

CHAPTER IV

RESULTS AND ANALYSIS -- THE MODEL

4.1 Introduction

These curves were for 5 types of alumina powder (samples #1 to #5 respectively). These 5 types of alumina powder differed in surface nature as well as pore size distribution. For each type of alumina powder, data obtained by method 1 and method 2 were plotted and compared. Then the phenol adsolubilization curves of method 2 (SDS adsorption first, phenol adsolubilization after the equilibrium of SDS adsorption) of these 5 alumina types were analyzed and compared, combined with the BET reports of pore size distribution of these 5 types of alumina powder. The adsolubilization kinetics curves were fit with a first order model, and an adsorption/adsolubilization model was proposed to explain the phenomena observed in the experiment.

All kinetics curves of phenol adsolubilizing into already-adsorbed SDS admicelles (by method 2) of the eight types of alumina powder used in the experiment show that the adsolubilization of phenol into SDS admicelles can be divided into two parts: a fast part and a slower part. In the fast part of the adsolubilization, the drop of phenol absorbance is very fast (within 1 minute). A similar result was reported by Yu in his thesis [Yu, C., Ph.D dissertation, University of Oklahoma]. Then the drop of phenol absorbance appears much slower. The processes of samples #1 to #5 are shown as below (Figures 4-2 -- 4-6).

4.2 The Supposed Adsolubilization Model

4.2.1 A Supposed Model inside the Pore

It is estimated that the theoretical length of fully extended hydrocarbon tail of SDS surfactant is 16 Angstrom and the diameter of its headgroup is 7.8 Angstrom [C. Lee, M.A. Yeskie, ..., Incorporation of Alcohols into Admicelles, Langmuir, Vol. 6, No. 12, 1990, 1758]. Thus in sufficiently small diameter pores, the morphology of SDS admicellar layer should be constrained by the pore in which it forms. This constraint may affect both adsolubilization kinetics and the amount of adsolubilization into those admicelles in pores. The adsolubilization phenol adsolubilized into SDS admicelles in alumina pores may be pictured as in the following:

The surfactant chain may be kinked itself and angular to the alumina surface to some extent according to the surface properties of the alumina and the properties of solution. So the transfer pore size of bilayer into monolayer probably can not be carried out simply by using the theoretical sizes of SDS headgroup and chain. Actually how is the practical morphology of SDS admicelles inside the pores on alumina powder and the adsolubilization of phenol in the admicelles needs to be identified by further experiment.

Supposed Adsorption/adsolubilization model

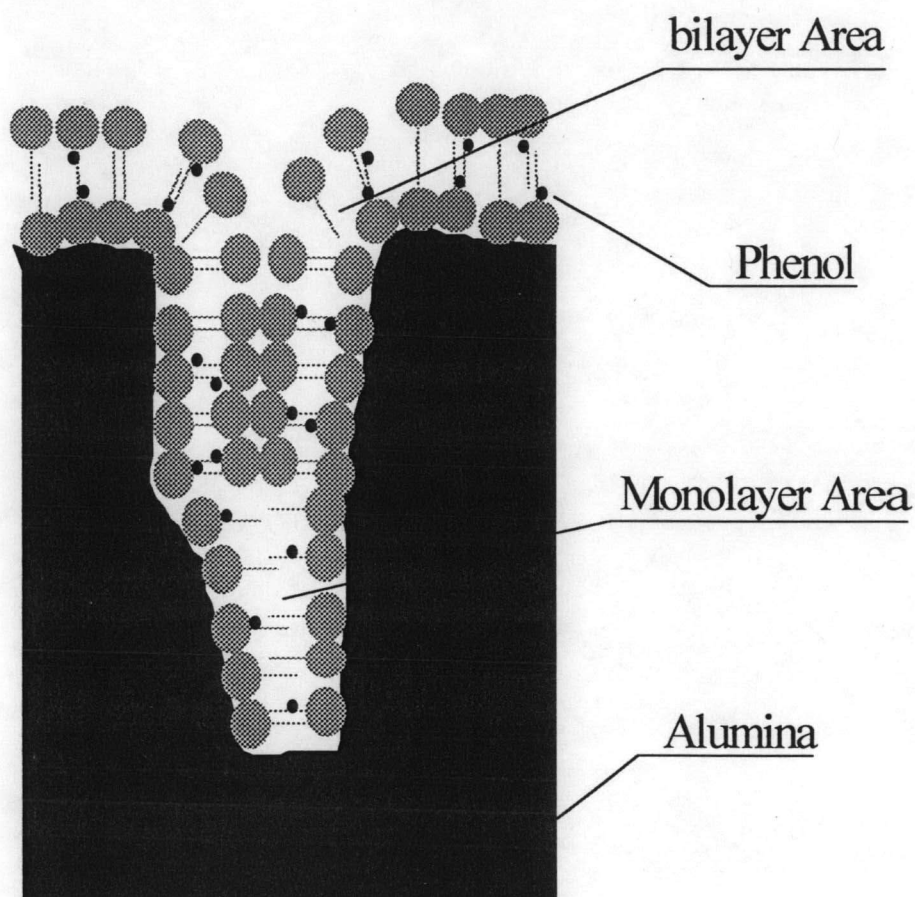


Figure 4.1 A supposed adsorption/adsolubilization model inside a pore.

4.2.2 Actual Cases

The actual cases of pore shapes and their distribution inside an alumina particle are much more complicated than the model shown in Fig. 4.1. A perfect model to describe the actual situations is not obtained in this experiment. It was confirmed by this experiment, however, that the adsolubilization of phenol into the admicelle - formed pores in alumina particles can be divided into two parts: a "fast" adsolubilization and a

“slow” adsolubilization. We hypothesize that the fast adsolubilization correspond to the diffusion in larger and smaller pores respectively. However, large particles of samples #7 and #8 were used in experiment, results show a decrease in fast part and an increase in slow adsolubilization. Since large and small particles of each sample have the same pore size distribution, this supports the explanations of hindered diffusion. As the particle size is increased, a smaller and smaller fraction of the particle is quickly reached by the diffusing phenol.

4.3 Data Analysis

4.3.1 First Order Model for the Slower Adsolubilization Part

A first-order model is used to match the slower part of adsolubilization, which is:

$$d(C)/dt = -k \cdot A \cdot C,$$

where

C is the bulk concentration of phenol in solution

k is the adsolubilization const.

A is the integration area of pores under transfer pore size

C is actually linearly proportional to the UV absorbance of phenol in solution because the concentration used in the experiment was not high, so if C is substituted by the Absorbance, the equation becomes as:

$$d(\text{Abs})/dt = -k \cdot A \cdot \text{Abs},$$

This equation can be solved to obtain:

$$\ln (\text{Abs}) = \ln (\text{Abs}_0) - k \cdot A \cdot t$$

Where Abs_0 is the initial UV absorbance of phenol in solution, t is the experiment time counted from the beginning. This first-order model fits the curves quite well, with numerically close slopes for those of the same (similar) surface properties, but different slopes for those of different surface properties, as shown in Figures 4-7 -- 4-11.

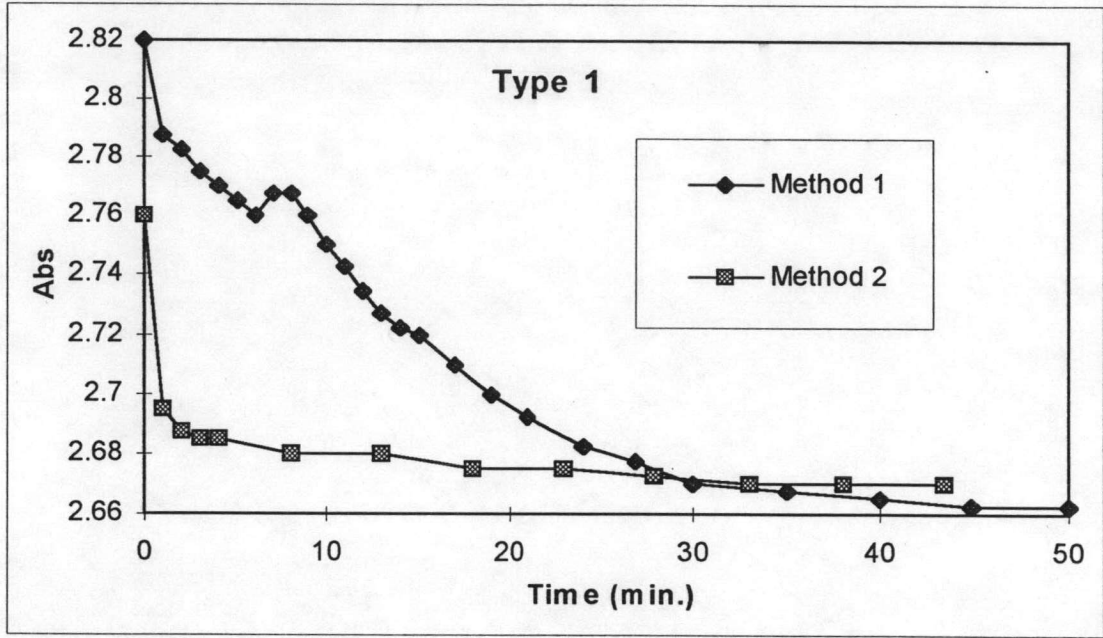


Figure 4-2

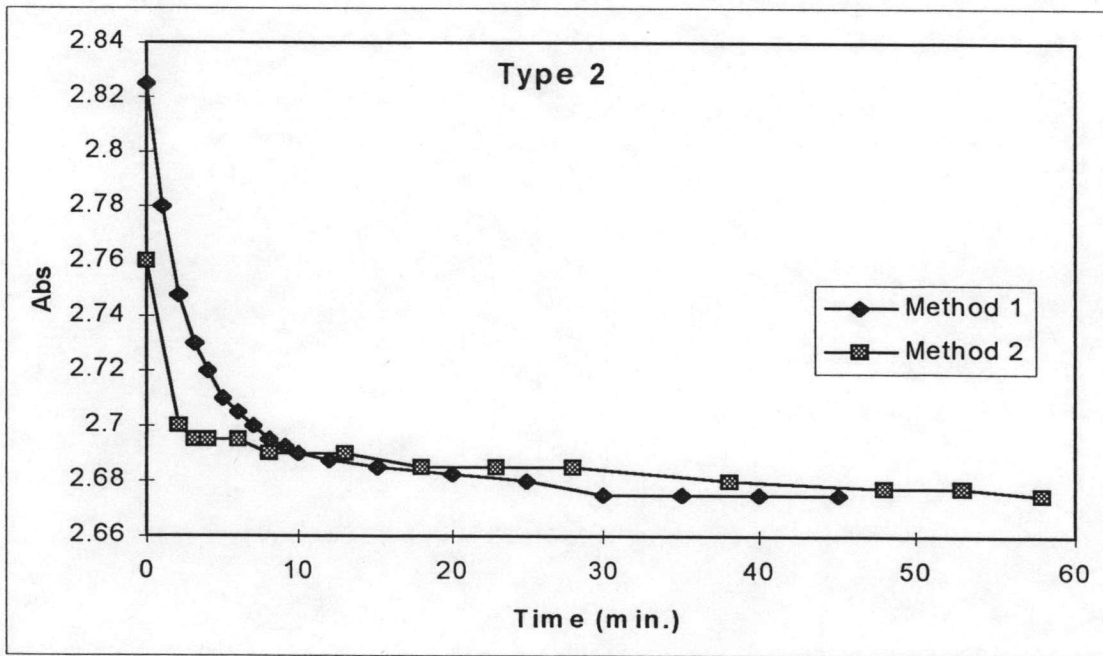


Figure 4-3

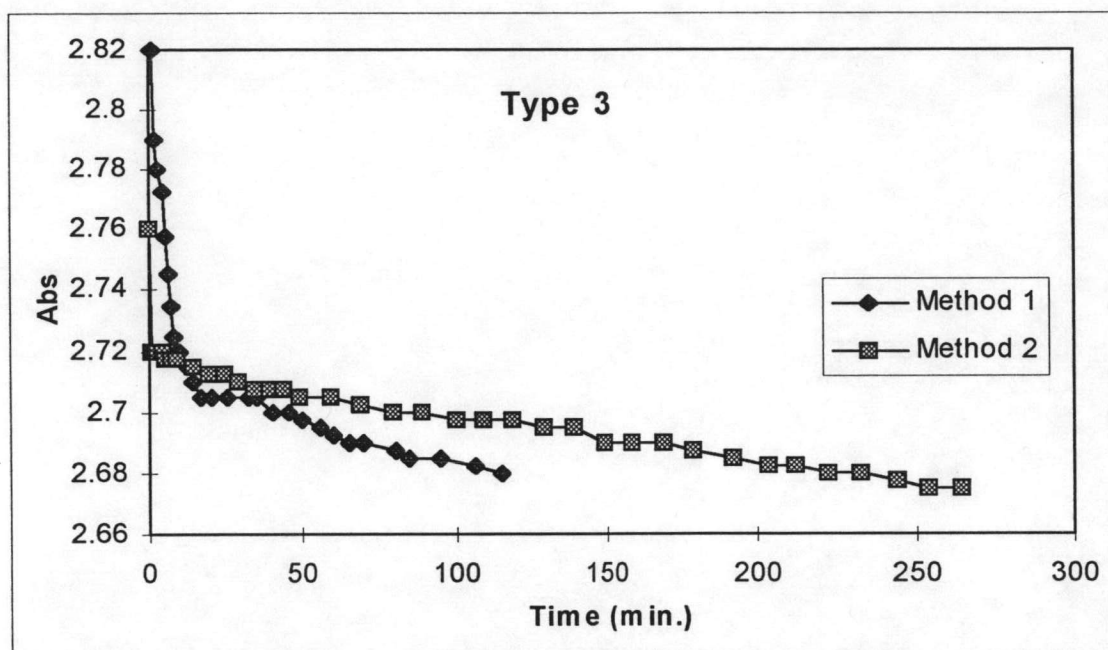


Figure 4-4

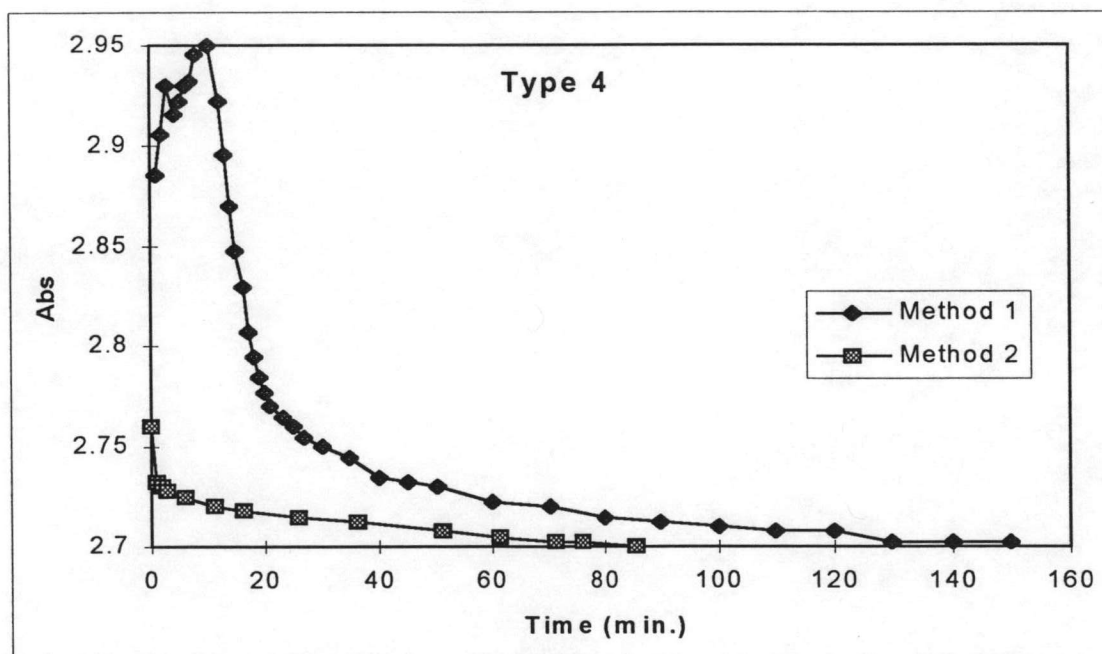


Figure 4-5

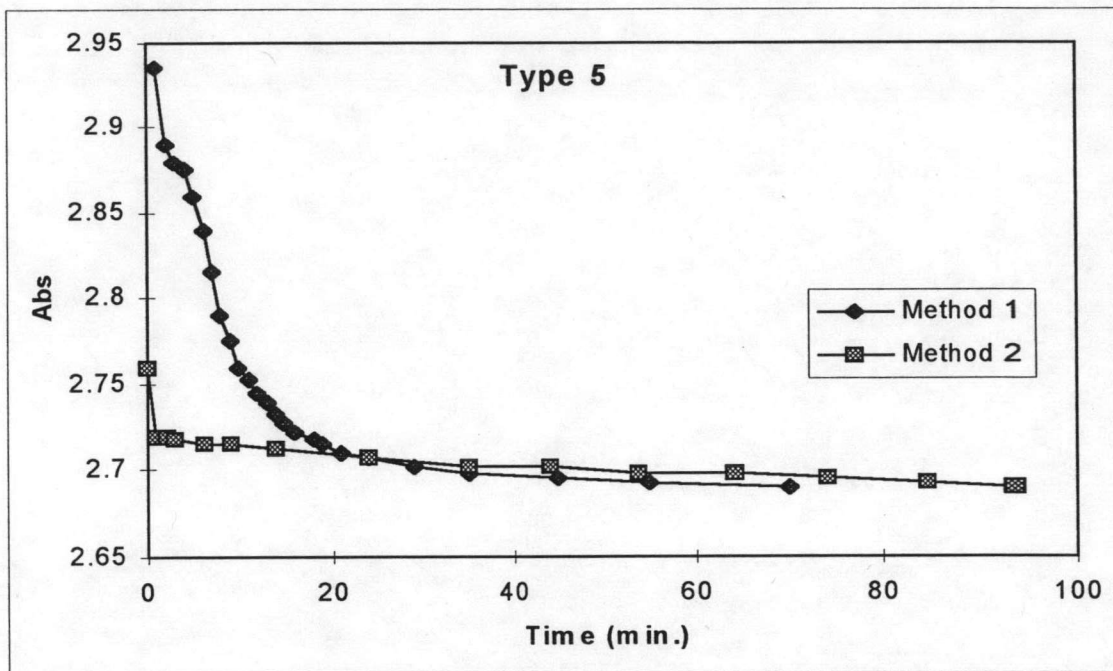


Figure 4-6

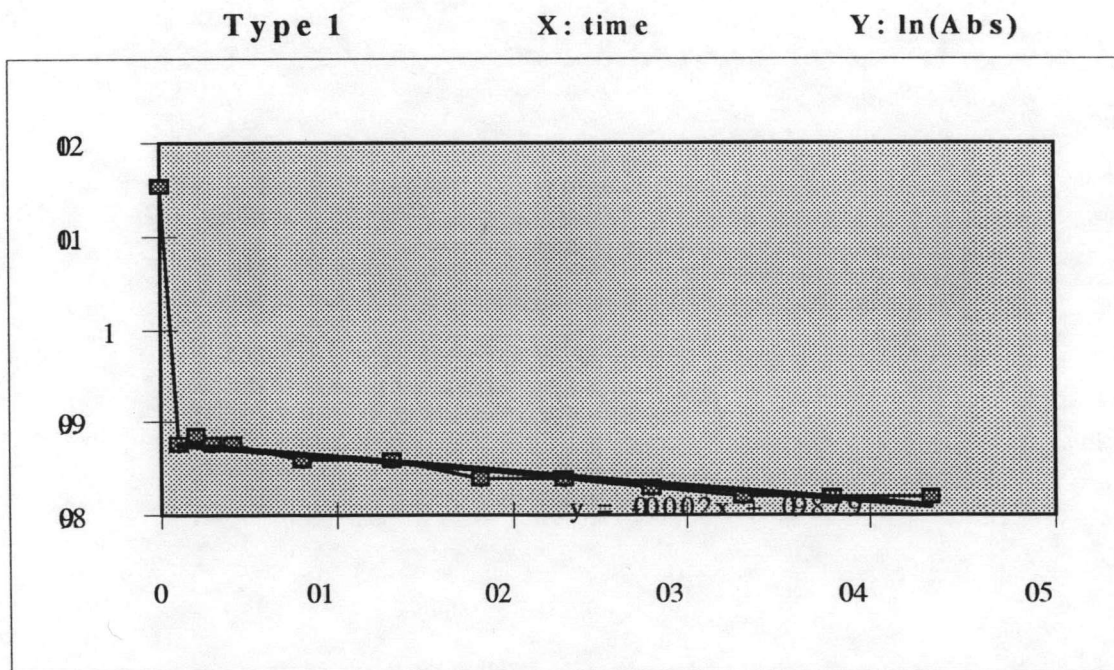


Figure 4-7

Type 2

X: time

Y: ln(abs)

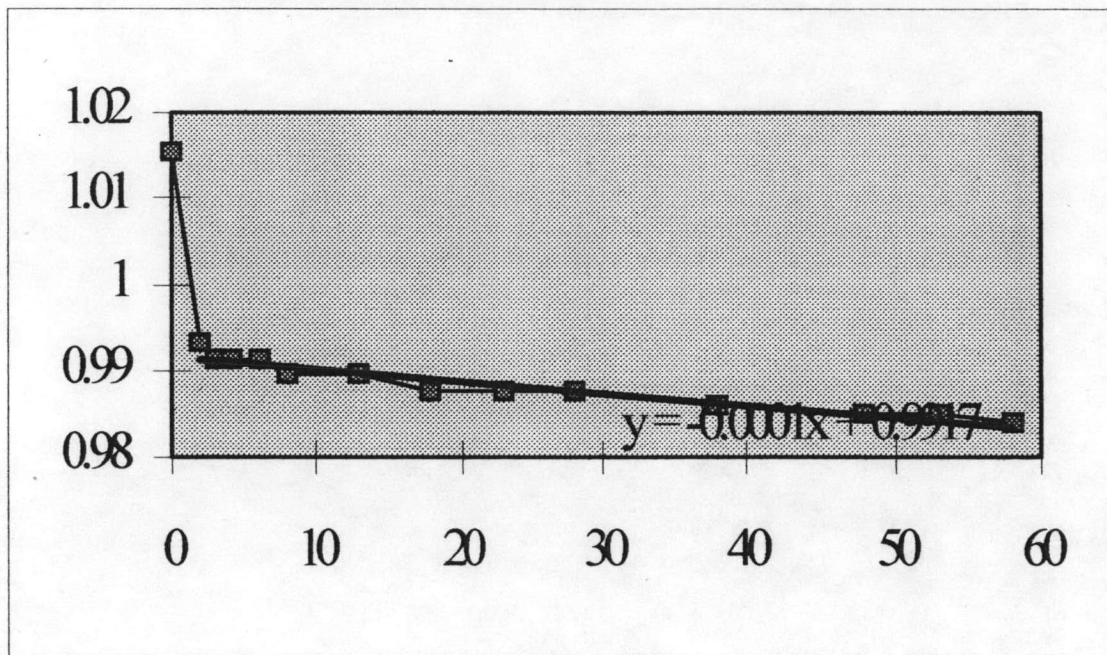


Figure 4-8

Type 3

X: time

Y: ln(abs)

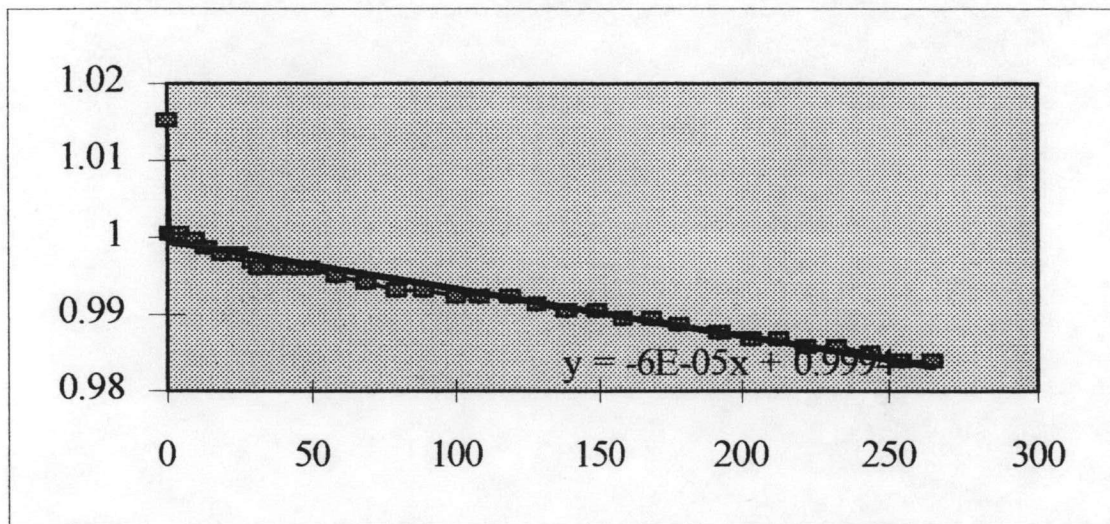


Figure 4-9

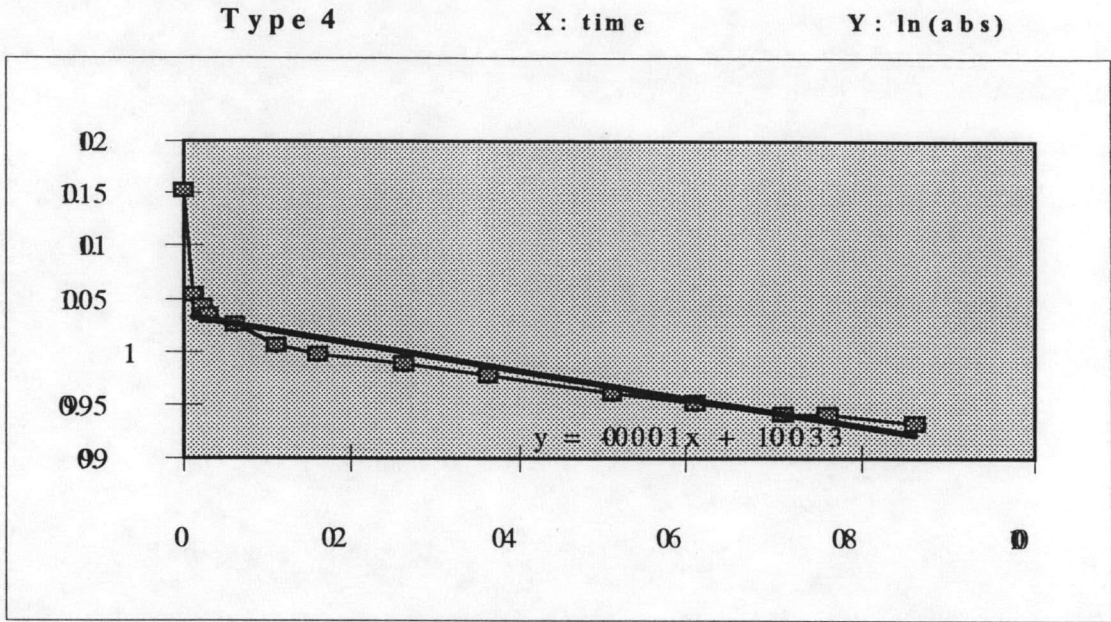


Figure 4-10

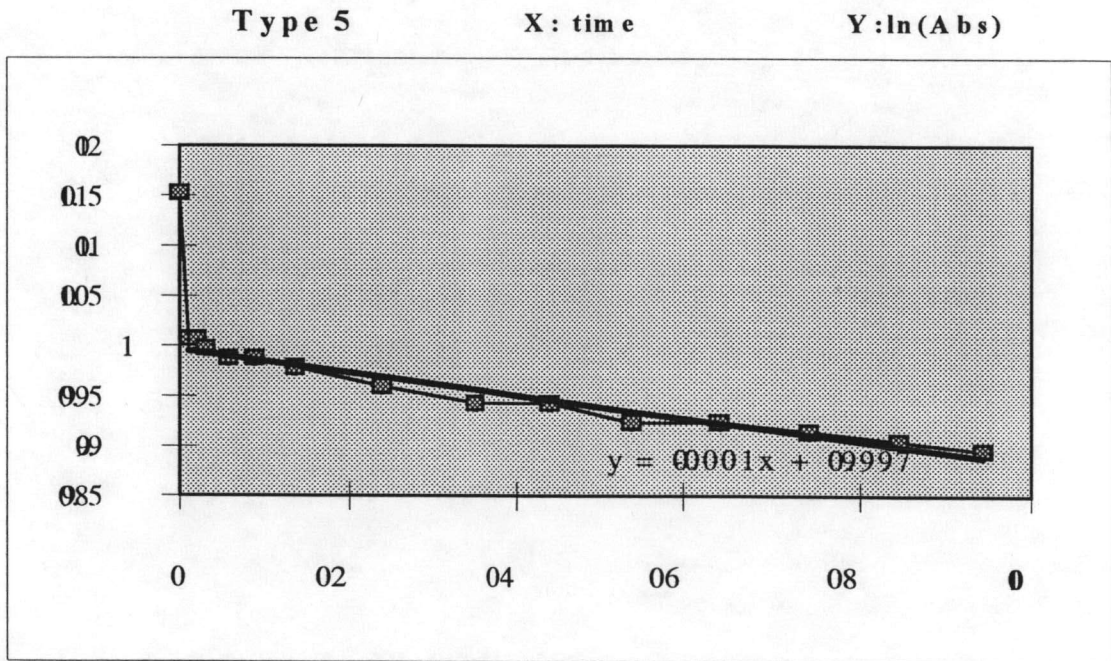


Figure 4-11

The following table is got from the curve fittings:

Table 4-1 Adsolubilization constants of various alumina types

ALUMINA TYPE	SLOPE
Type 1 (acidic)	0.000159
Type 2 (acidic)	0.000132
Type 3 (neutral)	0.0000672
Type 4 (calcined from acidic)	0.000128
Type 5 (acidic)	0.000117

The larger the slope the faster the adsolubilization of the slow part. The value is related to the rate of diffusion, i.e., the steeper the slope (larger k), the more rapid the diffusion.

4.3.2 The Calculation of Transfer Pore Size

The transfer pore size (dividing pores of fast adsolubilization from pores of slow adsolubilization) can be calculated as following:

E. g., for Type 1 alumina powder,

Assume fast adsolubilization is due to the bilayers at large pores and slow adsolubilization is due to the monolayers at small pores, and:

γ -- adsolubilization density of phenol in "slow pores", which is half that in "fast" pores

x -- surface area corresponding to the transfer pore size

from BET report as listed in Table 4.2, if the adsolubilization density of phenol in shallower area is twice that in deeper area, then,

$$(123.8 - x) \cdot 2 \cdot \gamma / (x \cdot \gamma) = 0.07 / 0.02$$

where 0.07 is the adsolubilization amount of fast part, and 0.02 is the adsolubilization amount of slower part. From the equation x is solved as

$$x = 45.02 \text{ m}^2/\text{g}$$

Table 4-2 Pore radius vs. pore surface area of #1 alumina

Radius (Angstrom)	Pore Surface Area (m ² /g)
16.98	21.82
19.03	47.5
21.44	73.07
...	...
684.46	123.8

Then from Table 4.2, the corresponding pore radius (Transfer pore size) can be obtained:

Transfer pore size = 18.5 Angstrom.

The calculated results for all 8 types of alumina powder are listed in Table 4.3.

Table 4-3 Transfer radii and mean pore sizes of all the alumina samples

Alumina Type	Transfer Radius (Angstrom)	Mean Pore Size (Angstrom)
1. Acidic	18.5	28.84
2. Acidic	19	28.96
3. Neutral	62	39.87
4. Calcined	120	113.4
5. Acidic	21	28.58
6. gamma	106	75.11
7. activated	30.3	41.97
8. gamma, incl. 3%C	30.5	40.89
7. (granule)	58.3	41.97
8. (granule)	109	40.89

4.4 The Effect of Surface Properties

Surface properties seem to have large effect on the kinetics of phenol adsolubilizing into SDS admicelles adsorbed on alumina surface. It was observed that on acidic alumina surface the first part of adsolubilization takes a larger ratio in the whole adsolubilization, and the slower part of adsolubilization on acidic surface also is faster than that on neutral surface. The calculated transfer pore size on neutral surface is larger than that on acidic surface, this may suggest a tighter packing of SDS admicelles on acidic alumina surface (with SDS chains more kinked and slant to the surface) and a relatively looser packing of SDS admicelles on neutral alumina surface (with SDS chains more straight and perpendicular to the surface).