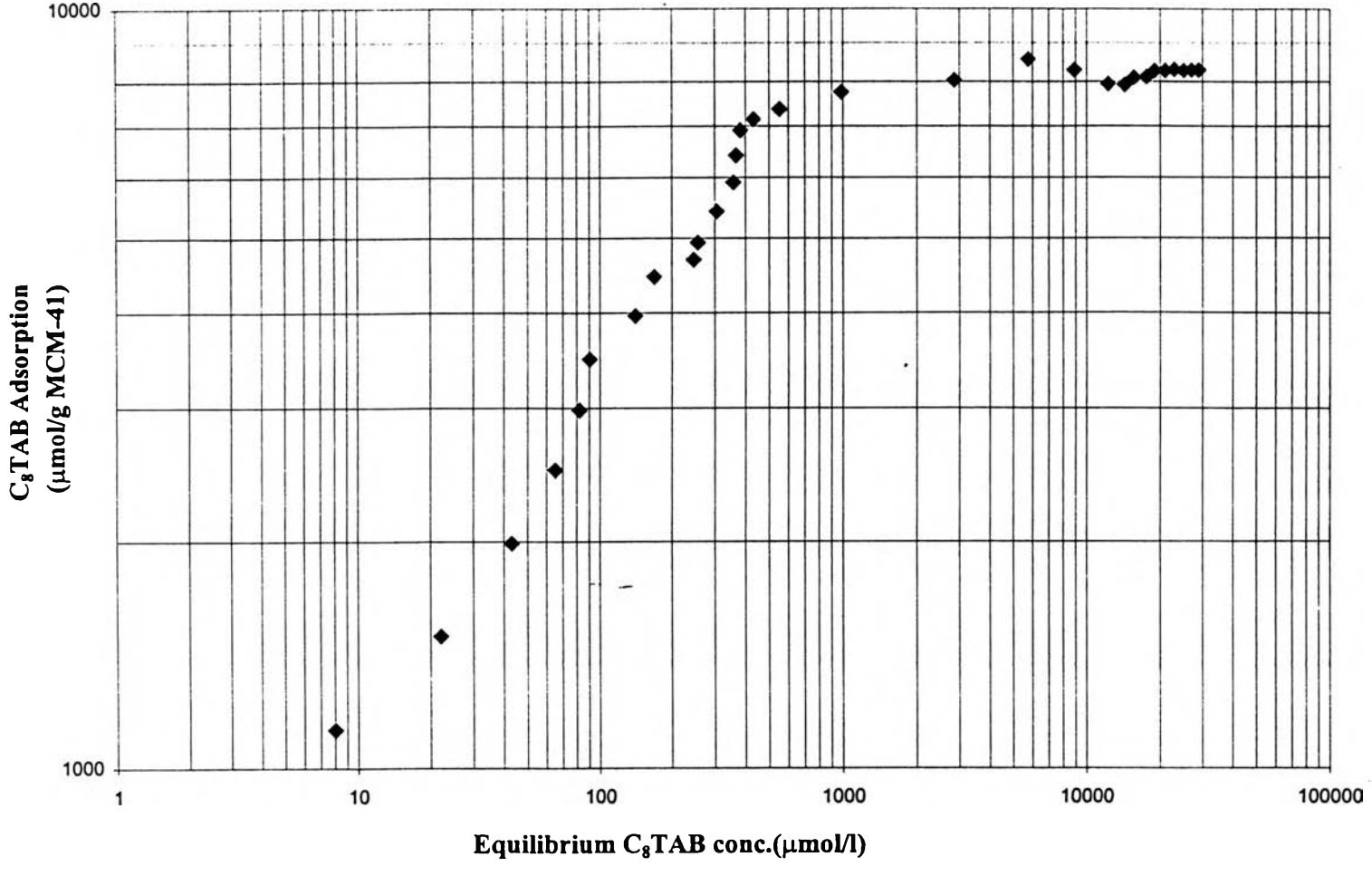

Figure 4-3 C_8TAB Adsorption Isotherm on MCM-41

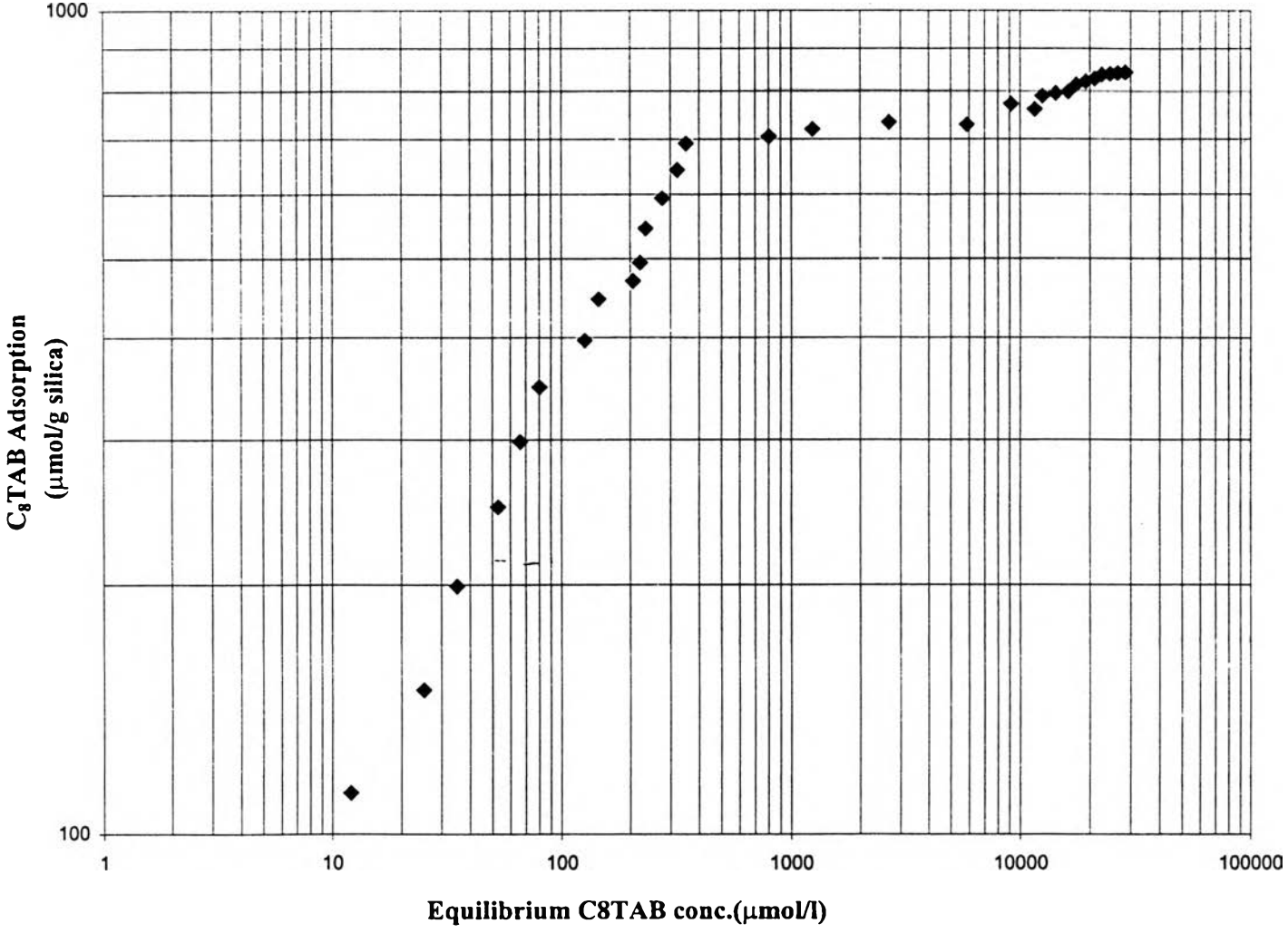

Figure 4-4 C_8TAB Adsorption Isotherm on Hi-Sil 255

4.2 Decyltrimethylammonium Bromide Adsorption Isotherm

The dynamic adsorptions of decyltrimethylammonium bromide on MCM-41 and Hi-Sil 255 are shown in Figures 4.5 and 4.6. For the adsorption isotherm of MCM-41, the slope of the isotherm is increased drastically in the range of the a concentration of decyltrimethylammonium bromide in the queous solution of 20 μM to 520 μM. For Hi-Sil 255, the same characteristic was observed at the decyltrimethylammonium bromide concentration of 18 μM to 700 μM. The two slopes indicate the onset of decyltrimethylammonium bromide on the surface of MCM-41 and Hi-Sil 255 respectively as shown in Figures 4.7 and 4.8, respectively. Although the two intervals of onset aggregation concentrations are almost the same but when based on monolayer coverage, MCM-41 gives a coverage of 4.79 molecule/mm^2 or 21 Å^2/molecule. Thus the hemimicelles were formed and took the area of 21 Å^2/molecule. This value can be implied for the admicelles that if successfully formed, they will take an area of around 42 Å^2/head group.[1] A coverage of 2.87 molecule/nm^2 or 35 Å^2/molecule was observed for Hi-Sil 255. As can be seen from Figure 4.5 and 4.6, the maximum adsorption for MCM-41 is almost 10 times higher than the one for Hi-Sil 255. This result was similar to the case of octyltrimethylammonium bromide. This highly adsorption characteristic of MCM-41 results from its high surface area.

4.3 Dodecyltrimethylammonium Bromide Adsorption Isotherm

Figures 4.9 and 4.10 show the dynamic adsorption behavior of dodecyltrimethylammonium bromide to be adsorbed on MCM-41 and Hi-Sil 255 which are similar to C_8TAB and C_9TAB. The adsorption isotherms of this

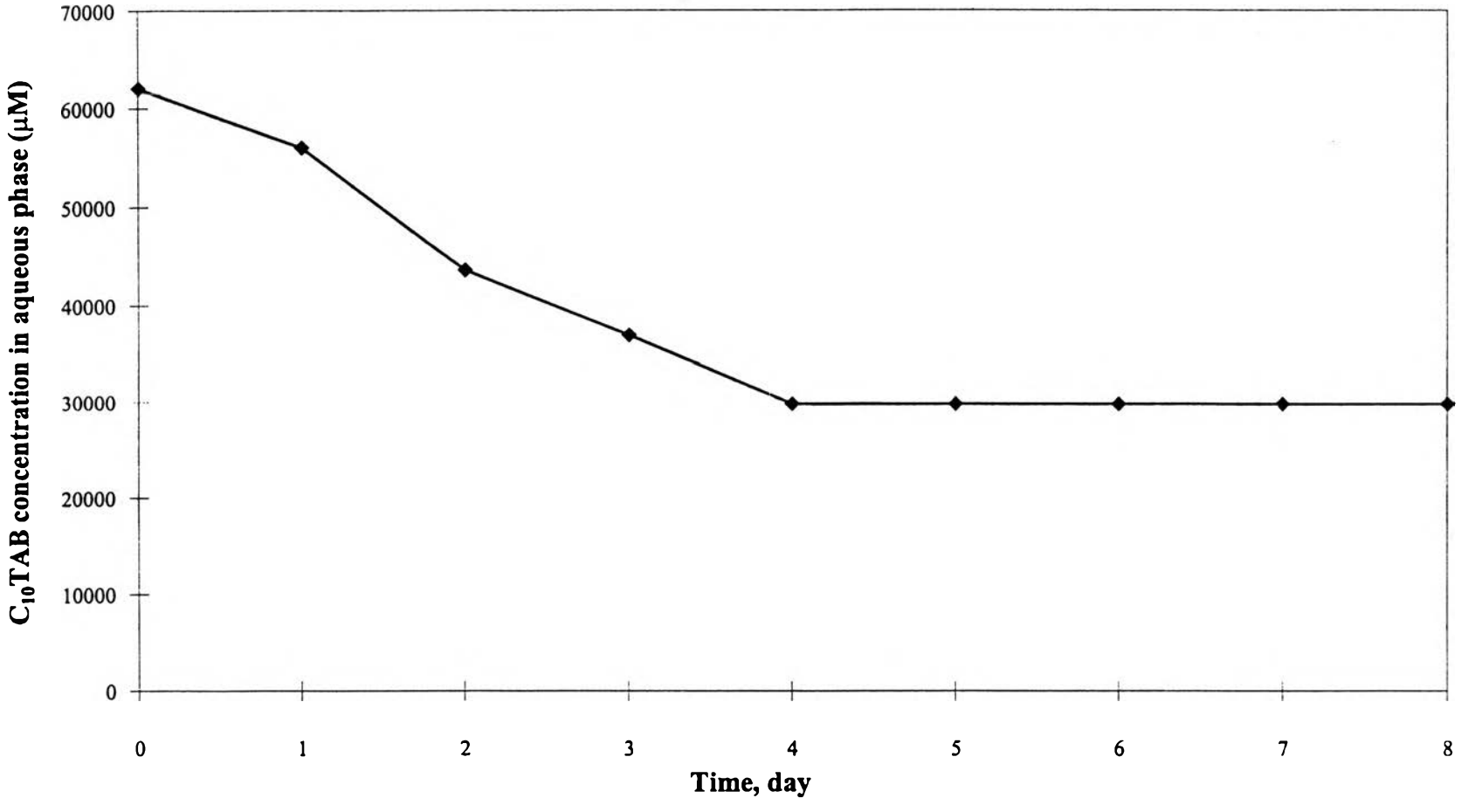

Figure 4-5 Dynamic adsorption of decyltrimethylammonium bromide (C_{10}TAB) on MCM-41

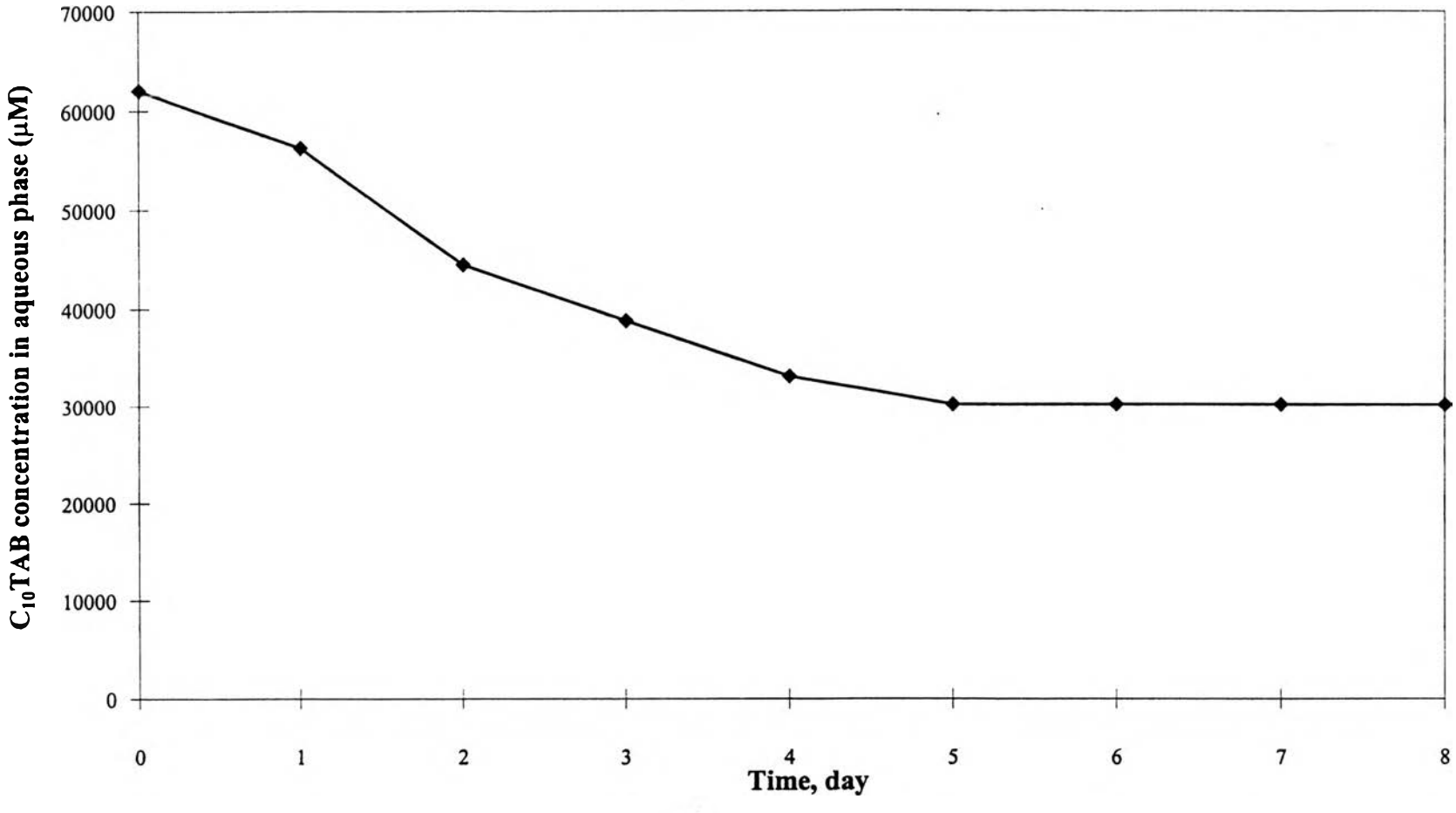

Figure 4-6 Dynamic adsorption of decyltrimethylammonium bromide (C_{10}TAB) on Hi-Sil 255

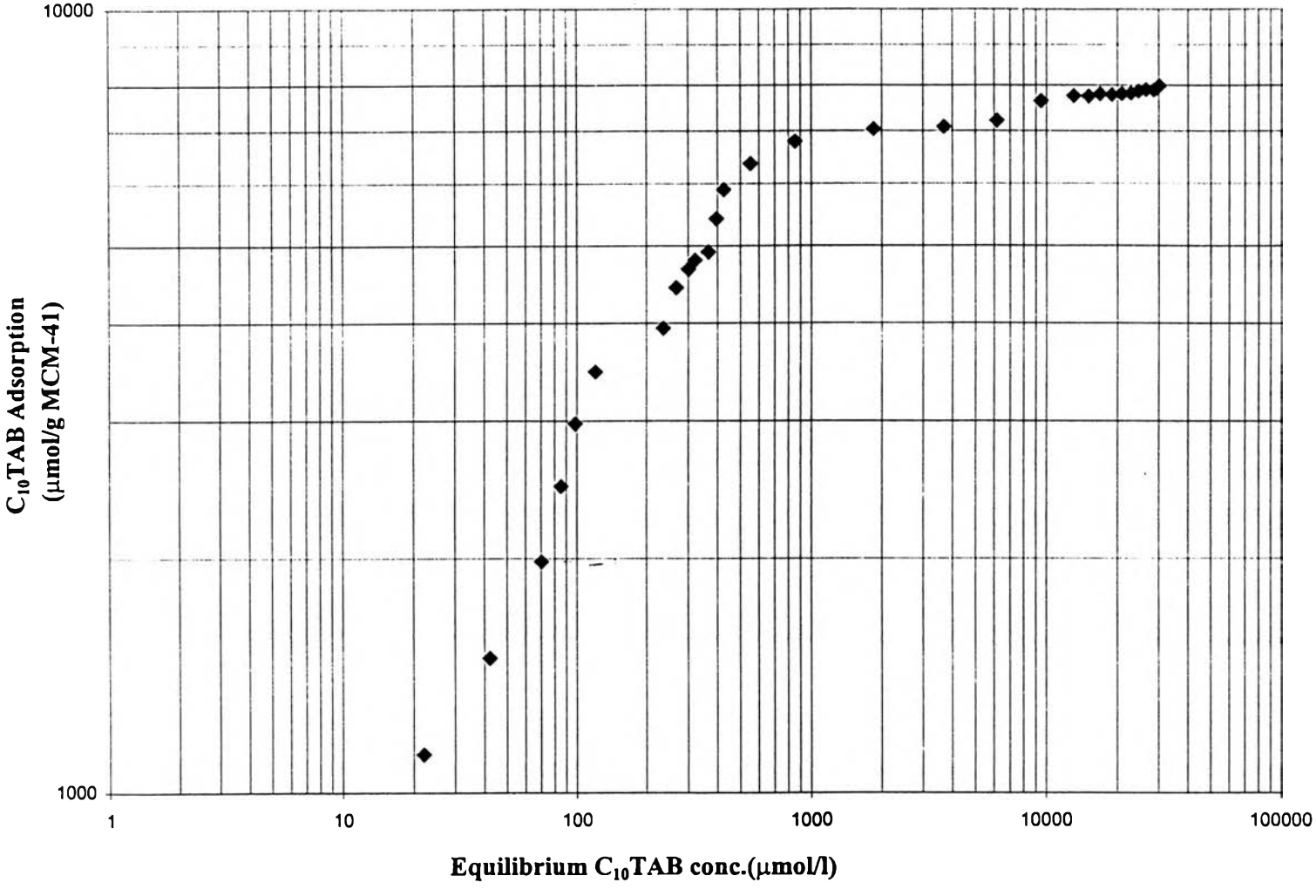

Figure 4-7 C_{10}TAB Adsorption Isotherm on MCM-41

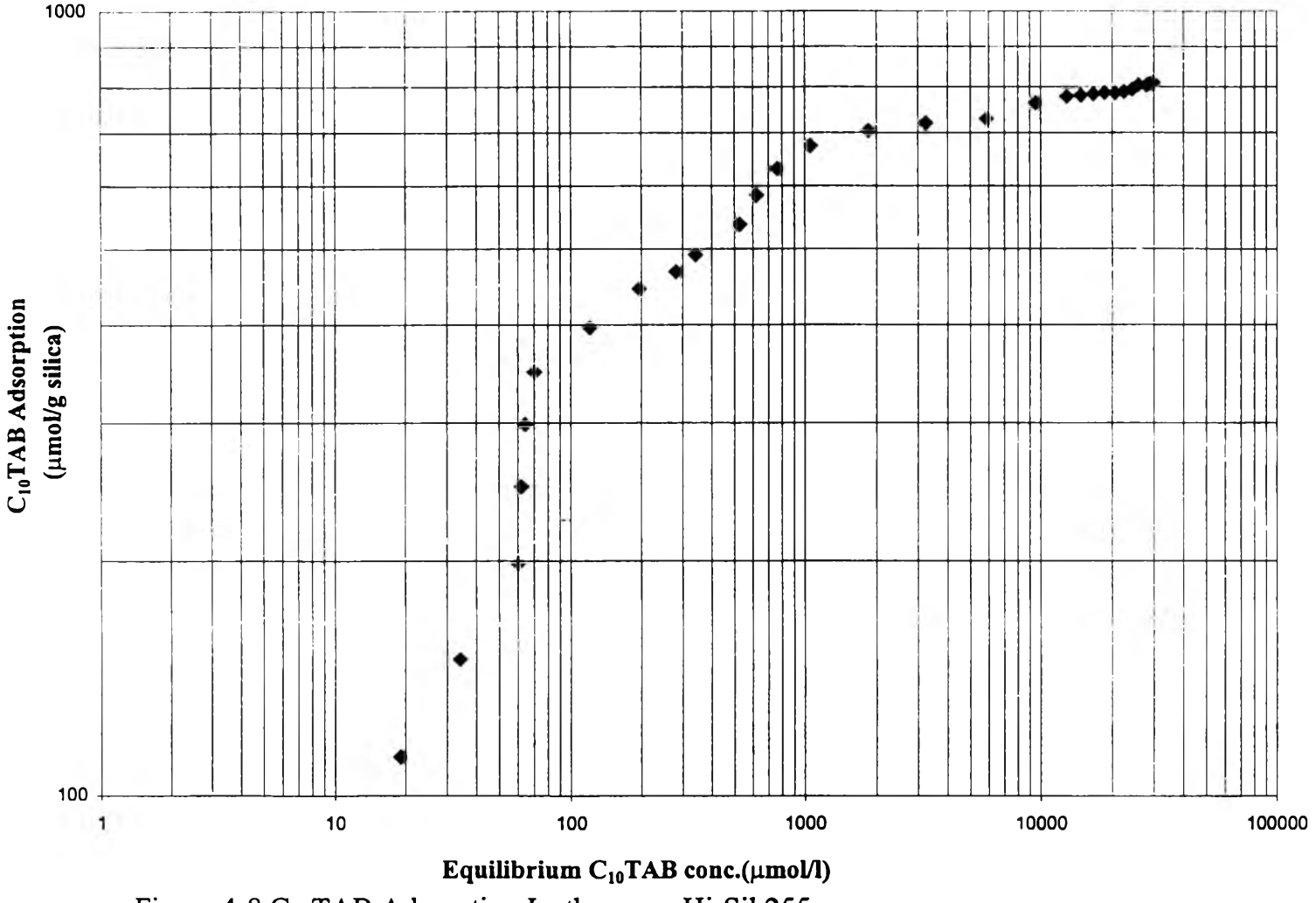

Figure 4-8 C_{10}TAB Adsorption Isotherm on Hi-Sil 255

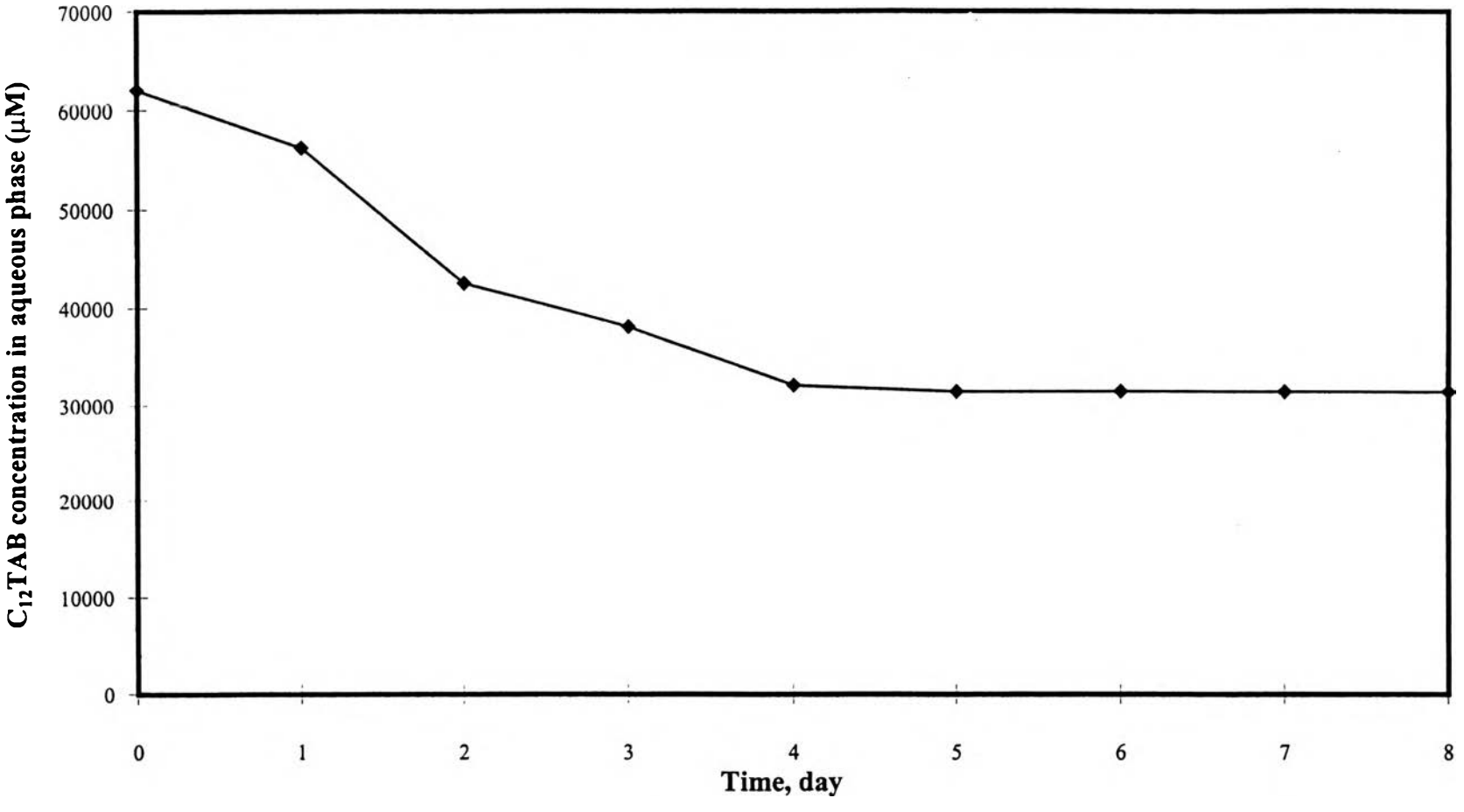

Figure 4-9 Dynamic adsorption of dodecyltrimethylammonium bromide (C_{12}TAB) on MCM-41

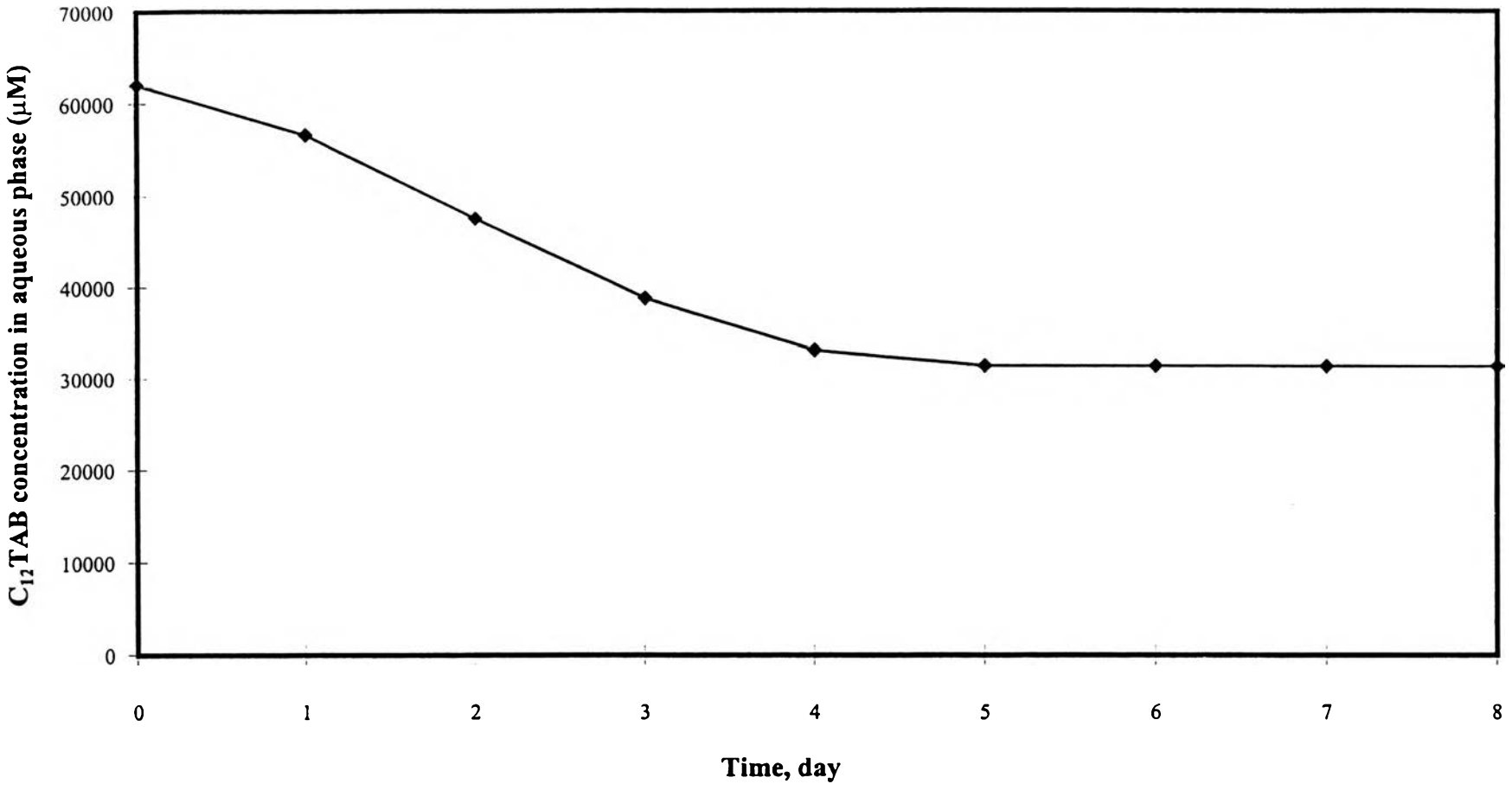

Figure 4-10 Dynamic adsorption of dodecyltrimethylammonium bromide (C_{12}TAB) on Hi-Sil 255

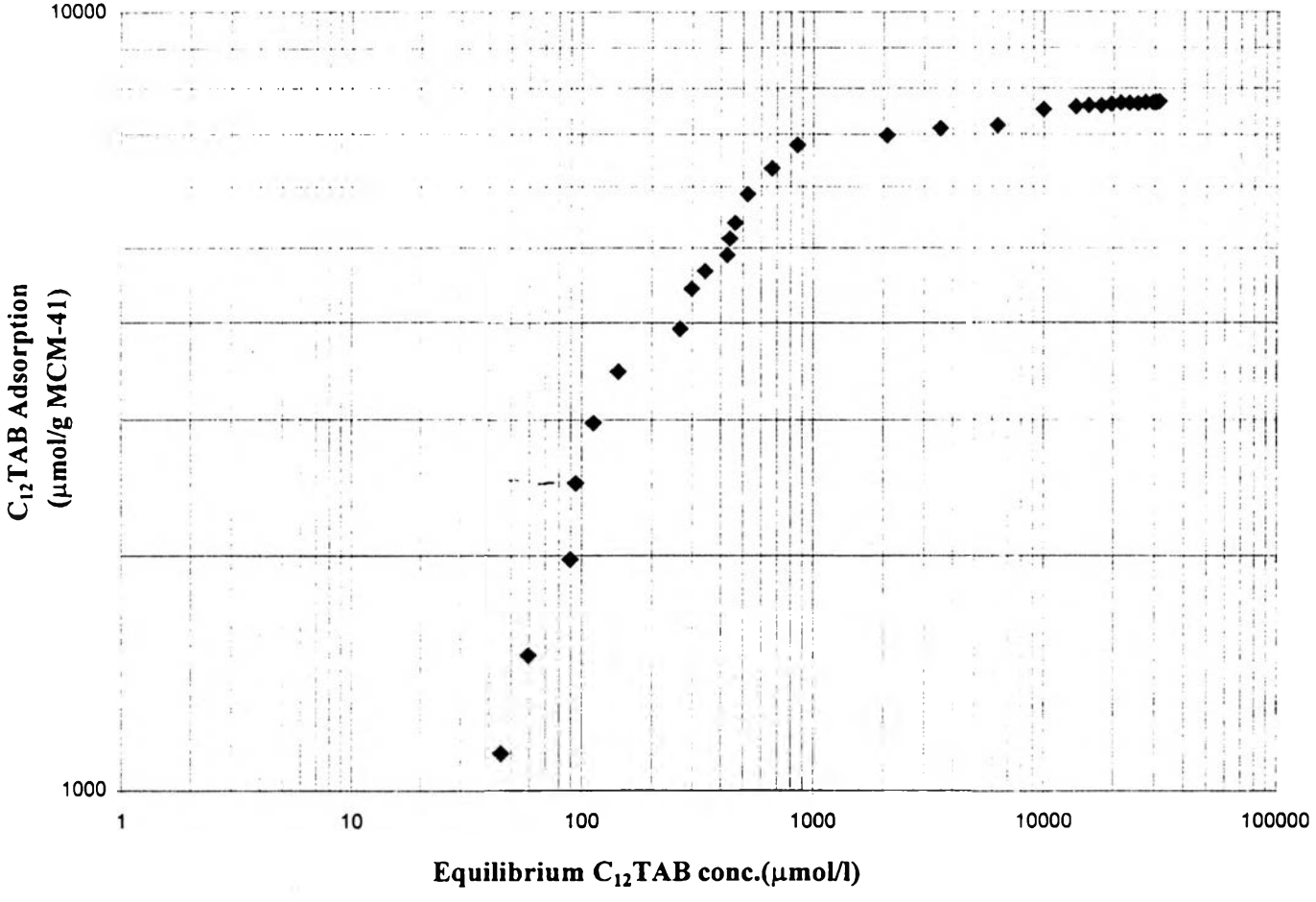

Figure 4.11 C_{12}TAB Adsorption Isotherm on MCM-41.

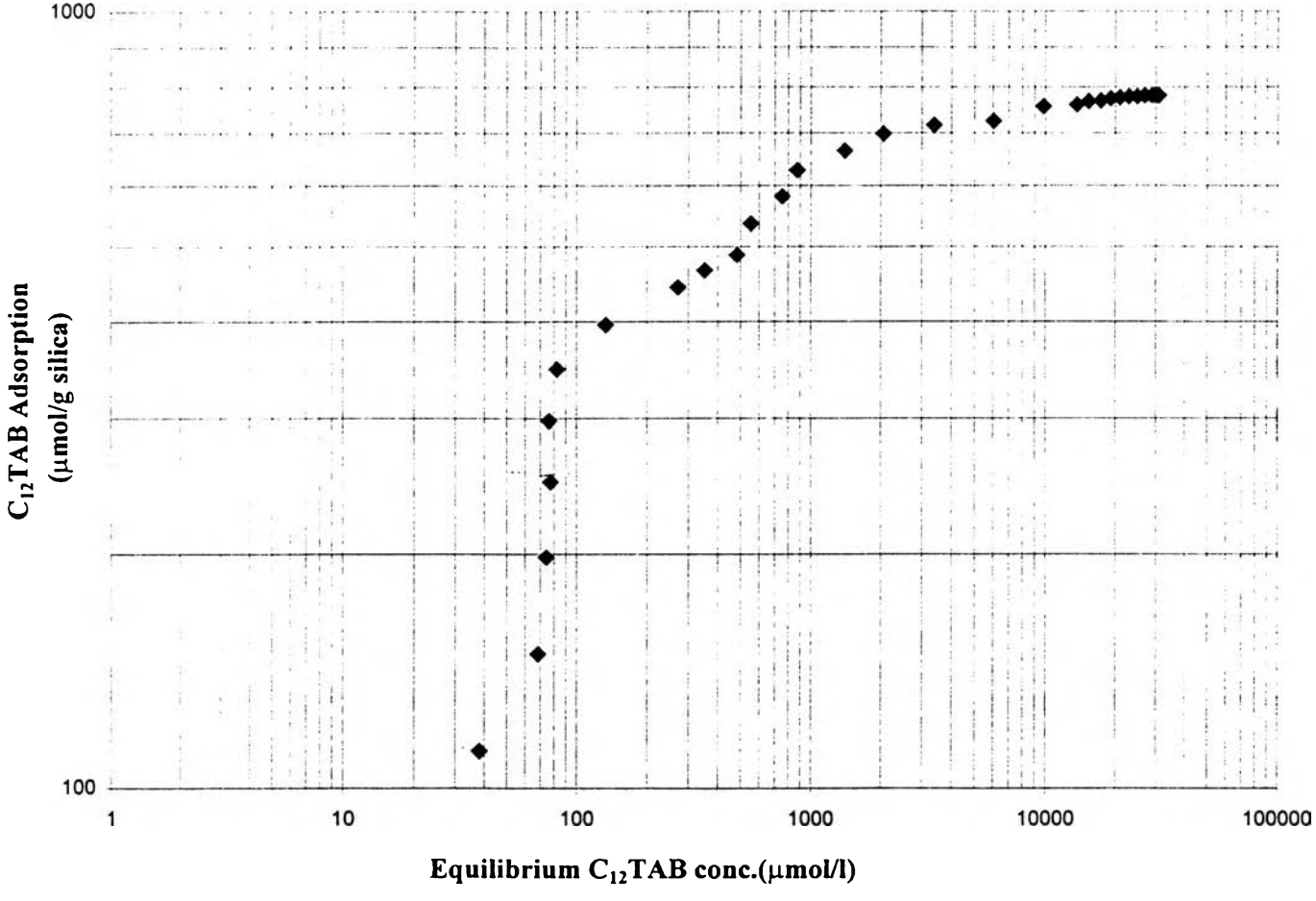

Figure 4.12 C_{12}TAB Adsorption Isotherm on Hi-Sil 255.

surfactant on MCM-41 and Hi-Sil 255 exhibit the characteristics of regions II, III, and IV (See Figures 4.11 and 4.12). For MCM-41,a shape slope is occured from the range of the dodecyltrimethylammonium bromide concentration in the aqueous solution of 45 μM to 570 μM as shown in Figure 4.11. For Hi-Sil 255, the concentration interval of 40 μM to 340 μM gives a shape increase in adsorptin of dodecyltri-methylammonium bromide on its surface as shown in Figure 4.12. When based on monolayer coverage, MCM-41 gives a 4.55 molecule/nm^2 or 22 $Å^2$/molecule which could be implied for the area of hemimicelle formation per molecule for dodecyltrimethylammonium bromide. For Hi-Sil 255, this solid allows a coverage of 2.76 molecule/nm^2 or 36 $Å^2$/molecule. Again, for the case of C_{10}TAB, the maximum adsorption of MCM-41 was much higher than the one of Hi-Sil 255.

4.4 Tetradecyltrimethylammonium Bromide Adsorption Isotherm

The dynamic adsorption behavior of tetradecyltrimethylammonium bromide to be adsorbed on MCM-41 and Hi-Sil are shown in Figures 4.13 and 4.14, respectively. The adsorption isotherms of tetradecyltrimethylammonium bromide on both MCM-41 and Hi-Sil 255 exhibit 3 regions of II, III and IV as shown in Figures 4.15 and 4.16, respectively. For the adsorption isotherm of tetradecyltrimethylammonium bromide on MCM-41, a shape increase in adsorption (region II) appeared at the concentration interval of 90 to 490 μM which is an onset of tetradecyltrimethylammonium bromide aggregation on the surface. For this surfactant, MCM-41 gives a monolayer coverage of 4.43 molecule/nm^2 or approximately 23 $Å^2$/molecule compared to Hi-Sil 255 which allows a coverage of 2.65 molecule/nm^2 or 38 $Å^2$/molecule.

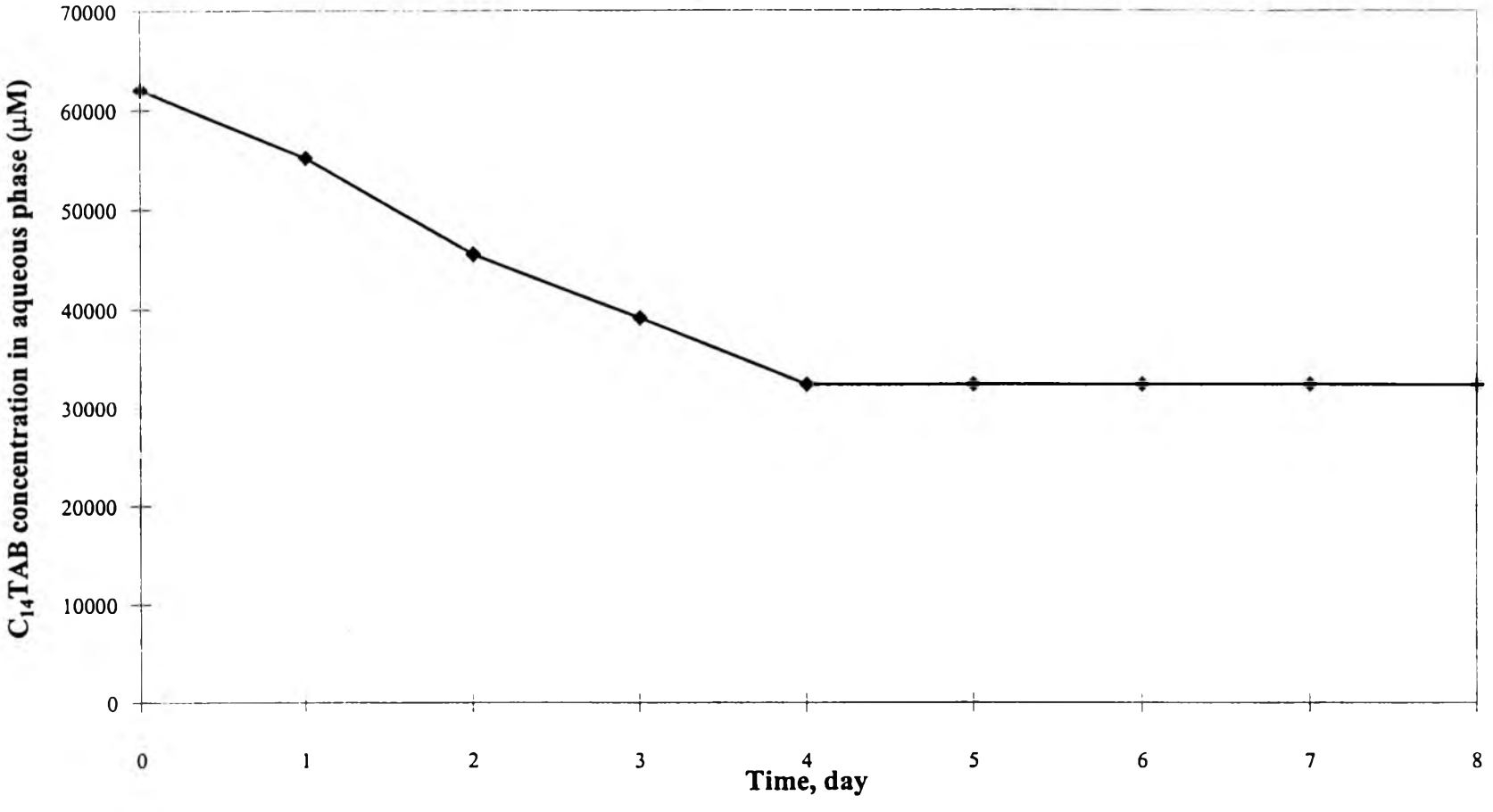

Figure 4-13 Dynamic adsorption of tetradecyltrimethylammonium bromide (C_{14}TAB) on MCM-41

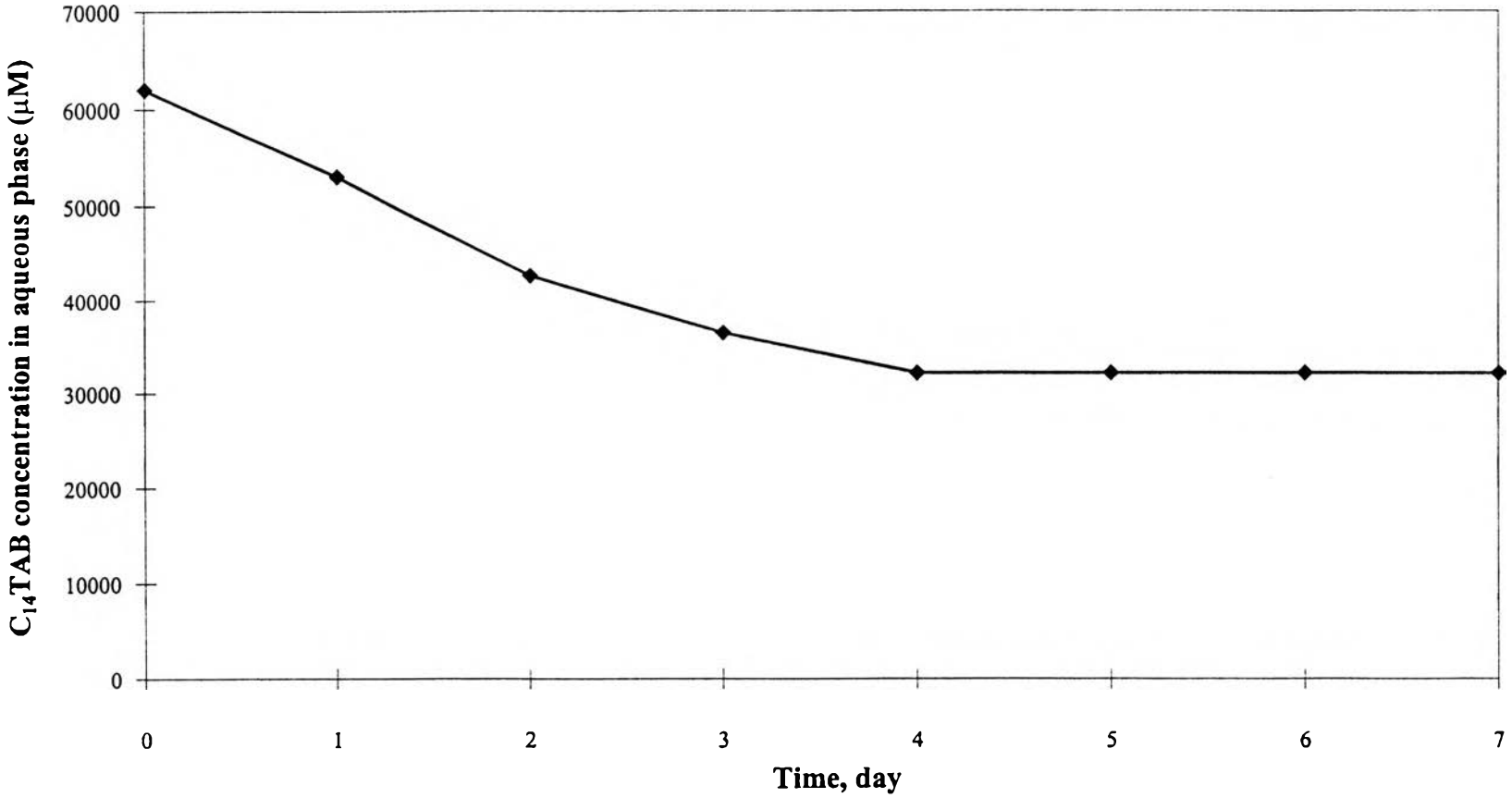

Figure 4-14 Dynamic adsorption oftetradecyltrimethylammonium bromide (C_{14}TAB) on Hi-Sil 255

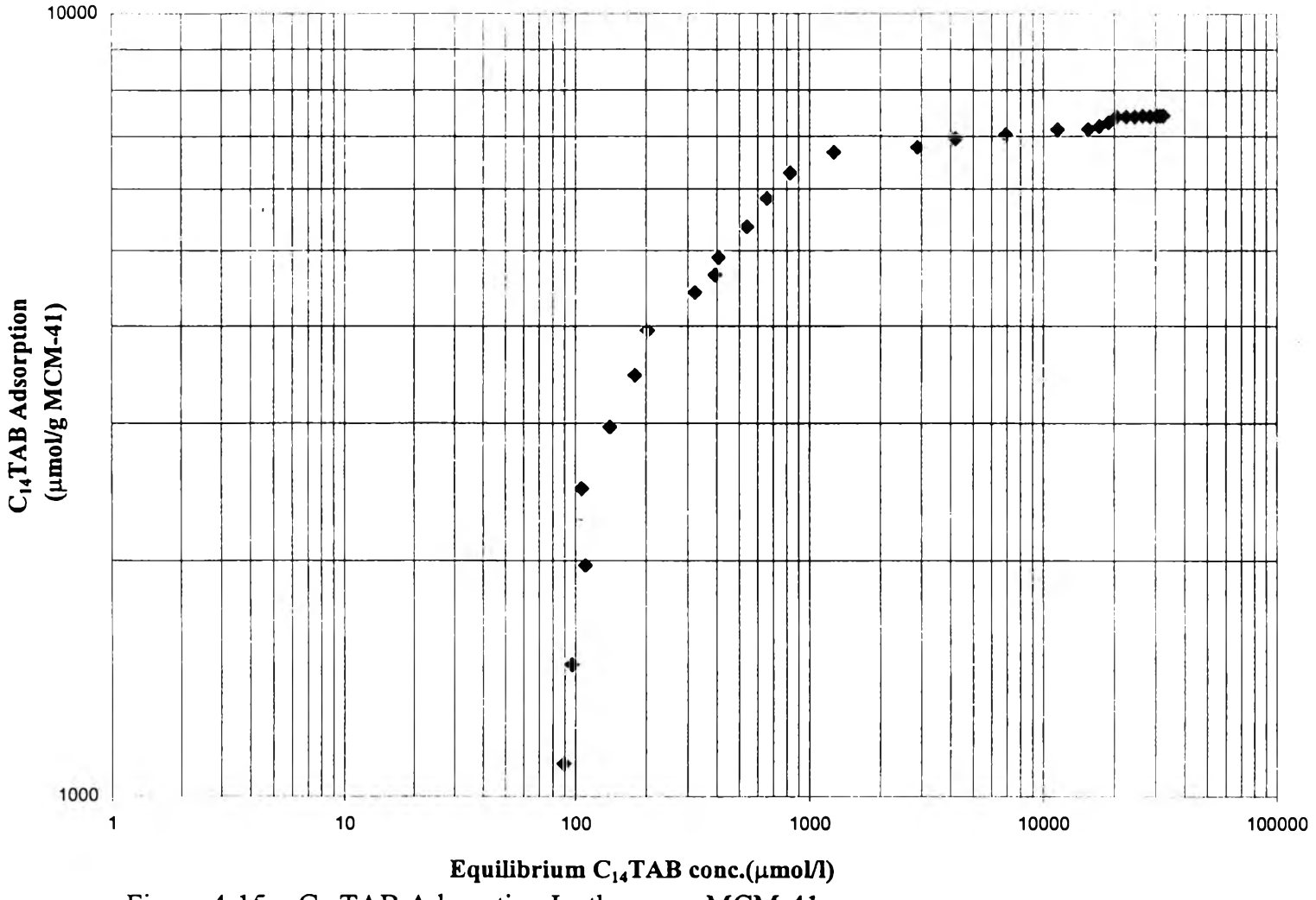

Figure 4-15 C_{14}TAB Adsorption Isotherm on MCM-41

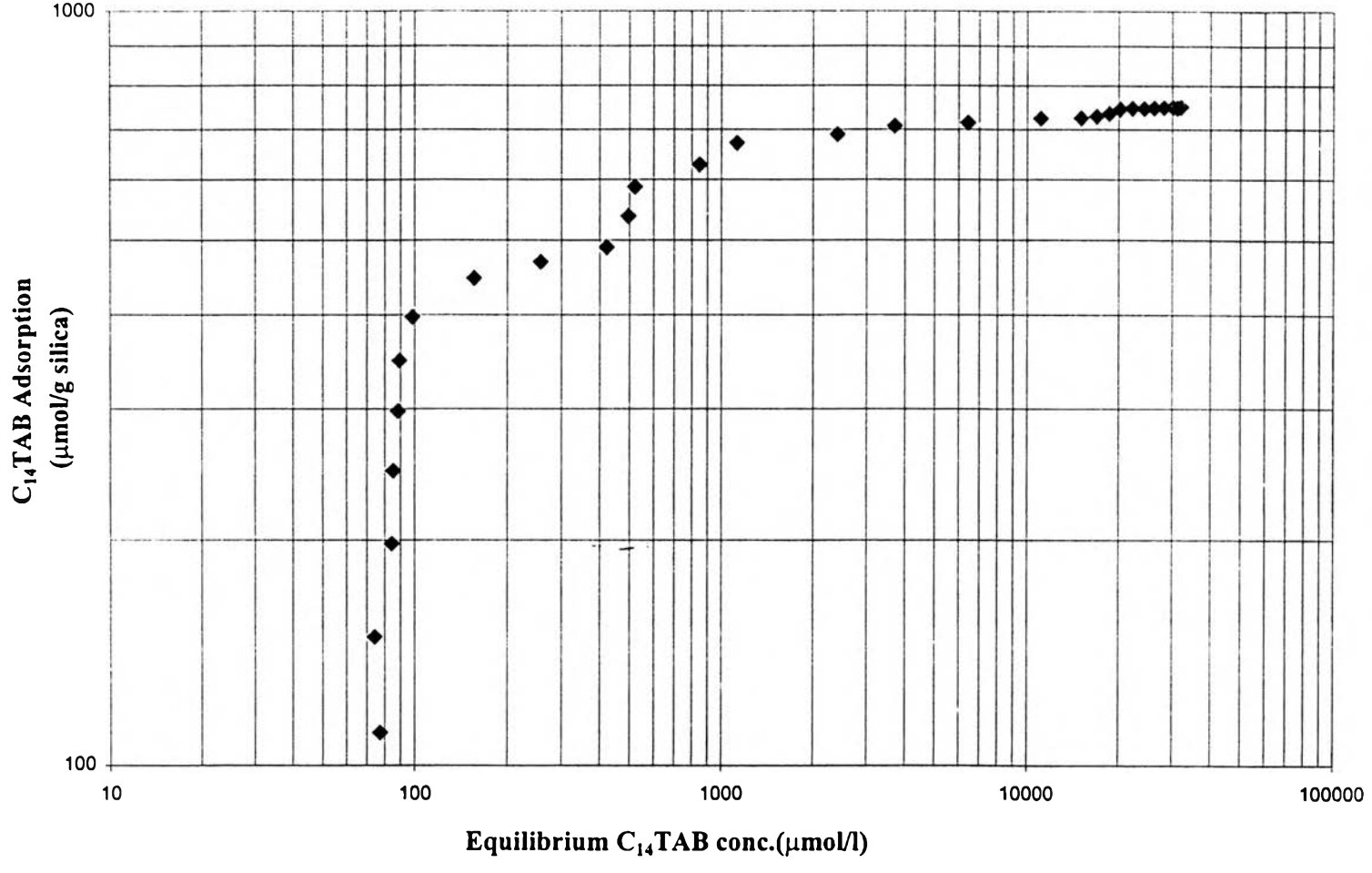

Figure 4-16 C_{14}TAB Adsorption Isotherm on Hi-Sil 255

4.5 Cetyltrimethylammonium Bromide Adsorption Isotherm

The dynamic adsorption behavior of cetyltrimethylammonium bromide adsorption on MCM-41 and Hi-Sil 255 are illustrated in Figures 4.17 and Figure 4.18, respectively. Figure 4.19 and 4.20 illustrate 3 regions of II, III and IV of the adsorption isotherms of both MCM-41 and Hi-Sil 255. In comparison to C_8TAB, C_{10}TAB, C_{12}TAB and C_{14}TAB, cetyltrimethylammonium bromide (C_{16}TAB) had the highest slope for the II region of the adsorption isotherm for both MCM-41 and Hi-Sil 255 as seen in Figure 4.19 and 4.20. This result indicates that C_{16}TAB has the strongest adsorption and the lowest measured equilibrium concentration (O'Haver et al,1994). The maximum adsorption of cetyltrimethylammonium bromide on MCM-41 and Hi-Sil 255 were approximately 7000 μmol/g. and 700 μmol/g., respectively. At plateau region, when based on monolayer coverage, MCM-41 could allow a coverage of 4.19 molecule/nm^2 or around 24 Å^2/molecule and Hi-Sil 255 gave a coverage of 2.55 molecule/nm^2 or 39 Å^2/molecule for cetyltrimethylammonium bromide .

4.6 Effect of number of carbons of surfactant tail on the adsorption density

From Figure 4.21, it is noticed that when the number of carbons in the surfactant tail is increased, at the transition point of the region II/III of any isotherms, the adsorption density of five cationic surfactants with different number of carbons (8, 10, 12, 14, and 16) is decreased. The adsorption density that could be read out from octyltrimethylammonium bromide (8 carbon atoms in the surfactant tail) isotherm at II/III transition point is about 3.83 molecule/nm^2, decyltrimethylammonium bromide (10 carbon atoms in the surfactant tail) is 3.71 molecule/nm2, dodecyltrimethylammonium bromide (12

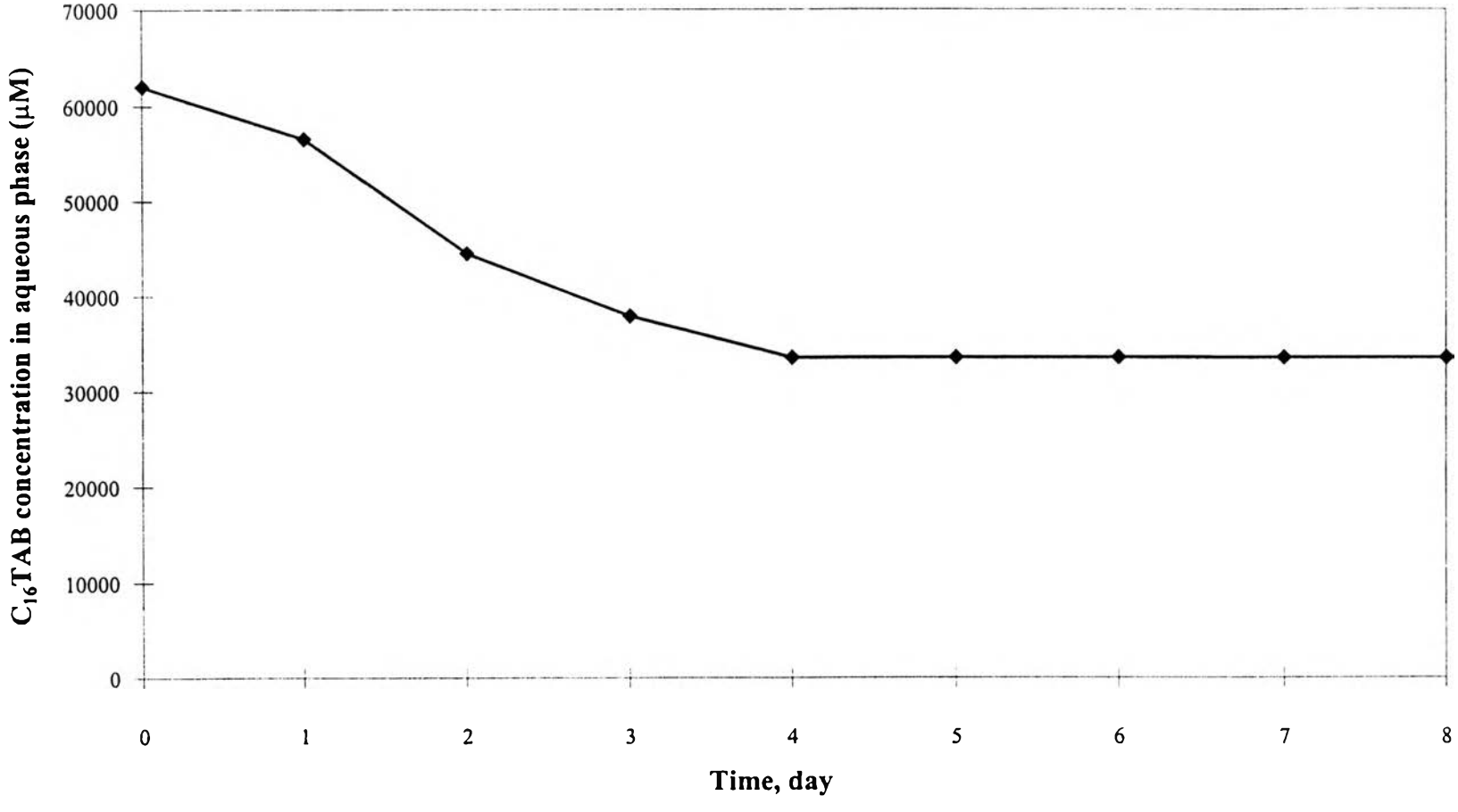

Figure 4-17 Dynamic adsorption of cetyltrimethylammonium bromide (C_{16}TAB) on MCM-41

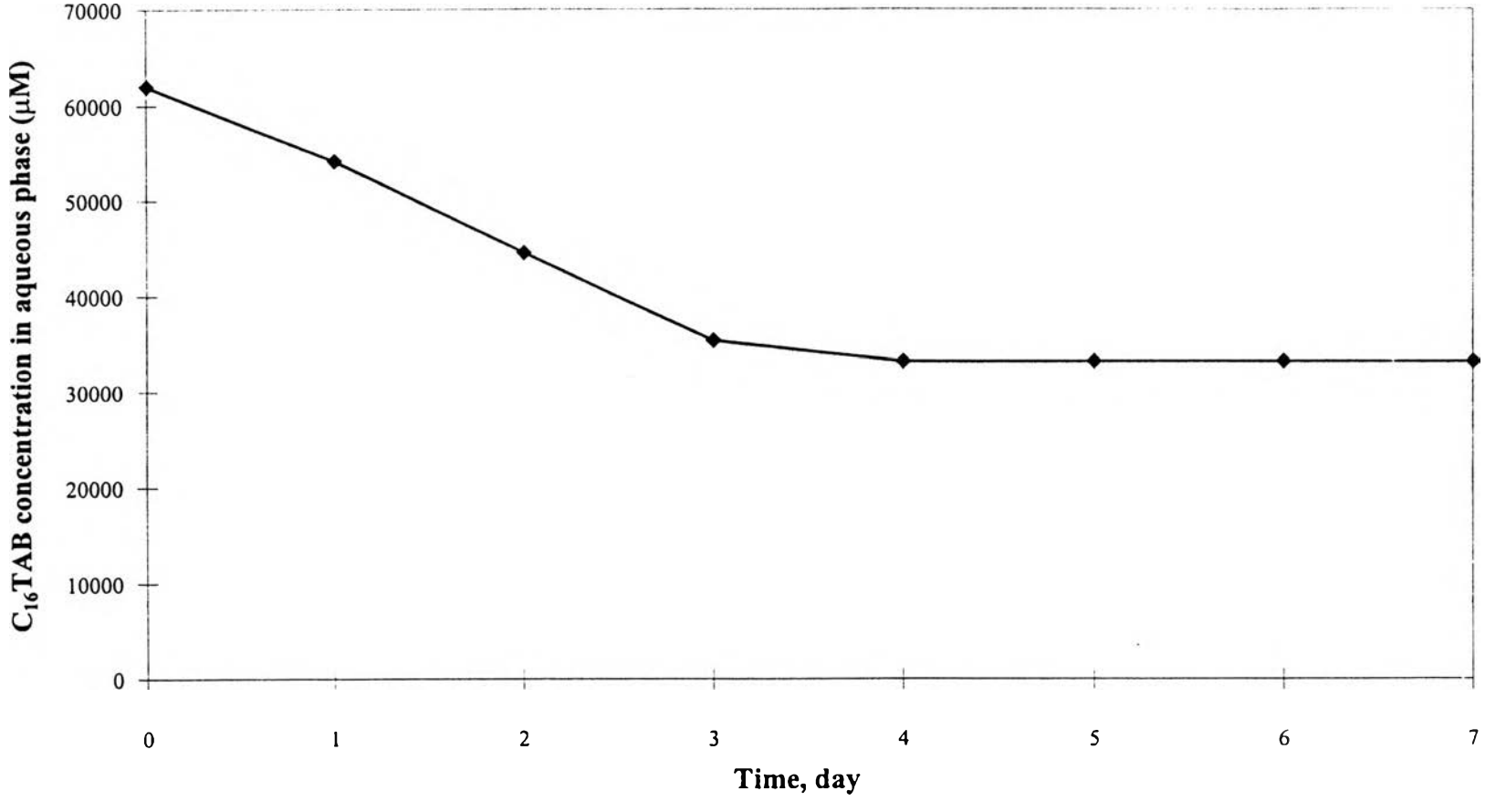

Figure 4-18 Dynamic adsorption of cetyltrimethylammonium bromide (C_{16}TAB) on Hi-Sil 255

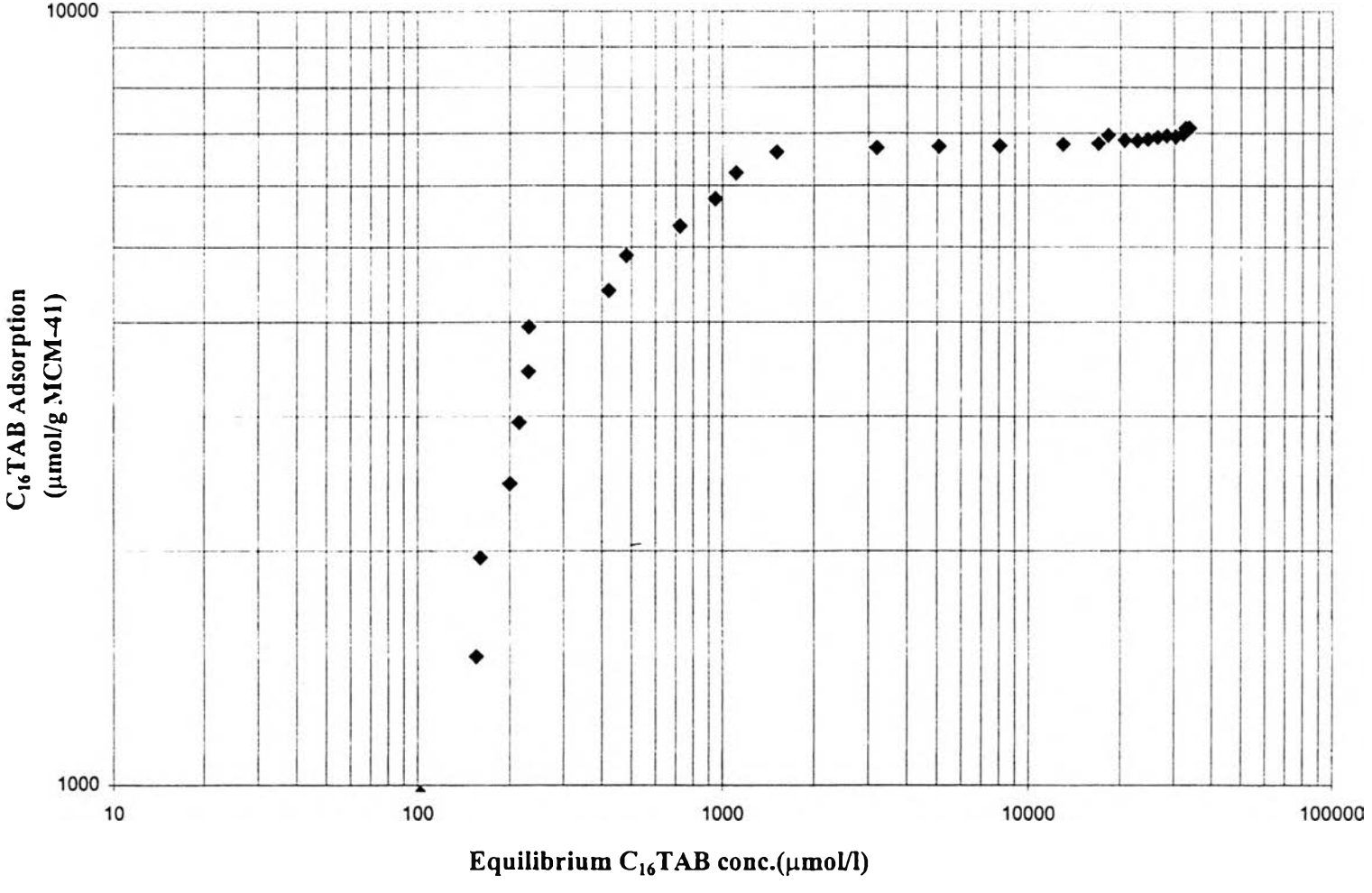

Figure 4-19 C_{16}TAB Adsorption Isotherm on MCM-41

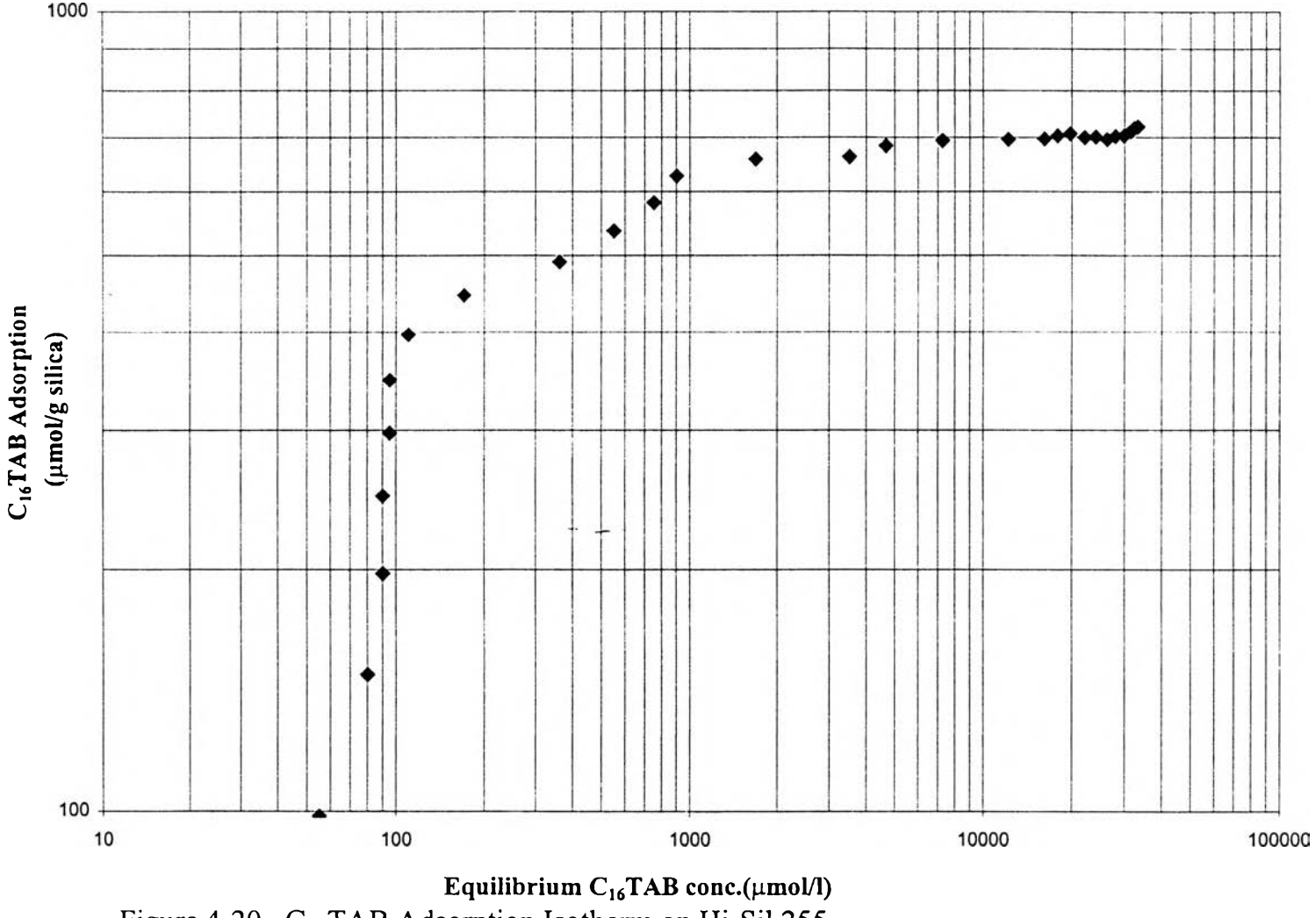

Figure 4-20 C_{16}TAB Adsorption Isotherm on Hi-Sil 255

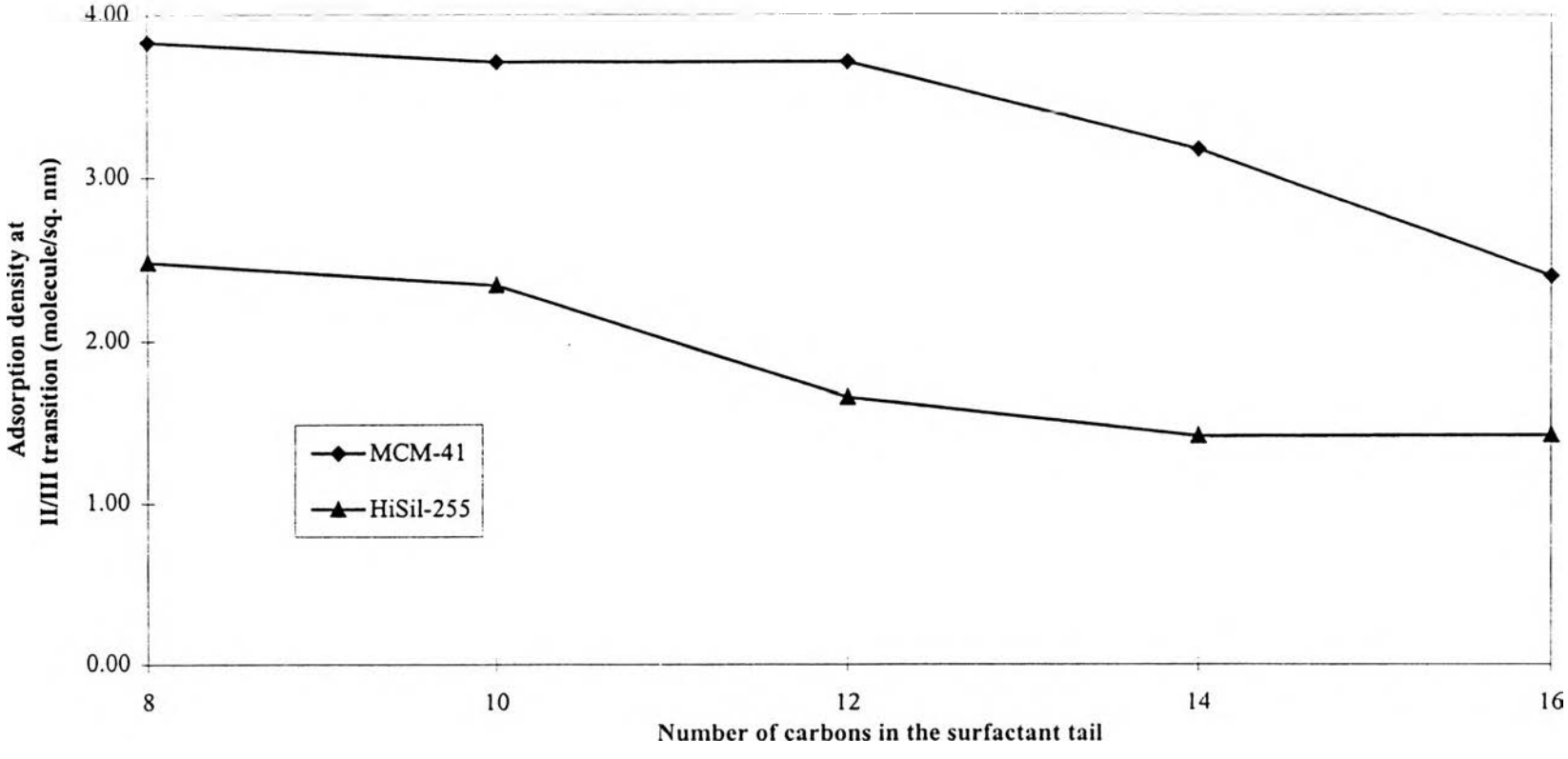

Figure 4-21 Adsorption density at region II/III transition of MCM-41 and HiSil-255 at different number of carbons in the surfactant tail

carbon atoms in the surfactant tail) is 3.71 molecule/nm^2, tetradecyltrimethyl-ammonium bromide is 3.17 molecule/nm^2 and cetyltrimethylammonium bromide is 2.40 molecule/nm^2 for MCM-41. A similar pattern of adsorption density was also observed for adsorption on Hi-Sil 255 when the number of carbons in surfactant tail was increased as the following values: 2.48, 2.34, 1.65, 1.41, and 1.42 molecule/nm2 for octyltrimethylammmonium bromide, decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and cetyltrimethylammonium bromide, respectively.

For the adsorption density at the III/IV transition point which is the point that indicates the successfully formed of admicelles on the solid was found to be decreased when the number of carbons in the surfactant tail is increased the same as detected at the transition point of region II/III as shown in Figure 4.22. The values of adsorption density are 4.73, 4.43, 4.37, 4.19, and 2,40 molecule/nm^2 for MCM-41 and 2.76, 2.49, 2.36, 2.23, and 1.42 for Hi-Sil 255. Both groups of adsorption density values are referred to octyltrimethyl-ammonium bromide, decyltrimethylammonium bromide, dodecyltrimethyl-ammonium bromide, tetradecyltrimethylammonium bromide, and cetyltri-methylammonium bromide, respectively. So it can be implied that the pore size distribution of MCM-41 is more uniform than that of Hi-Sil 255.

4.7 The Effect of Surfactant Tail Length on Adsorption Density

Due to the C-C bond length in the surfactant tail is around 1.1Å thus octyltrimethylammonium bromide has 8.8 Å tail length, decyltri-methylammonium bromide has 11 Å tail length, dodecyltrimethylammoniuim bromide has 13.2 Å tail length, tetradecyltrimethylammonium bromide has 15.4

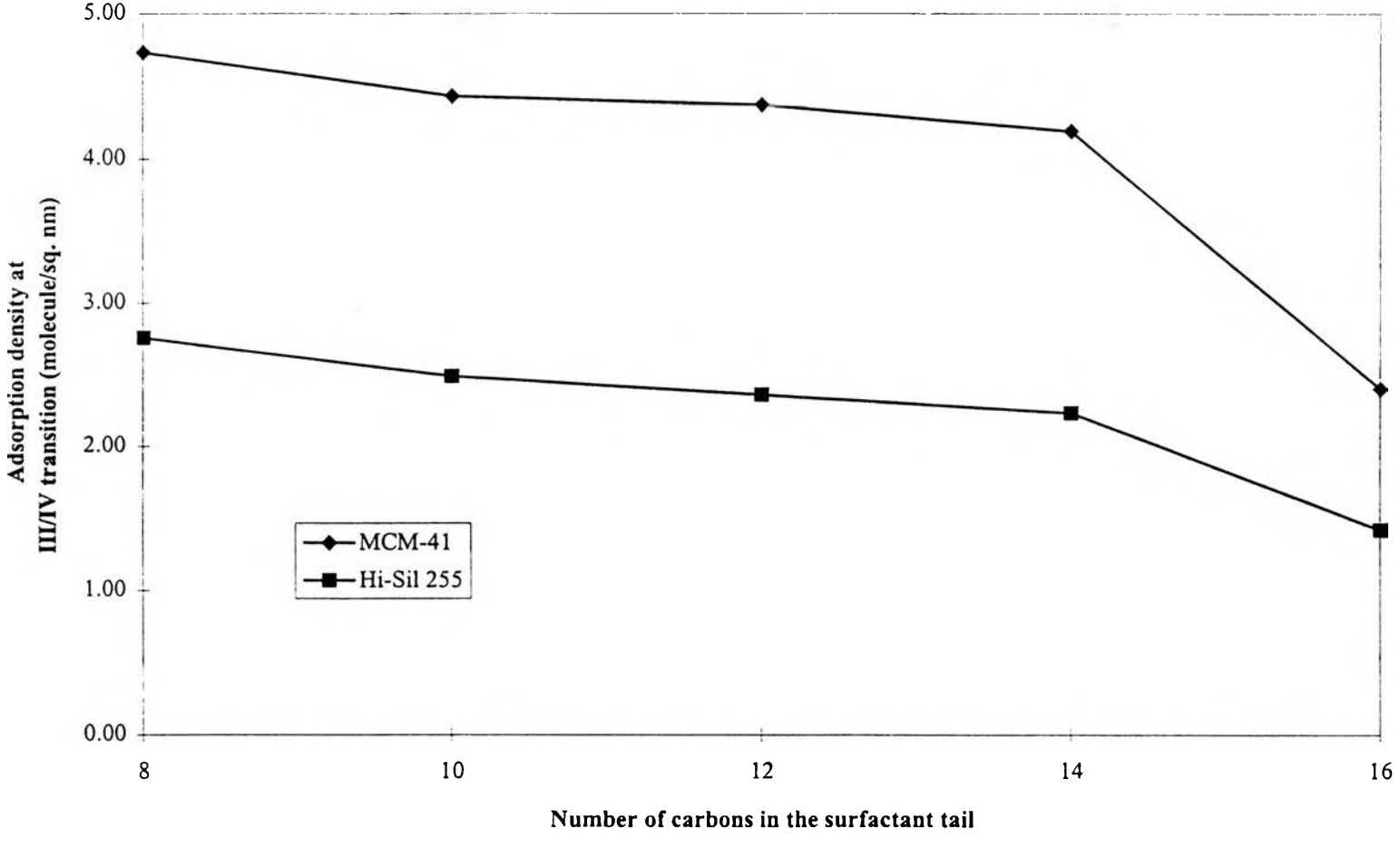

Figure 4-22 Adsorption density at region III/IV transition of MCM-41 and Hi-Sil 255 at different number of carbons in the surfactant tail

Å tail length and cetyltrimethylammonium has 17.6 Å tail length. The longer the tail length of the surfactant will cause the lower in adsorption density on both MCM-41 and Hi-Sil 255 as be shown in Figures 4.23-4.25.

Figure 4.23 which is a plot between the number of carbons in the surfactant tail and the maximum adsorption density of each surfactant on MCM-41 and Hi-Sil 255. It is observed that when the number of carbon atoms in the surfactant tail length was increased an increased in the surfactant tail length, the adsorption density of each surfactant decreased linearly. For octytrimethylammonium bromide which is the shortest surfactant tail length in this experiment, it gave the maximum adsorption densities on both MCM-41 and Hi-Sil 255 with the values of 4.91 and 2.98 molecule/nm^2 compared to the minimum values of 4.19 and 2.55 molecule/nm^2 for cetyltrimethylammonium bromide, respectively. The decrement of adsorption density is clearly due to the effect of the tail length of the surfactant that causes other surfactant monomers hardly enter into the pores of the solid substrate as shown in Figures 4.24 and 4.25 for MCM-41 and Hi-Sil 255, respectively. It can be seen that for MCM-41 which has the average pore diameter of 36 Å, when the ratio of the length of surfactant ion to the diameter of the average pore increases, the adsorption density decreases. For Hi-Sil 255 that possesses the average pore diameter around 194 Å (from N_2-BET adsorption), when the length to diameter ratio increases, the adsorption density will also declines. As a result, the longer the surfactant tail length results in the lower the adsorption density.

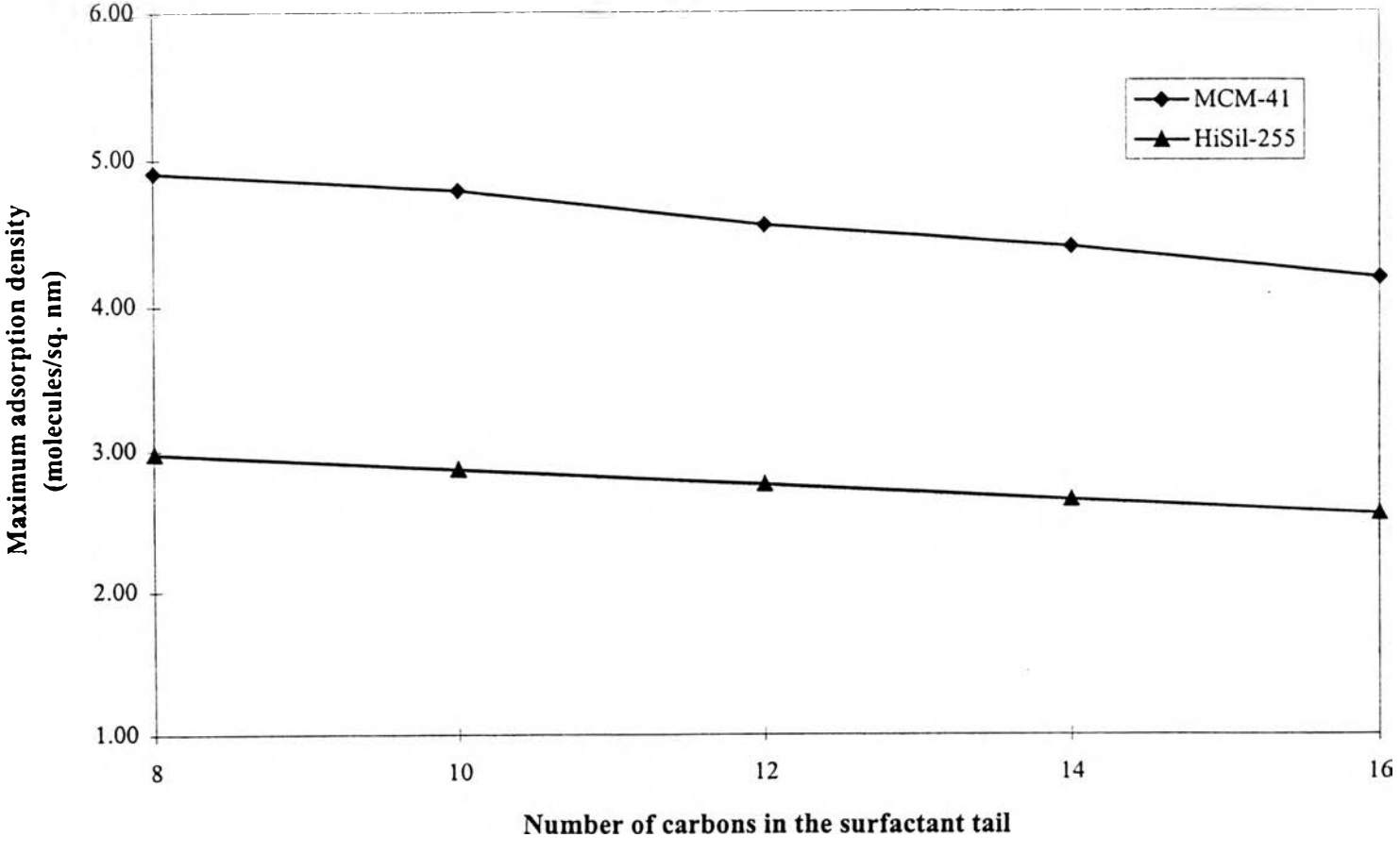

Figure 4-23 Maximum adsorption density of MCM-41and Hi-Sil 255 at different number of carbons in the surfactant tail

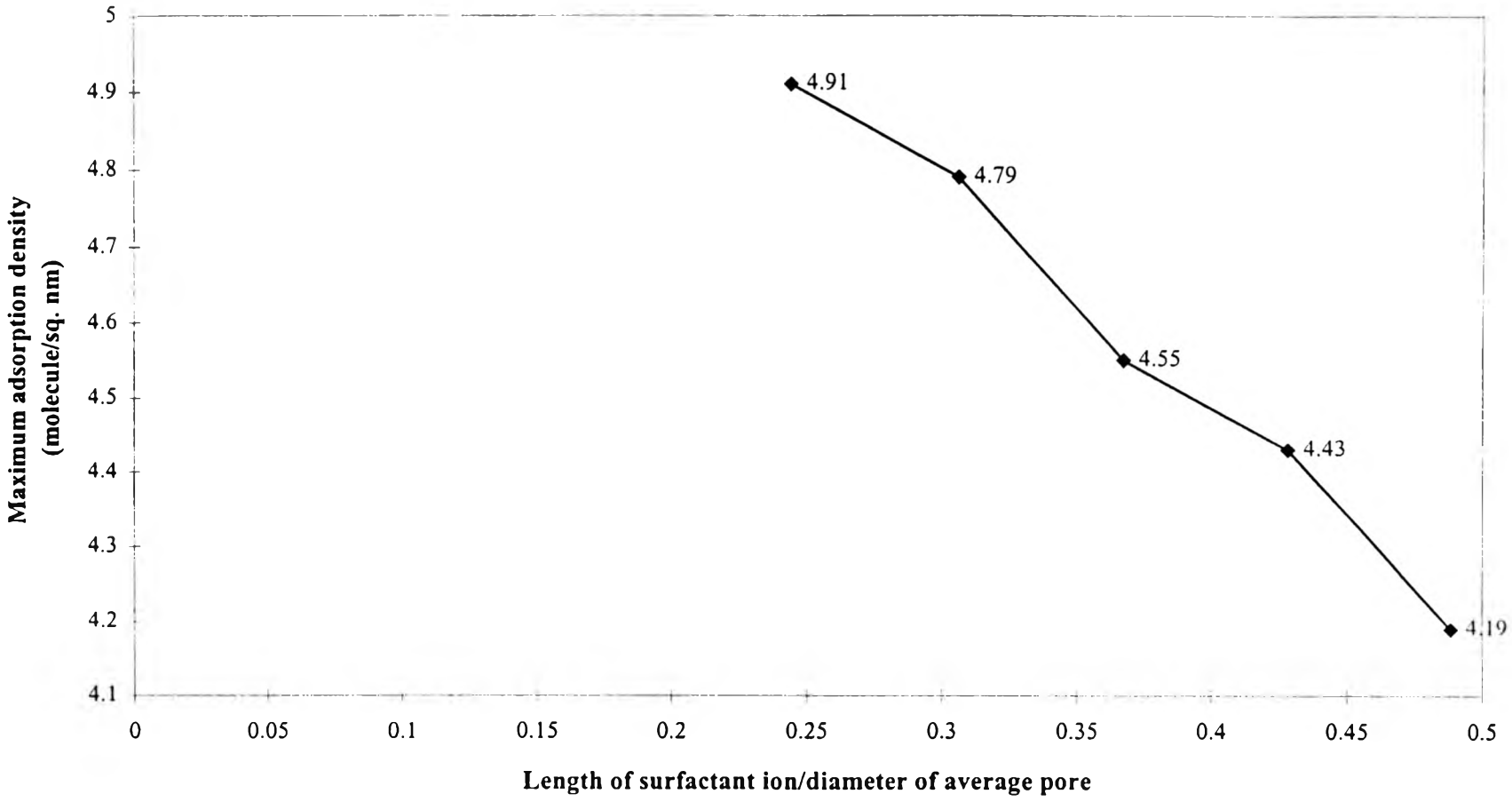

Figure 4-24 Maximum adsorption density of MCM-41at different length of surfactant ion/diameter of the average pore

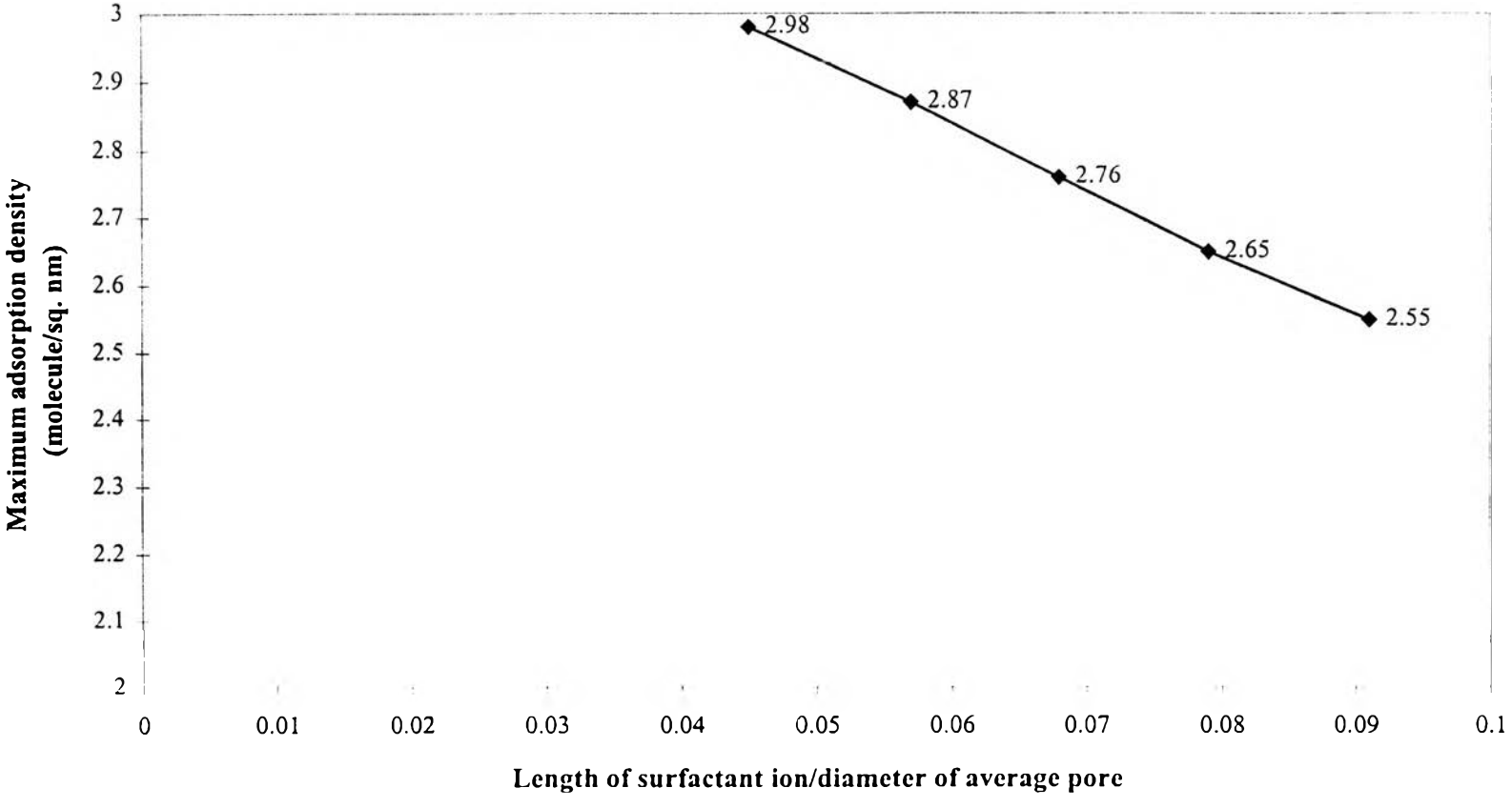

Figure 4-25 Maximum adsorption density of Hi-Sil 255 at different length of surfactant ion/diameter of the average pore