CHAPTER III

RESULTS

Physicochemical Properties of Various Aluminum Hydroxide Gels at Initial Condition

Physical Properties

1. Transmission Electron Microscope

The particle morphology of various samples of aluminum hydroxide gel in this study were examined by high resolution transmission electron microscope. Figures 11A-17A showed the particle morphology of gels 1-7 at the initial condition, respectively. All gels appeared to be an amorphous form composed of spherule primary particles. The approximate size of these primary particles of each gel obtained from photomicrographs are listed in Table 2.

2. Infrared Spectrum

The IR spectra of gels at initial condition are shown in Figures 18A-24A. In all cases, broad band at about 3,460 cm^{-1} was observed which is corresponding to the O-H stretching frequency of structural hydroxyl and adsorbed water. In addition, the absorption bands associated with carbonate adsorbed on gel surface also appeared for gels 1,3-7 at 1,525, 1,410, 1,090 and 850 cm^{-1}. In the case of gel 2, the previously mentioned carbonate

Table 2

The estimate range of initial particle size* of aluminum hydroxide gel from various sources

SAMPLE	Particle size (angstrom)
GEL 1	200 - 300
GEL 2	450 - 550
GEL 3	350 - 500
GEL 4	320 - 510
GEL 5	180 - 250
GEL 6	150 - 230
GEL 7	200 - 300

* = from transmission electron microscope

Figure 11 Transmission electron photomicrographs of Gel 1 (Key : A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

Figure 12 Transmission electron photomicrographs of Gel 2 (Key ; A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

Figure 13 Transmission electron photomicrographs of Gel 3 (Key ; A=initial condition, B=after storage at - ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

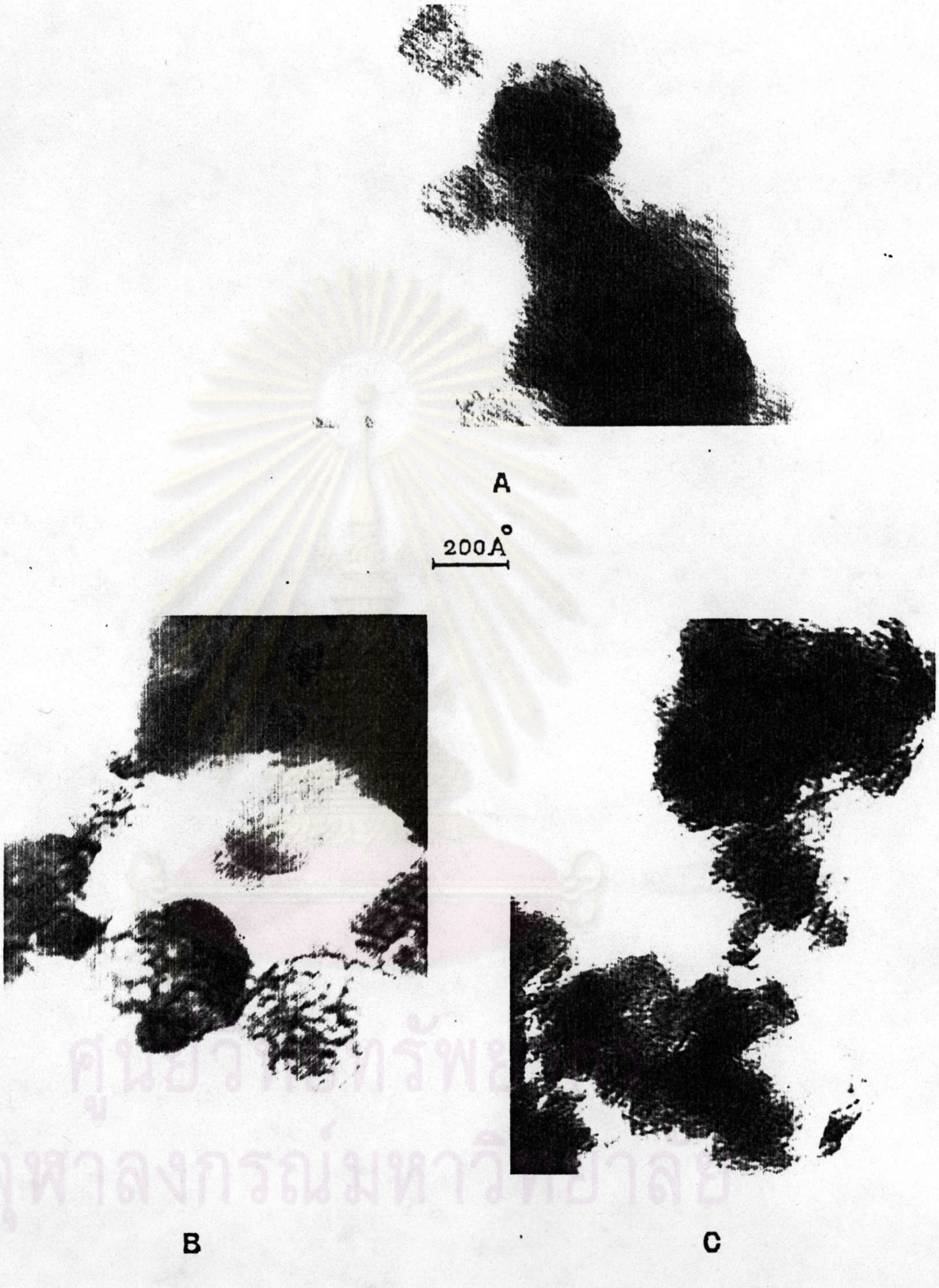

Figure 14 Transmission electron photomicrographs of Gel 4 (Key ; A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

Figure 15 Transmission electron photomicrographs of Gel 5 (Key ; A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

Figure 16 Transmission electron photomicrographs of Gel 6 (Key ; A=initial condition, B=after storage at - ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

Figure 17 Transmission electron photomicrographs of Gel 7 (Key ; A=initial condition, B=after storage at - ambient temperature for 6 months, C=after storage at 45°c for 6 months) X270,000

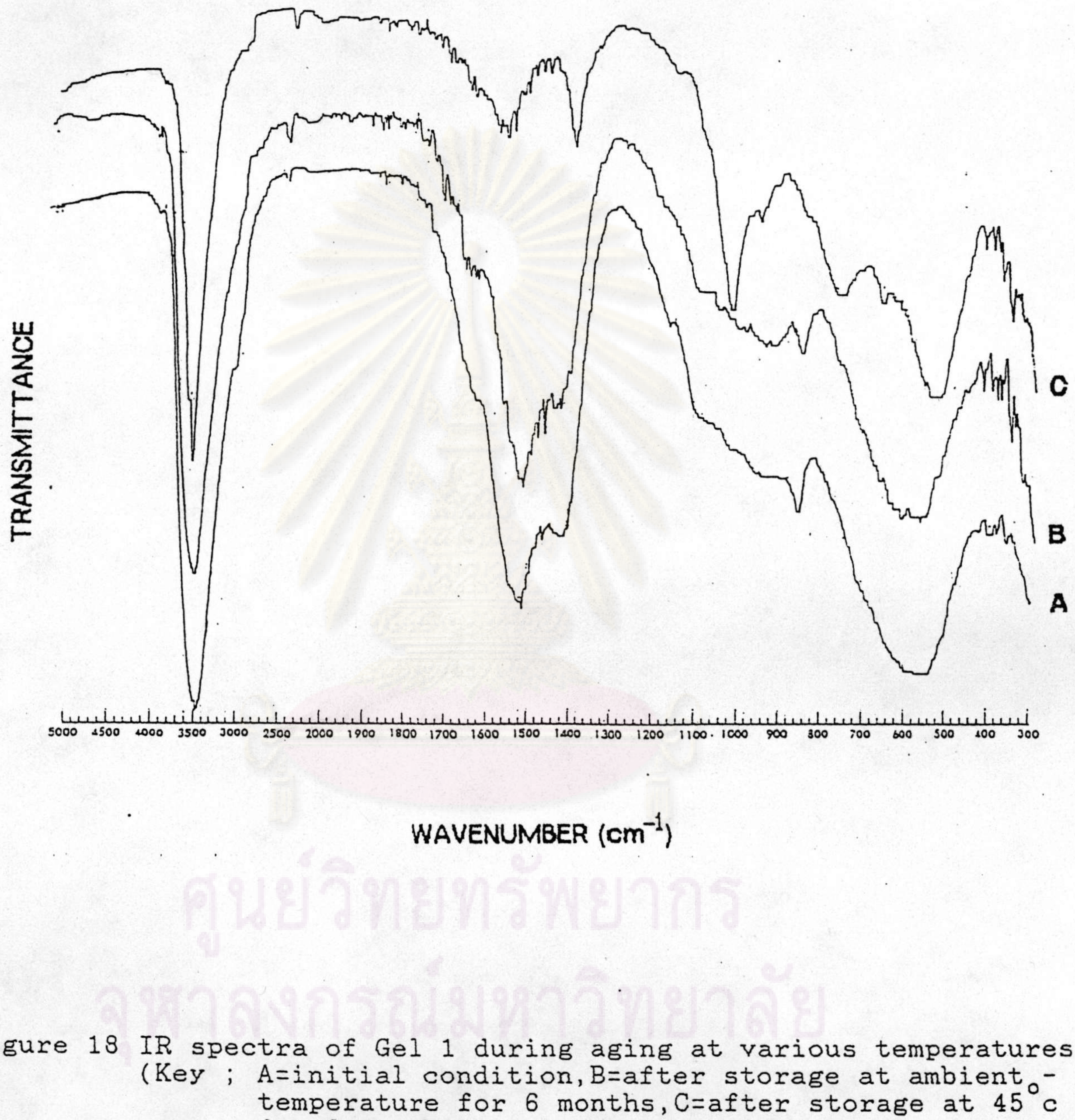

Figure 18 IR spectra of Gel 1 during aging at various temperatures (Key ; A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45 °c for 6 months)

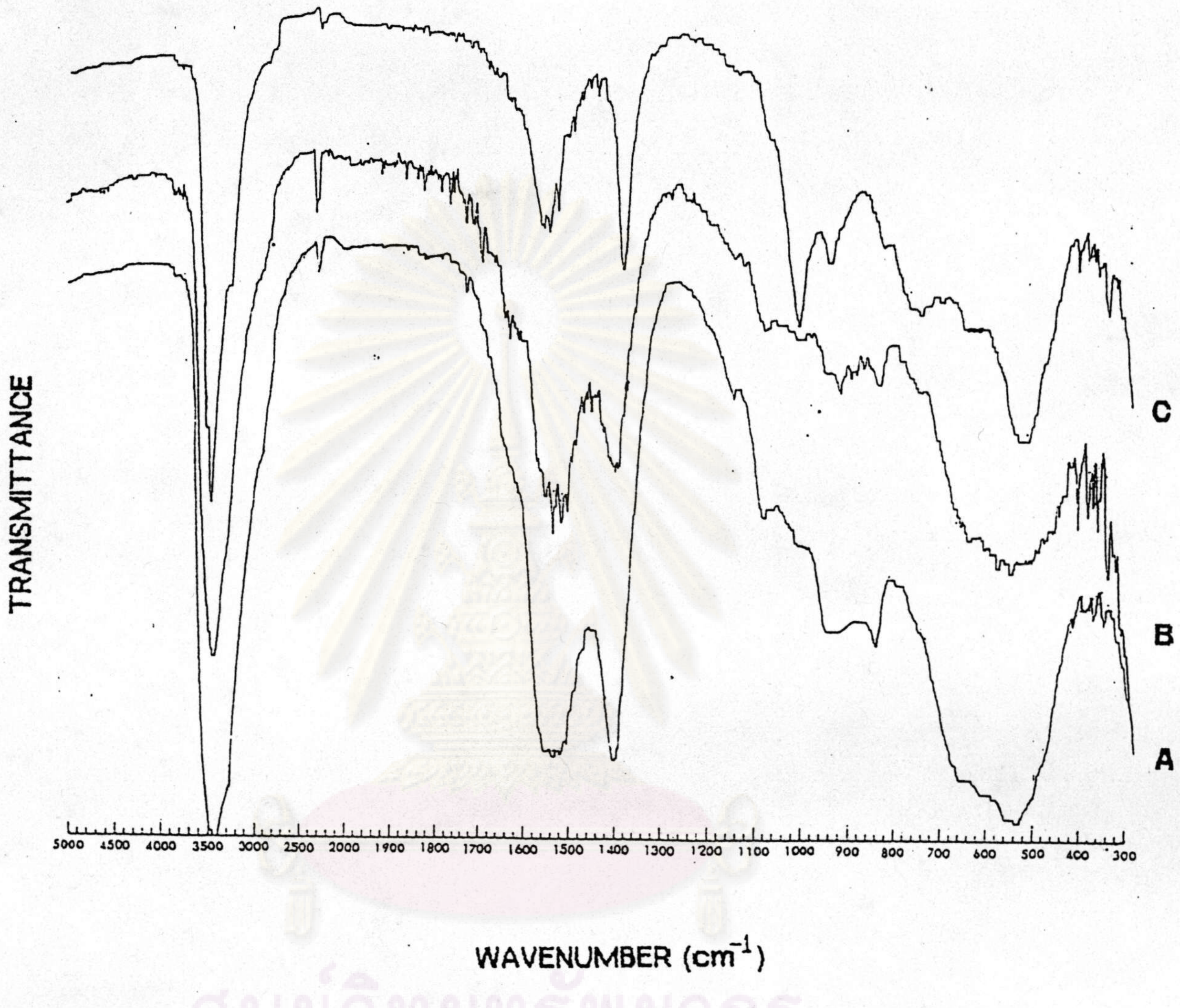

Figure 19 IR spectra of Gel 2 during aging at various temperatures (Key ; A=initial condition, B=after storage at ambient-temperature for 6 months, C=after storage at 45°c for 6 months)

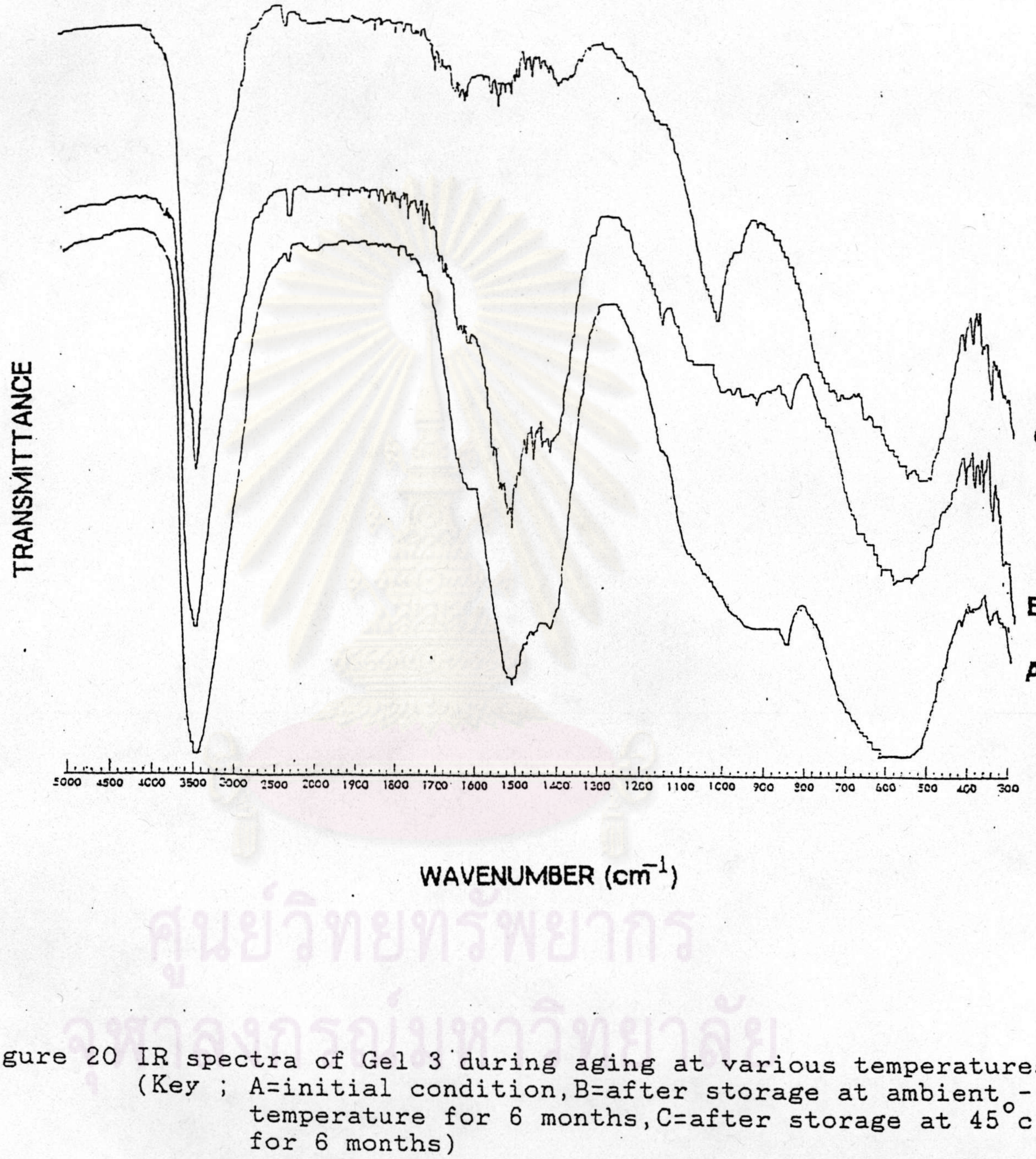

Figure 20 IR spectra of Gel 3 during aging at various temperatures (Key ; A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45°c for 6 months)

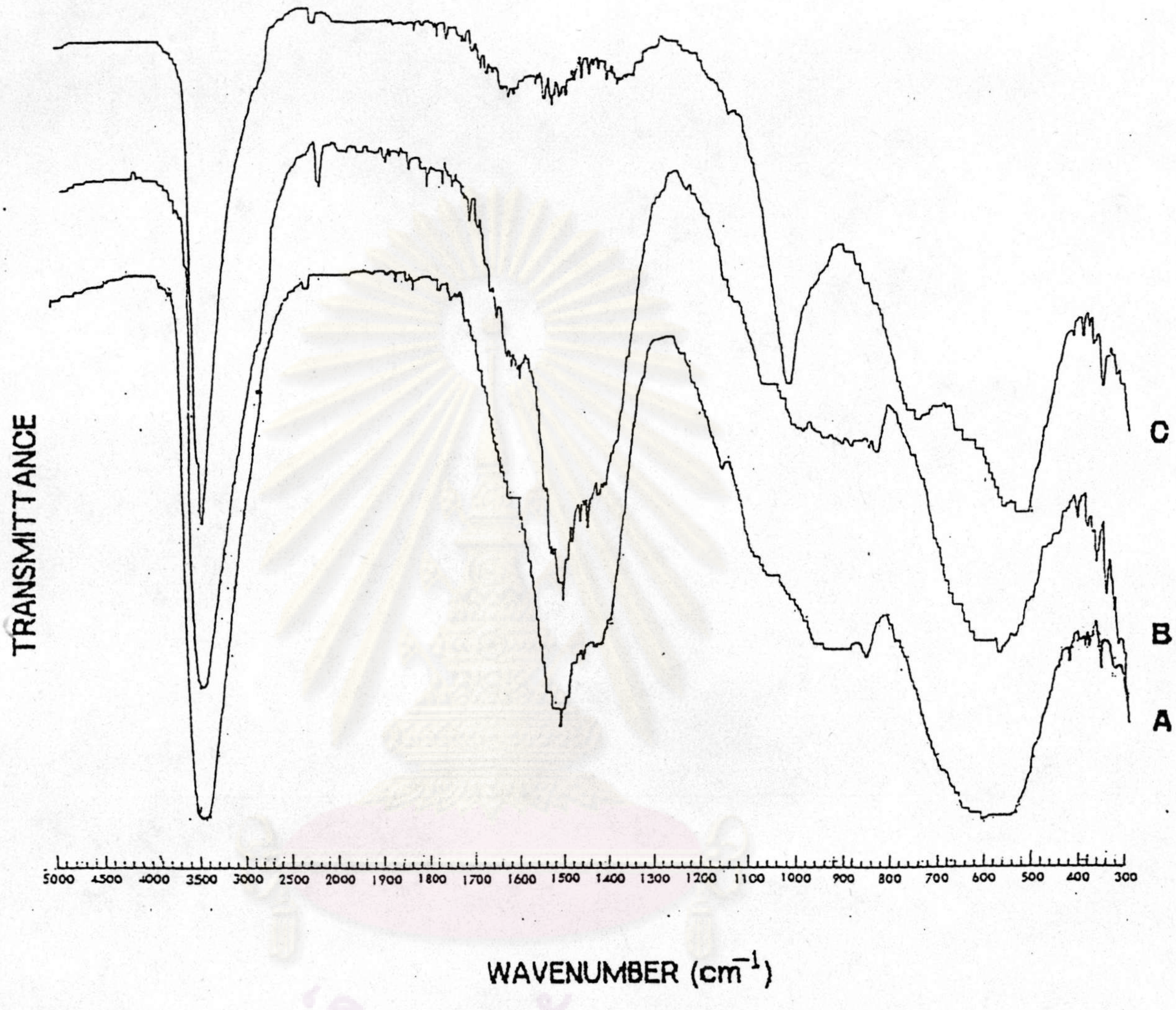

Figure 21 IR spectra of Gel 4 during aging at various tempertures (Key ; A=initial condition, B=after storage at ambient-temperature for 6 months, C=after storage at 45°c for 6 months)

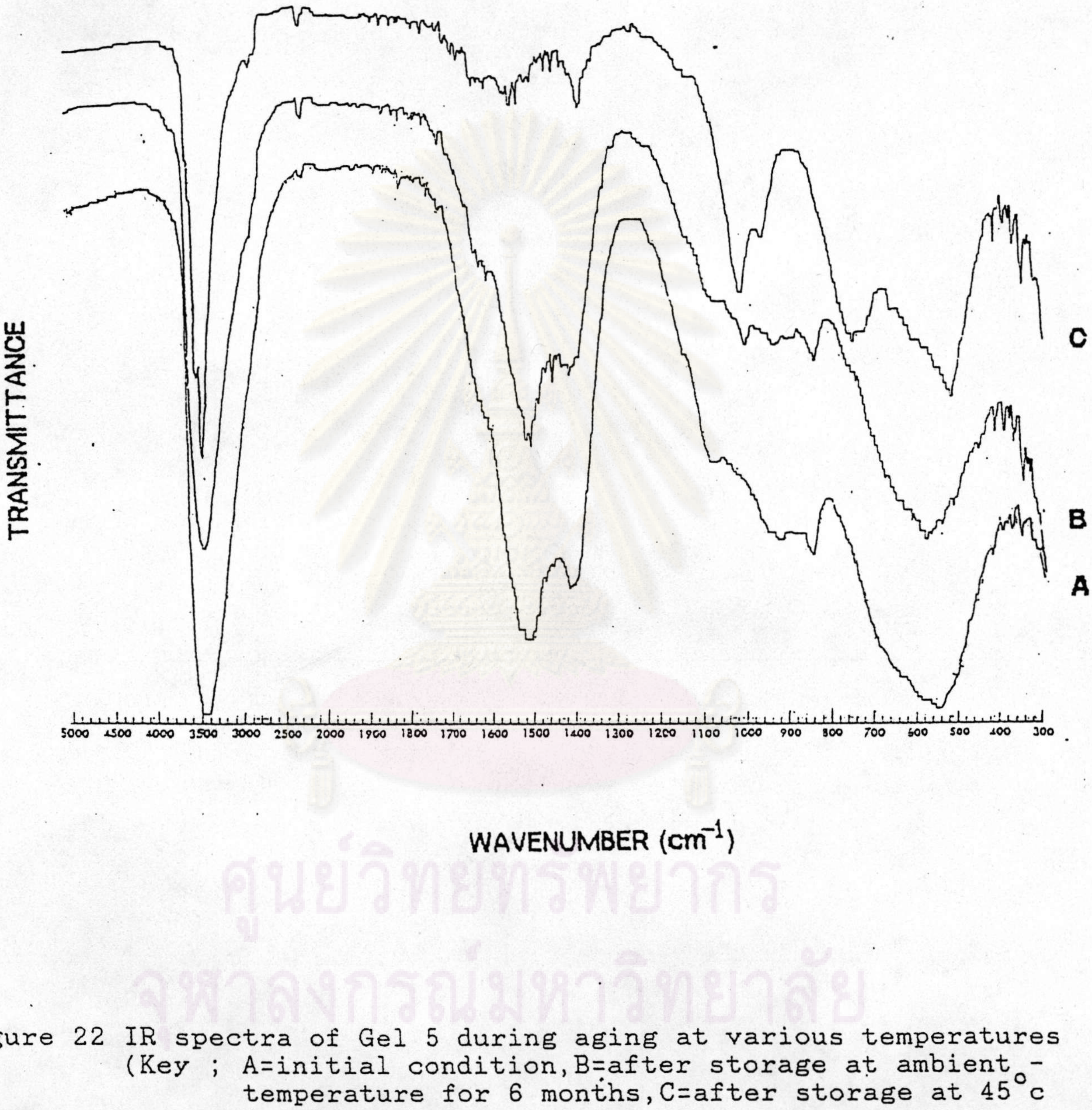

Figure 22 IR spectra of Gel 5 during aging at various temperatures (Key ; A=initial condition, B=after storage at ambient temperature for 6 months, C=after storage at 45°c for 6 months)

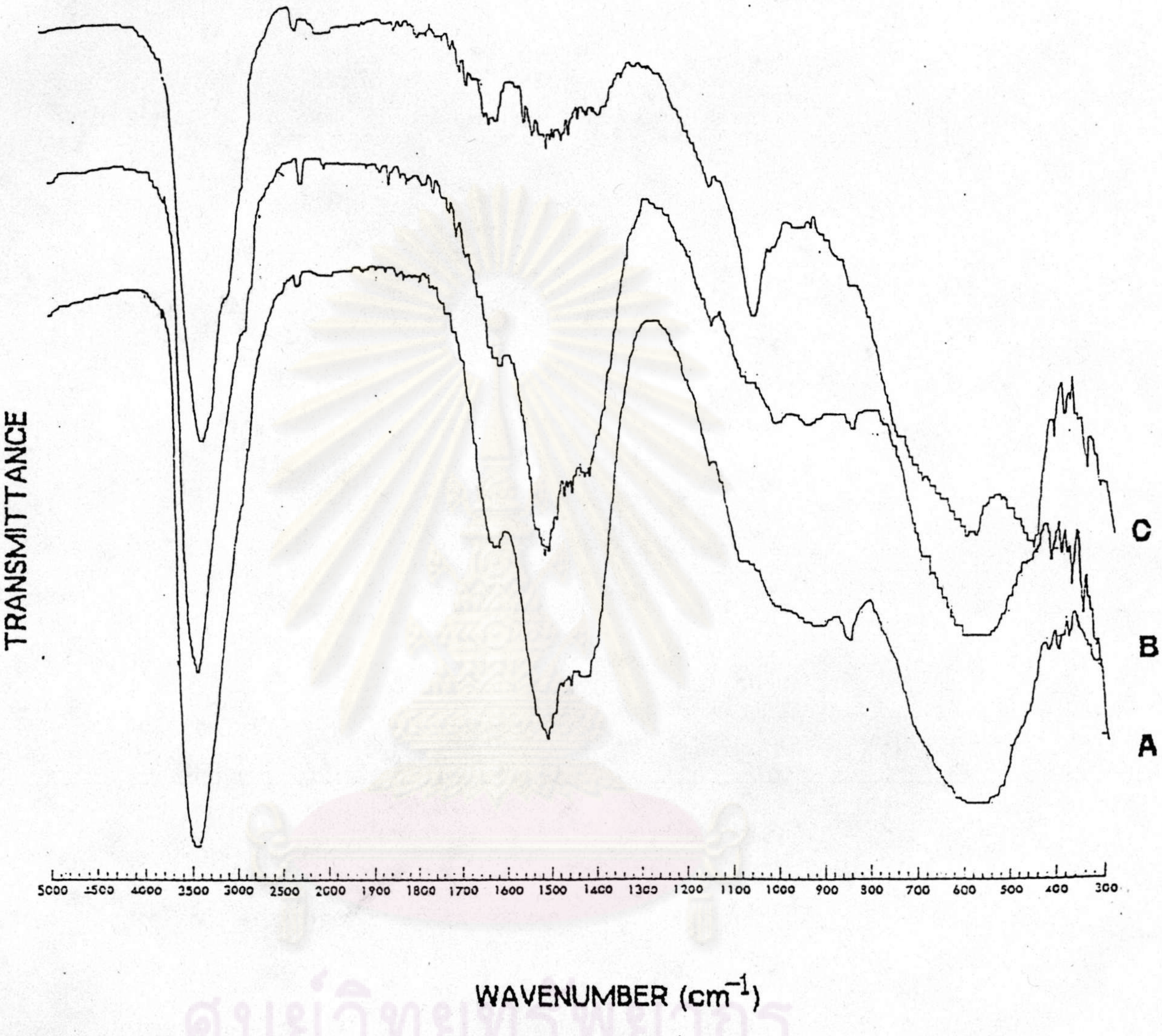

Figure 23 IR spectra of Gel 6 during aging at various temperatures (Key ; A=initial condition, B=after storage at ambient-temperature for 6 months, C=after storage at 45^{o}c for 6 months)

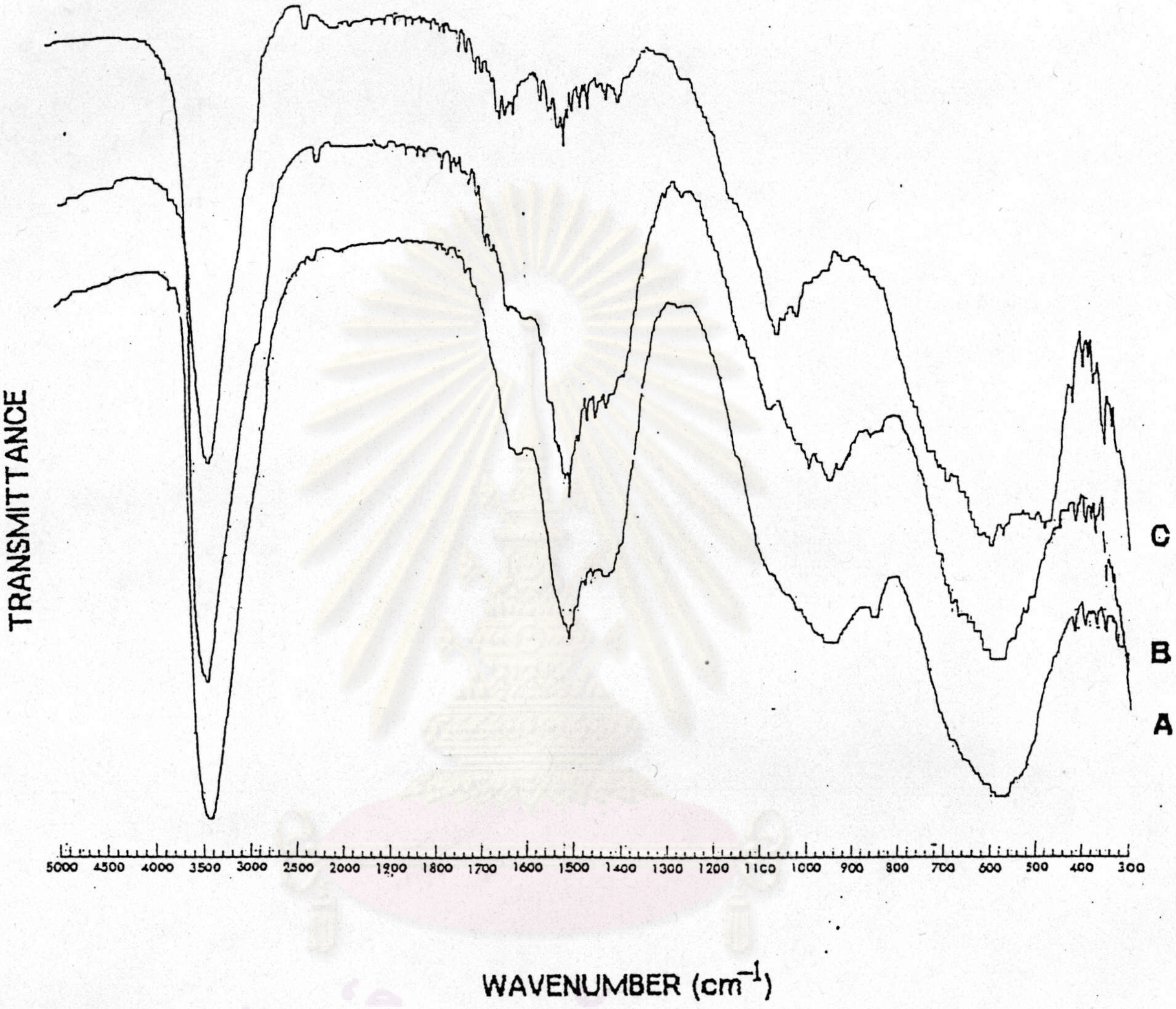

Figure 24 IR spectra of Gel 7 during aging at various temperatures (Key ; A=initial condition, B=after storage at ambient-temperature for 6 months, C=after storage at 45 °c for 6 months)

bands, however occurred at 1,540, 1,400, 1,090 and 850 cm^{-1}.

3. <u>X-Ray Diffraction</u>

X-ray diffractograms of gels at initial condition are given in Figures 25A-31A. For gels 1,3-7, they were not shown any particular indicated peak which indicated crystalline form, while x-ray diffractogram of gel 2 revealed a small peak at about 15^o 2θ. Gels 1-6, however exhibited the broad background reflection between 35 and 22^o 2θ.

<u>Chemical Properties</u>

The determinations of chemical properties of aluminum hydroxide gel were preliminary antacid test, acid neutralizing capacity test, reaction velocity test, hydroxide to aluminum ratio and PZC, respectively. All aluminum hydroxide gel from various sources showed good antacid properties at initial condition. These results are given in Tables 5, 7, 11, 13 and 15 for preliminary antacid test, acid neutralizing capacity test, reaction velocity test, hydroxide to aluminum ratio and PZC, respectively.

<u>Effect of Aging at Ambient Temperature and at 45</u>^oC

<u>Physical Properties</u>

1. <u>Transmission Electron Microscope</u>

The change in morphology of gels are illustra-

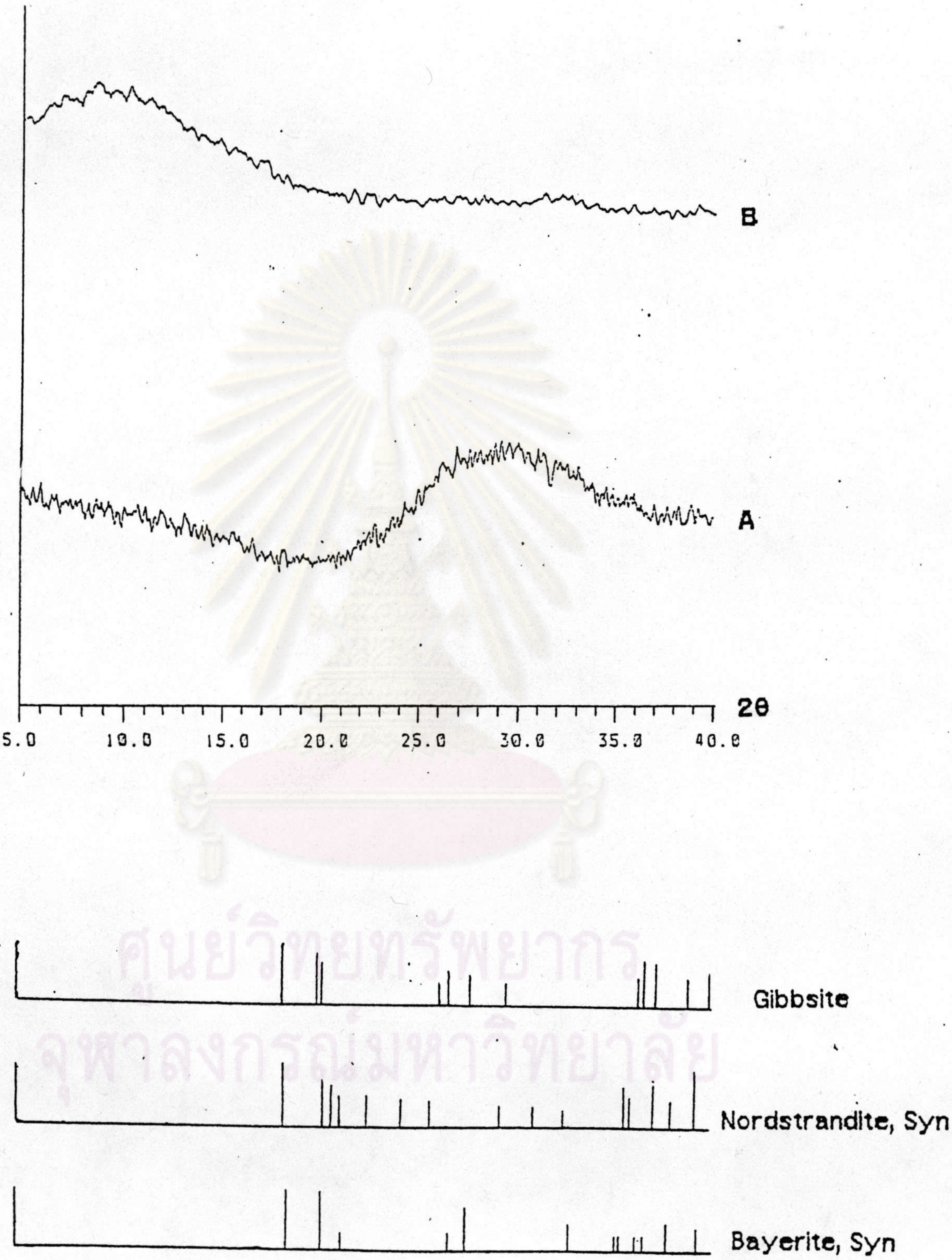

Figure 25 X-ray diffraction patterns of Gel 1 during aging at ambient temperature (Key; A=initial condition, B=after storage for 6 months)

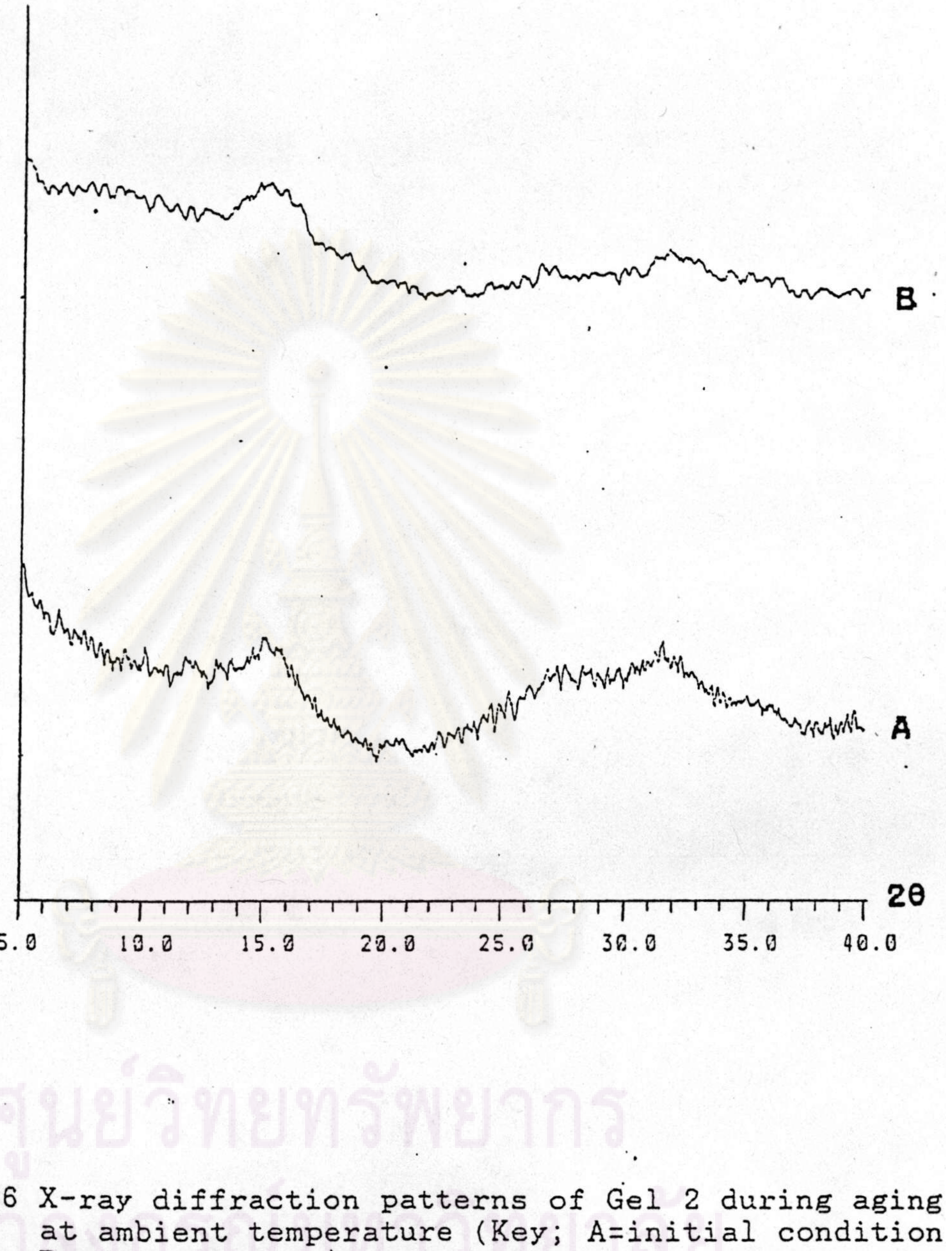

Figure 26 X-ray diffraction patterns of Gel 2 during aging at ambient temperature (Key; A=initial condition, B=after storage for 6 months)

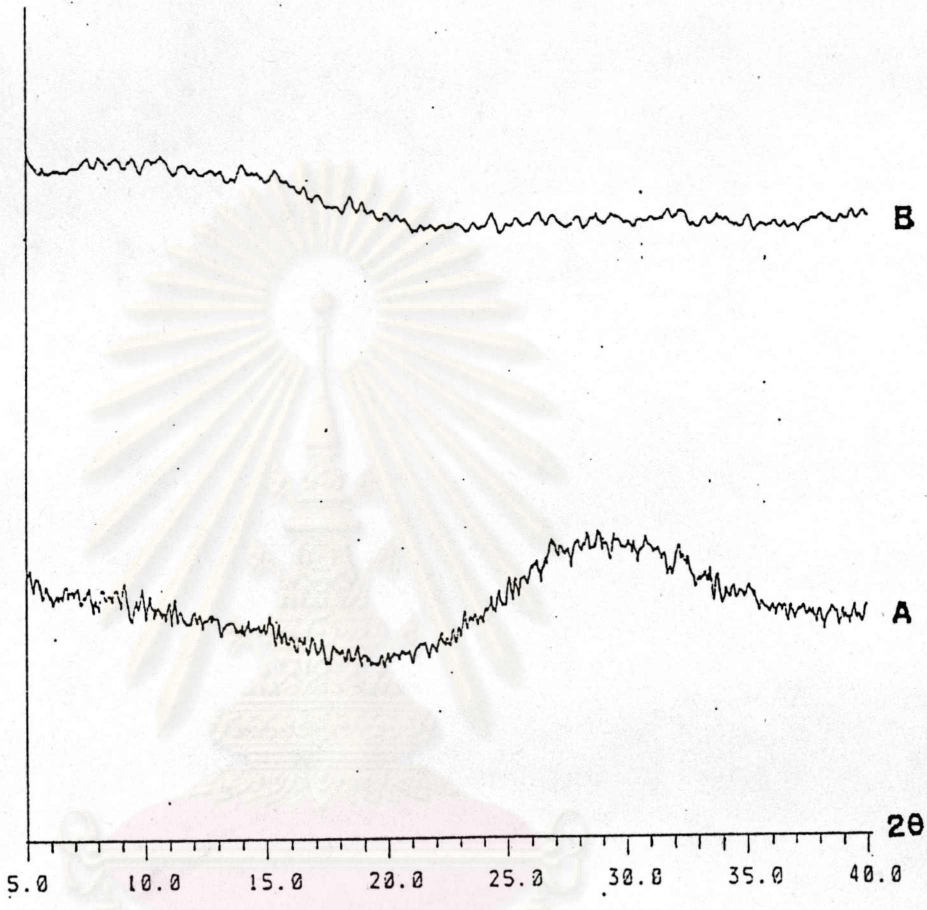

Figure 27 X-ray diffraction patterns of Gel 3 during aging at ambient temperature (Key; A=initial condition, B=after storage for 6 months)

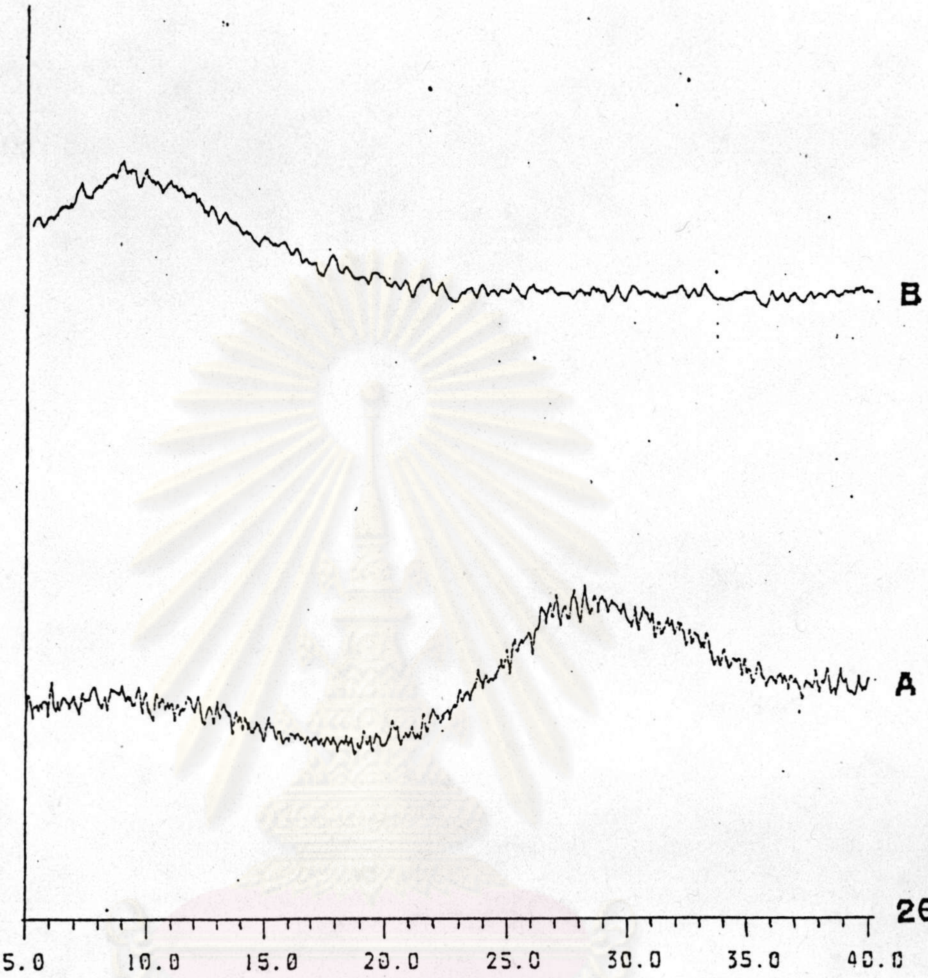

Figure 28 X-ray diffraction patterns of Gel 4 during aging at ambient temperature (Key; A=initial condition, B=after storage for 6 months)

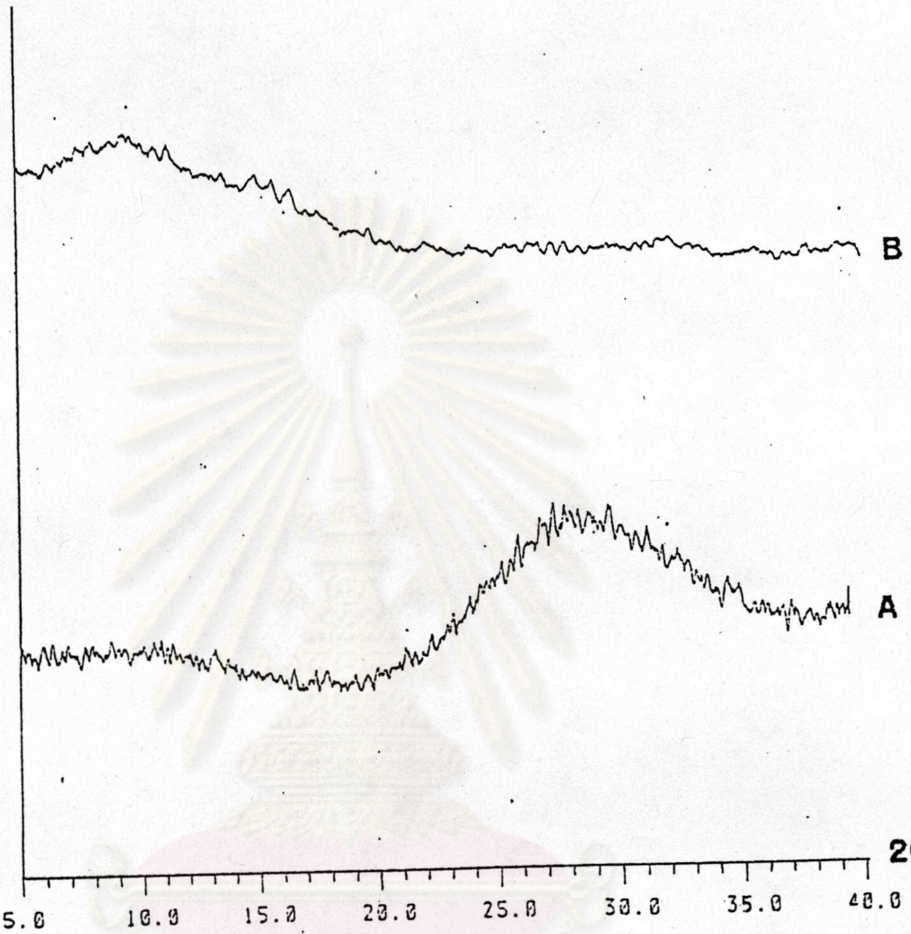

Figure 29 X-ray diffraction patterns of Gel 5 during aging at ambient temperature (Key; A=initial condition, B=after storage for 6 months)

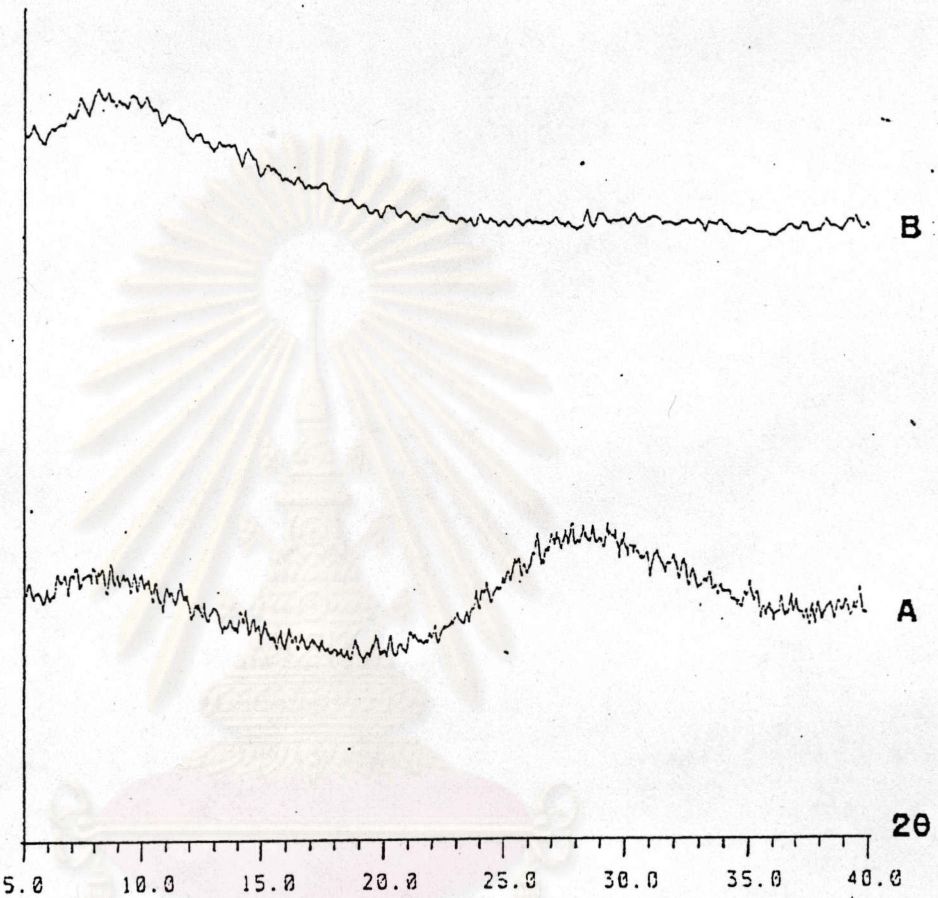

Figure 30 X-ray diffraction patterns of Gel 6 during aging at ambient temperature (Key; A=initial condition, B=after storage for 6 months)

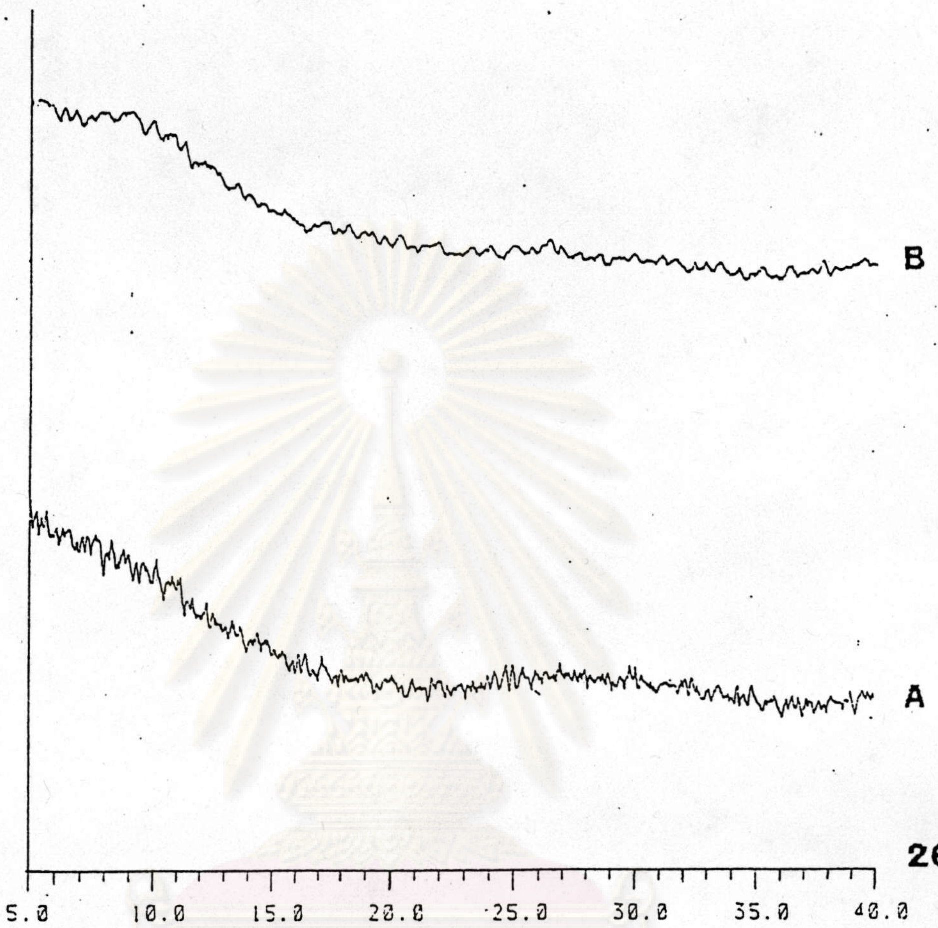

Figure 31 X-ray diffraction patterns of Gel 7 during aging at ambient temperature (Key; A=initial condition; B=after storage for 6 months)

ted in Figures 11B-17B after storage at ambient temperature for six months. It was observed that the particle size of primary particles were increased for all gels after aging. In the case of aging for six months at 45^{o}C, morphology of the primary particles of aluminum hydroxide showed the increasing in ordered of crystallinity as indicated from photomicrographs (Figures 11C-17C). The change in morphology at 45^{o}C were well defined as compared with the ambient temperature.

2. Infrared Spectrum

Figures 18B-24B presented the IR spectra of all gels after storage at ambient temperature for six months. These spectra indicated that the center of all peaks still appeared at the same wavenumber. However, the absorption of carbonate band were changed as indicated by decreasing the intensity. For the IR spectra of the gels after aging at 45^{o}C for six months (Figures 18C-24C), the broad peak at 3,460 cm^{-1} became sharper except for gels 6 and 7, which showed the same. At this condition, peak at 1,020 cm^{-1} and small peak at 970 cm^{-1} started to occurred, by this time there was no evidence of a peak at 850 cm^{-1}. In addition, the large decreased in the intensity of carbonate bands were observed. For gel 6, the intense peak at 1,070 cm^{-1}, small peak at 1,150 cm^{-1} and two strong absorption bands at about 610 and 470 cm^{-1} occurred. In the case of gel 7, the bands at 600 and 480

cm^{-1} appeared, together with the band at 1,055 cm^{-1}. However, the above mentioned bands for gels 6 and 7 were not observed for gels 1-5.

3. X-Ray Diffraction

X-ray diffractograms (Figures 25B-31B) showed no changed after storage at ambient temperature for six months. But, the broad background reflection between 35 and 22° 2θ for gels 1-6 were absented.

4. pH

The decreased in pH values of aluminum hydroxide gels with aged were detected. These are listed in Tables 3 and 4 for the gels aging at ambient temperature and at 45°C, respectively. The pH values, however were decreased faster for the gel storage at 45°C.

Chemical Properties

1. Preliminary Antacid Test

The preliminary antacid test of each aluminum hydroxide gel after storage at ambient temperature and at 45°C are listed in Tables 5 and 6, respectively. It was seen that the pH of preliminary antacid test were decreased during aging. Decreasing of pH for preliminary antacid test after storage at 45°C was more than storage at ambient temperature.

Table 3

The pH values of aluminum hydroxide gel* from various sources during aging at ambient temperature

SAMPLE	pH of sample* after storage at AT** for (months)						
	0	1	2	3	4	5	6
GEL 1	8.06	8.03	8.00	7.99	8.00	7.98	7.97
GEL 2	7.90	7.80	7.74	7.70	7.68	7.62	7.56
GEL 3	7.56	7.48	7.42	7.39	7.35	7.30	7.27
GEL 4	7.55	7.49	7.40	7.35	7.33	7.30	7.24
GEL 5	8.31	8.25	8.21	8.22	8.20	8.13	8.08
GEL 6	7.59	7.54	7.53	7.55	7.50	7.47	7.40
GEL 7	7.53	7.48	7.49	7.45	7.43	7.38	7.32

* 4% Aluminum oxide suspension
** ambient temperature

Table 4

The pH values of aluminum hydroxide gel* from various sources during aging at 45°c and stabilization effect of sorbitol

SAMPLE	pH of sample* after storage at 45°c for(months)				
	0	1	2	3	4
GEL 1	8.06	8.04	7.93	7.90	7.82
GEL 2	7.90	7.77	7.70	7.68	7.44
GEL 3	7.56	7.45	7.33	7.26	7.19
GEL 4	7.55	7.38	7.30	7.25	7.16
GEL 5	8.31	8.20	8.00	7.91	7.82
GEL 6	7.59	7.55	7.49	7.36	7.31
GEL 7	7.53	7.40	7.21	7.17	7.14
GEL 1+2% **	8.12	8.08	7.95	7.99	7.94
GEL 1+5% **	8.16	8.12	8.06	8.00	7.98
GEL 2+2% **	7.94	7.90	7.88	7.85	7.81
GEL 2+5% **	7.98	7.95	7.92	7.90	7.88

* 4% Aluminum oxide suspension
** percent of sorbitol added

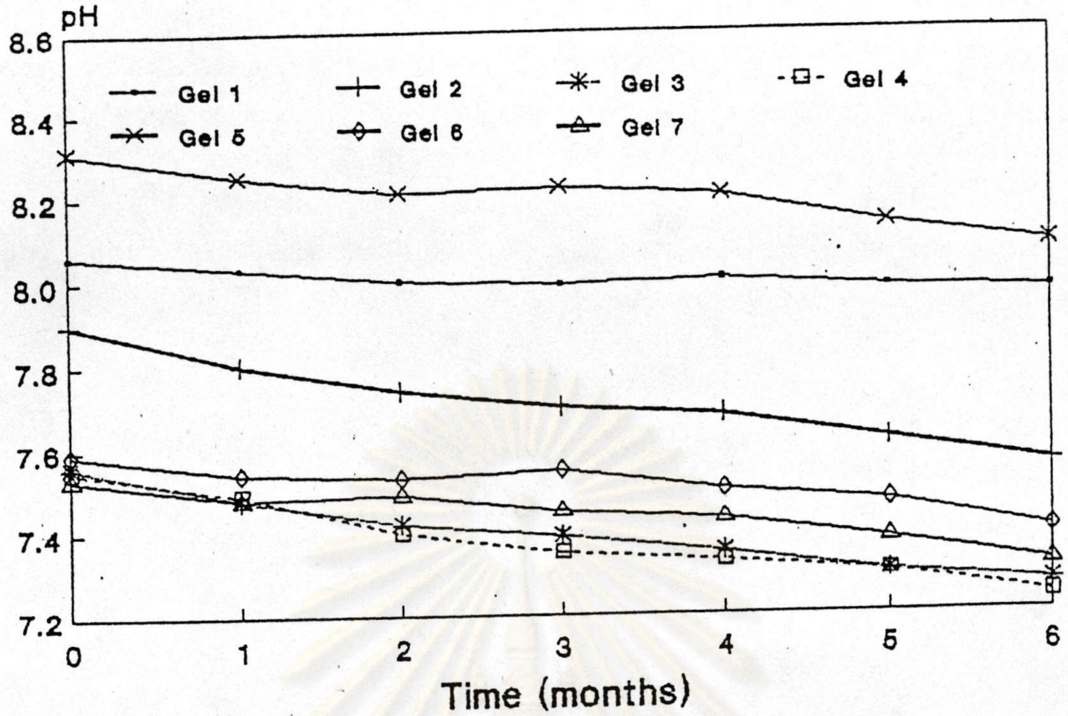

Figure 32 Change in pH values of aluminum hydroxide gel from various sources during aging at ambient temperature

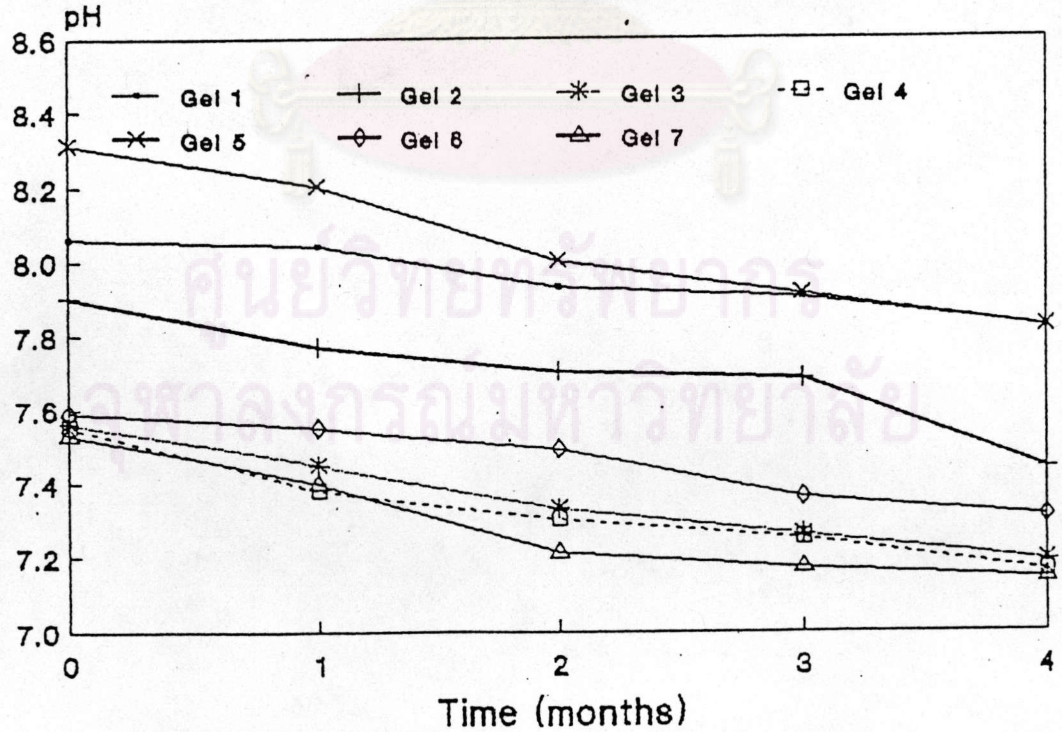

Figure 33 Change in pH values of aluminum hydroxide gel from various sources during aging at 45°c

Table 5

The preliminary antacid test of aluminum hydroxide gel from various sources during aging at ambient temperature

SAMPLE	Preliminary antacid test after storage at AT* for (months)						
	0	1	2	3	4	5	6
GEL 1	4.10	4.05	4.01	3.98	3.99	3.90	3.87
GEL 2	4.05	3.99	3.98	3.95	3,91	3.87	3.80
GEL 3	4.04	3.99	3.94	3.90	3.84	3.82	3.64
GEL 4	4.06	4.00	3.92	3.85	3.81	3.77	3.58
GEL 5	4.06	3.99	3.96	3.92	3.90	3.89	3.84
GEL 6	4.08	4.04	4.01	4.00	3.98	3.91	3.86
GEL 7	4.00	3.98	3.99	3.95	3.90	3.88	3.82

* ambient temperature

Table 6

The preliminary antacid test of aluminum hydroxide gel from various sources during aging at 45°c and stabilization effect of sorbitol

SAMPLE	Preliminary antacid test after storage at 45°c for(months)				
	0	1	2	3	4
GEL 1	4.10	3.99	3.97	3.87	3.80
GEL 2	4.05	3.98	3.94	3.52	2.96
GEL 3	4.04	3.97	3.76	3.63	2.15
GEL 4	4.06	3.97	3.72	3.59	2.11
GEL 5	4.06	3.94	2.95	2.55	1.68
GEL 6	4.08	3.99	3.98	3.84	3.78
GEL 7	4.00	3.88	3.44	2.95	1.57
GEL 1+2% *	4.00	3.98	3.96	3.92	3.90
GEL 1+5% *	3.98	3.98	3.96	3.97	3.94
GEL 2+2% *	3.99	3.97	3.97	3.95	3.89
GEL 2+5% *	3.99	3.97	3.98	3.97	3.93

* percent of sorbitol added

2. Acid Neutralizing Capacity

The acid neutralizing capacity was given as a percent of theoretical as indicated in USP XXII. The data are listed in Tables 7 and 8 for the gels aging at ambient temperature and at 45°C, respectively. Plots of the ln of the percent of theoretical acid neutralizing capacity of the gel as a function of times at ambient temperature and at 45°C were shown in Figures 34 and 35. Linear regression method was employed and the kinetics appeared to be first order. The coefficient of determination (r^2) was also listed (Tables 9, 10). It could be concluded that the decreasing of acid neutralizing capacity of all gels followed first order kinetics.

The rate constant of each aluminum hydroxide gel are shown in Tables 9 and 10. The degree of increment was orderly ranked by the following Gel 1 < Gel 6 < Gel 5 < Gel 7< Gel 2< Gel 3< Gel 4 and Gel 1 < Gel 2 < Gel 6 < Gel 4 < Gel 3 < Gel 5 < Gel 7 for the gels aging at ambient temperature and at 45°C, respectively.

3. Reaction Velocity

Tables 11 and 12 list the reaction velocity of various aluminum hydroxide gels after storage at ambient temperature and at 45°C, respectively. It may be seen that the reaction velocity decreased after storage and

Table 7

Percent of Theoretical Acid Neutralizing Capacity(TANC) of aluminum hydroxide gel from various sources during aging at ambient temperature

SAMPLE	Percent of TANC after storage at AT* for (months)						
	0	1	2	3	4	5	6
GEL 1	95.51	94.66	92.11	90.61	88.82	87.23	85.67
GEL 2	98.22	94.16	91.19	89.33	85.11	82.23	79.56
GEL 3	94.52	88.34	82.60	77.23	72.12	65.64	63.09
GEL 4	96.14	85.59	76.20	70.01	60.40	53.77	47.86
GEL 5	98.23	94.62	89.98	88.01	85.91	83.18	80.54
GEL 6	98.23	97.22	93.64	92.09	89.15	87.05	85.08
GEL 7	93.59	93.36	87.47	84.66	82.01	79.44	78.05

* ambient temperature

Table 8

Percent of Theoretical Acid Neutralizing Capacity(TANC) of aluminum hydroxide gel from various sources during aging at 45°c and stabilization effect of sorbitol

SAMPLE	Percent of TANC after storage at 45°c for (months)				
	0	1	2	3	4
GEL 1	95.51	90.28	86.51	79.01	76.26
GEL 2	98.22	81.86	66.17	54.84	44.59
GEL 3	94.52	74.97	51.27	37.76	27.86
GEL 4	96.14	75.24	61.77	45.76	36.06
GEL 5	98.23	65.94	44.67	30.25	22.41
GEL 6	98.23	77.12	62.53	50.04	37.32
GEL 7	93.59	65.52	49.48	30.27	20.73
GEL 1+2% *	95.53	93.41	90.54	87.99	86.42
GEL 1+5% *	95.36	95.06	94.24	93.47	92.31
GEL 2+2% *	97.49	94.86	91.35	87.62	85.58
GEL 2+5% *	96.88	95.26	93.22	91.64	91.15

* percent of sorbitol added

Table 9

Rate constant of aluminum hydroxide gel from various sources during aging at ambient temperature

SAMPLE	Rate Constant at AT* $K \times 10^{2}$ ($month^{-1}$)	Y-intercept	Correlation Coefficient (r^2)
GEL 1	1.88	4.5628	0.9941
GEL 2	3.47	4.5852	0.9947
GEL 3	6.94	4.5507	0.9960
GEL 4	11.62	4.5703	0.9978
GEL 5	3.21	4.5789	0.9878
GEL 6	2.50	4.5932	0.9910
GEL 7	3.33	4.5462	0.9713

* ambient temperature

Table 10

Rate constant of aluminum hydroxide gel from various sources during aging at 45°c and stabilization effect of sorbitol

SAMPLE	Rate Constant at 45°c $K \times 10^{2}$ ($month^{-1}$)	Y-intercept	Correlation Coefficient (r^2)
GEL 1	5.84	4.5619	0.9837
GEL 2	19.80	4.5933	0.9995
GEL 3	31.29	4.5781	0.9961
GEL 4	24.58	4.5754	0.9967
GEL 5	37.35	4.5658	0.9975
GEL 6	23.68	4.5938	0.9964
GEL 7	37.87	4.5703	0.9930
GEL 1+2%*	2.60	4.5598	0.9931
GEL 1+5%*	0.82	4.5605	0.9635
GEL 2+2%*	3.40	4.5818	0.9926
GEL 2+5%*	1.61	4.5712	0.9696

* percent of sorbitol added

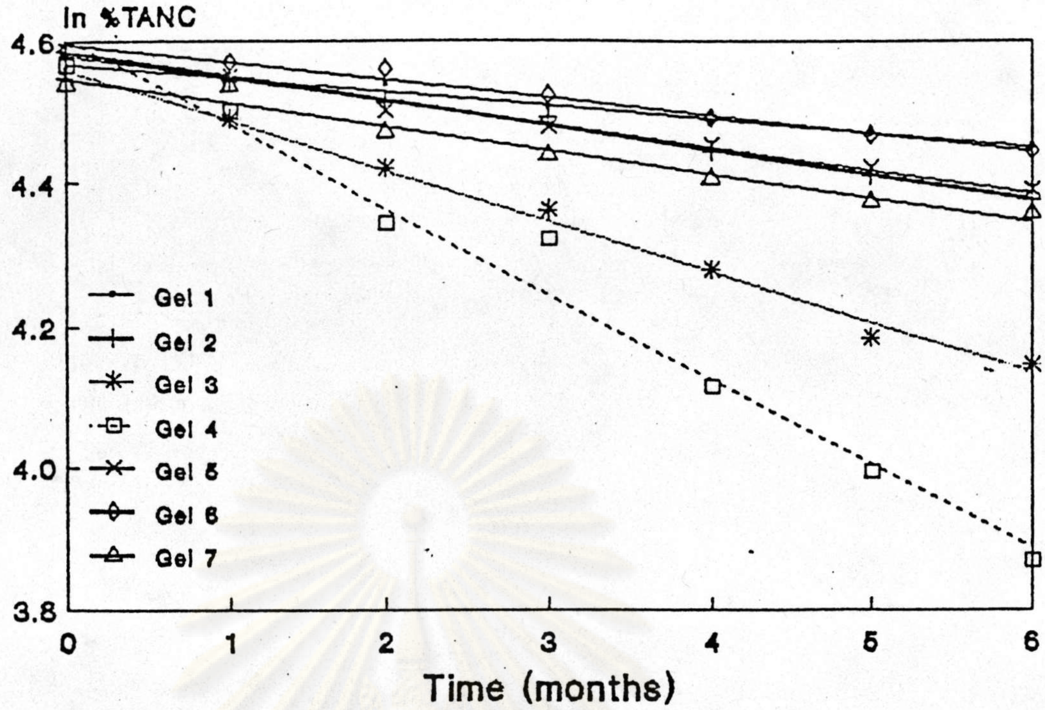

Figure 34 Change in Acid Neutralizing Capacity of aluminum hydroxide gel from various sources during aging at ambient temperature

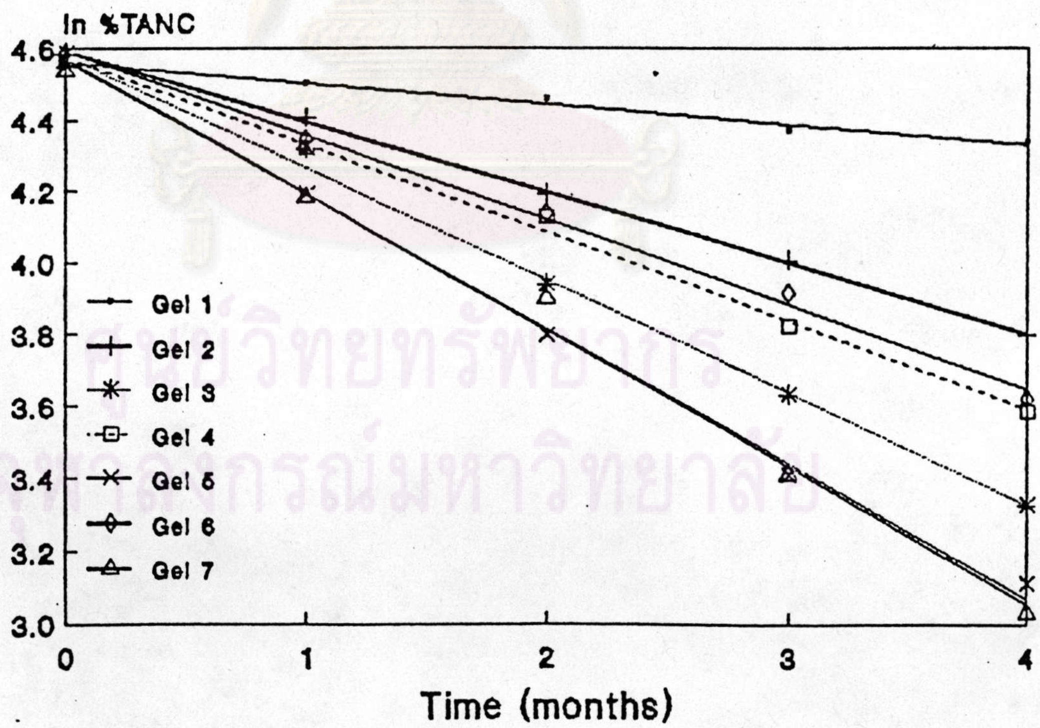

Figure 35 Change in Acid Neutralizing Capacity of aluminum hydroxide gel from various sources during aging at 45°c

Table 11

The reaction velocity test of aluminum hydroxide gel from various sources during aging at ambient temperature

SAMPLE	Time to reach pH 3.5(seconds)after storage at AT* for(months)						
	0	1	2	3	4	5	6
GEL 1	32	34	54	77	90	100	120
GEL 2	10	12	16	27	30	47	55
GEL 3	77	225	238	265	276	330	564
GEL 4	90	189	232	296	326	351	673
GEL 5	45	121	145	173	198	200	250
GEL 6	47	72	116	185	195	205	211
GEL 7	95	170	187	217	230	242	263

* ambient temperature

Table 12

The reaction velocity test of aluminum hydroxide gel from various sources during aging at 45°c and stabilization effect of sorbitol

SAMPLE	Time to reach pH 3.5(seconds) after storage at 45°c for(months)				
	0	1	2	3	4
GEL 1	32	37	139	182	254
GEL 2	10	16	36	758	NR
GEL 3	77	590	666	782	NR
GEL 4	90	594	630	889	NR
GEL 5	45	299	571	NR	NR
GEL 6	47	272	280	422	NR
GEL 7	95	561	622	NR	NR
GEL 1+2% *	75	88	94	150	200
GEL 1+5% *	115	123	136	171	210
GEL 2+2% *	20	25	28	31	40
GEL 2+5% *	23	30	37	50	71

NR = not reach pH 3.5 within 30 minutes
* = percent of sorbitol added

some of them which stored at 45°C could not reach pH 3.5 within 30 minutes.

4. Hydroxide to Aluminum Ratio

The molar ratio of bound hydroxide to aluminum for gels 1-7 during aging at ambient temperature and at 45°C are shown in Tables 13 and 14, respectively. The ratio increased as the gels aged. At ambient temperature the change in hydroxide to aluminum ratios as a function of times are illustrated in Figure 36. The ratios for gels 1, 5 and 6 remained relatively unchange. The plots of hydroxide to aluminum ratio of gels aging at 45°C versus times are revealed in Figure 37.

5. Point of Zero Charge (PZC)

The PZC of aluminum hydroxide gels were determined after storage at an ambient temperature for three months interval. Plots of pH values and the amount of acid or base added (ml) are illustrated in Figures 38-44 for gels 1-7 at the initial condition. The calculation of PZC was carried out by using computer program. The same method was utilized to calculated the PZC of the gels after storage for three and six months. The observed PZC values are listed in Table 15. The PZC of various gels were increased as a function of the gel aged.

Table 13

The Hydroxide to Aluminum ratio of aluminum hydroxide gel from various sources during aging at ambient temperature

SAMPLE	Hydroxide to Aluminum ratio after storage at AT* for(months)						
	0	1	2	3	4	5	6
GEL 1	2.48	2.48	2.50	2.58	2.57	2.58	2.60
GEL 2	2.52	2.54	2.56	2.57	2.58	2.63	2.67
GEL 3	2.41	2.50	2.56	2.60	2.64	2.69	2.71
GEL 4	2.47	2.51	2.56	2.61	2.66	2.72	2.74
GEL 5	2.54	2.56	2.57	2.58	2.59	2.60	2.62
GEL 6	2.54	2.55	2.56	2.57	2.57	2.58	2.61
GEL 7	2.43	2.55	2.57	2.58	2.59	2.60	2.65

* ambient temperature

Table 14

The Hydroxide to Aluminum ratio of aluminum hydroxide gel from various sources during aging at 45^{o}c and stabilization effect of sorbitol

SAMPLE	Hydroxide to Aluminum ratio after storage at 45^{o}c for(months)				
	0	1	2	3	4
GEL 1	2.48	2.55	2.60	2.61	2.70
GEL 2	2.52	2.56	2.70	2.70	2.75
GEL 3	2.41	2.56	2.60	2.72	2.82
GEL 4	2.47	2.60	2.69	2.75	2.79
GEL 5	2.54	2.67	2.78	2.81	2.86
GEL 6	2.54	2.57	2.56	2.72	2.80
GEL 7	2.43	2.71	2.73	2.77	2.81
GEL 1+2% *	2.50	2.52	2.55	2.57	2.62
GEL 1+5% *	2.45	2.50	2.53	2.56	2.57
GEL 2+2% *	2.51	2.54	2.56	2.58	2.58
GEL 2+5% *	2.48	2.52	2.55	2.57	2.56

* percent of sorbitol added

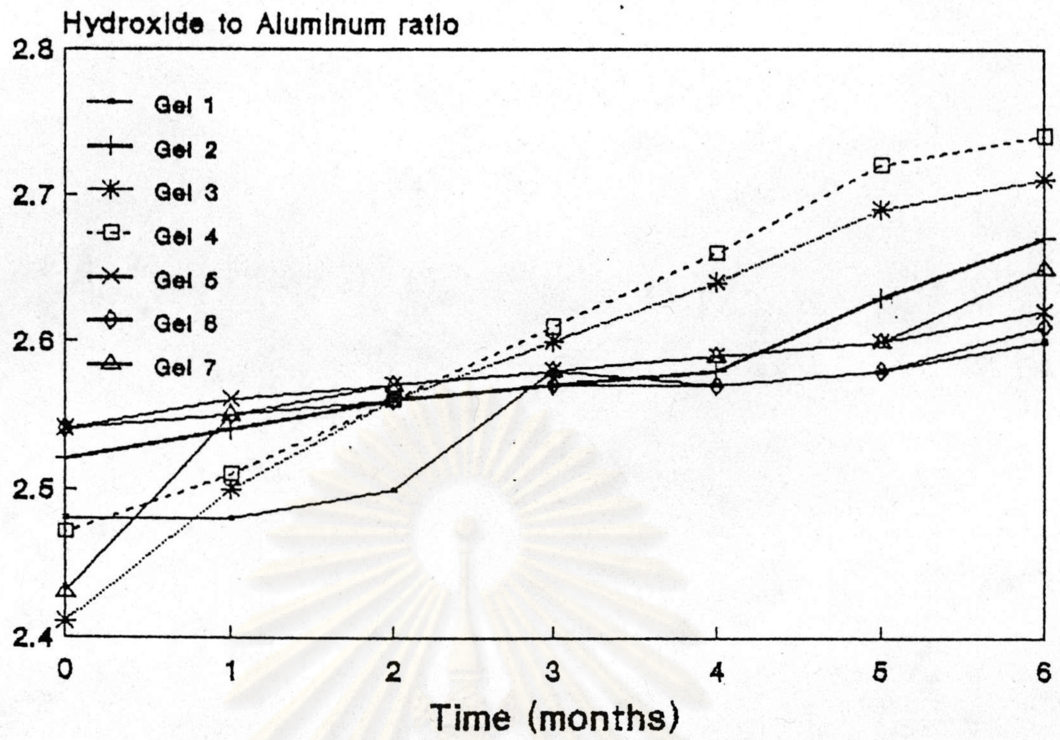

Figure 36 Change in Hydroxide to Aluminum ratio of aluminum hydroxide gel from various sources during aging at ambient temperature

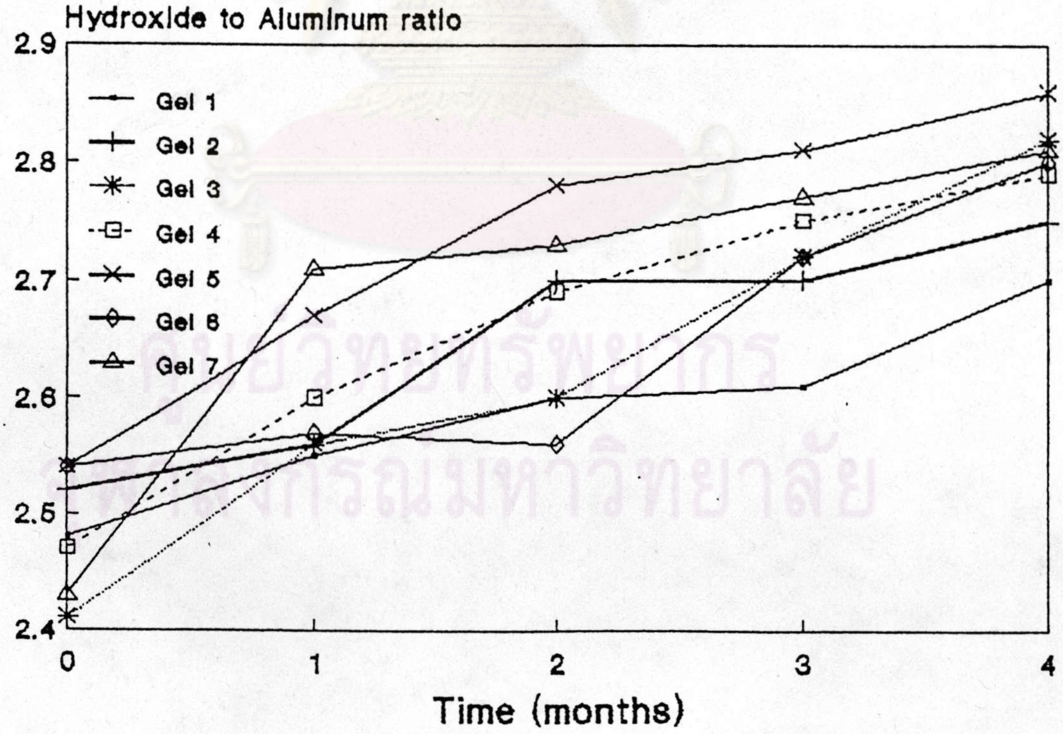

Figure 37 Change in Hydroxide to Aluminum ratio of aluminum hydroxide gel from various sources during aging at 45°c

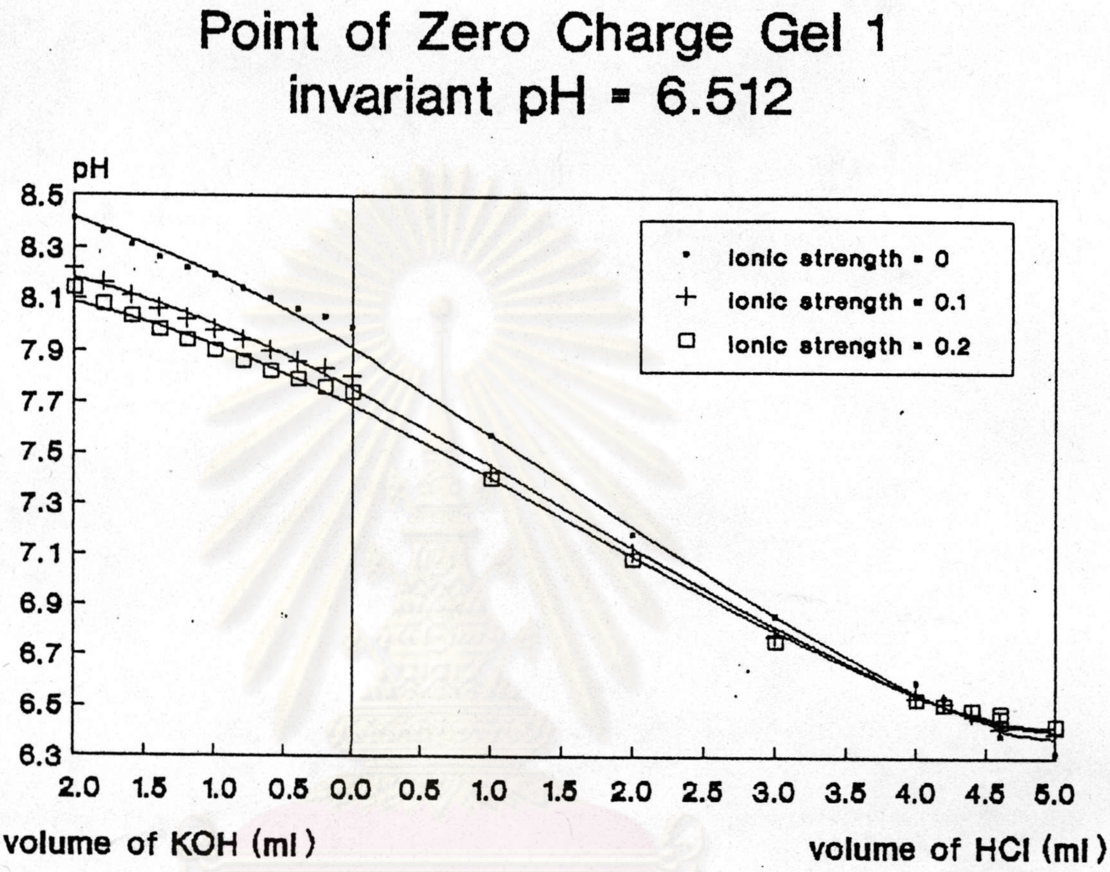

Figure 38 Determination of the Point of Zero Charge (PZC) of Gel 1 at initial condition

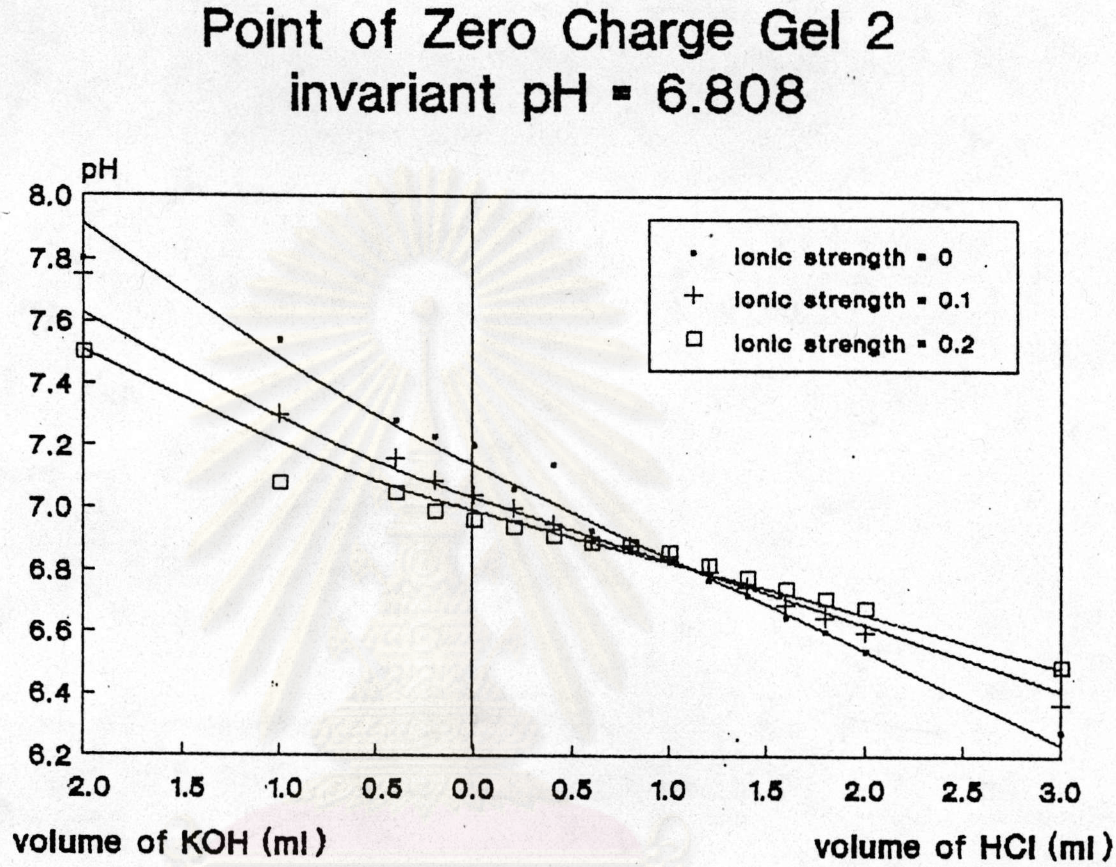

Figure 39 Determination of the Point of Zero Charge (PZC) of Gel 2 at initial condition

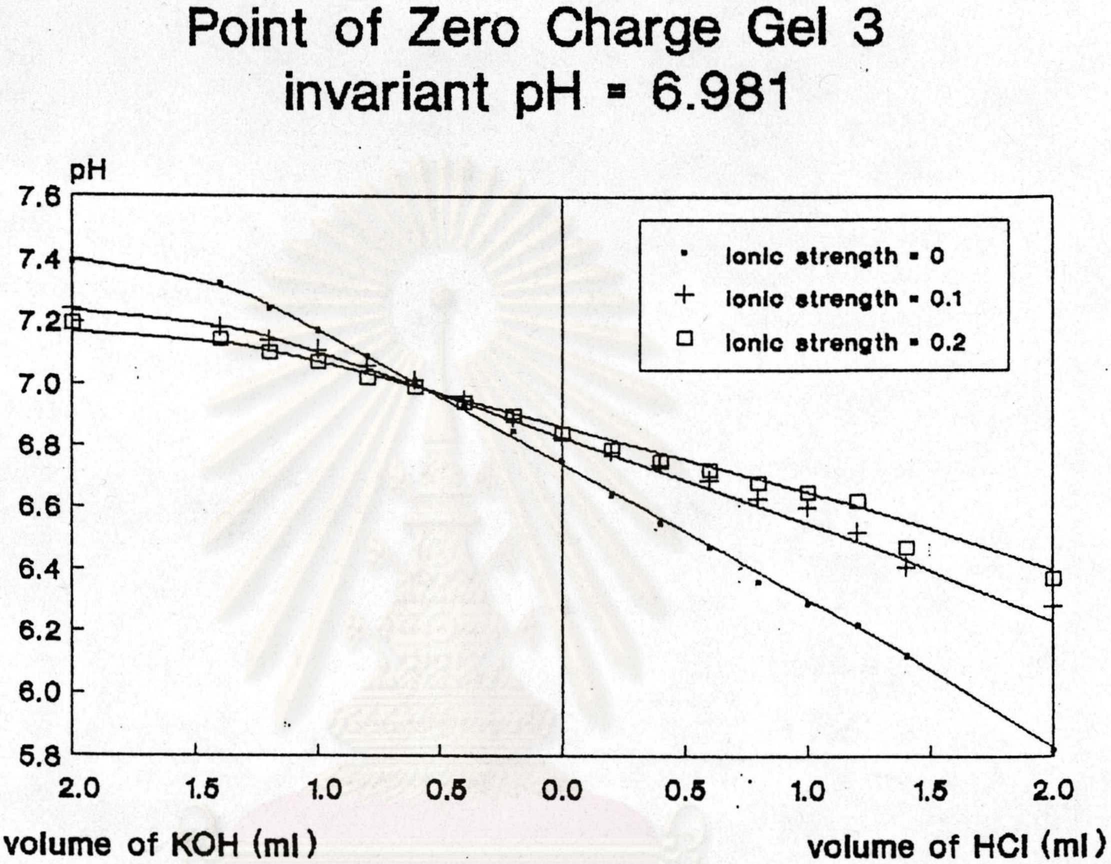

Figure 40 Determination of the Point of Zero Charge (PZC) of Gel 3 at initial condition

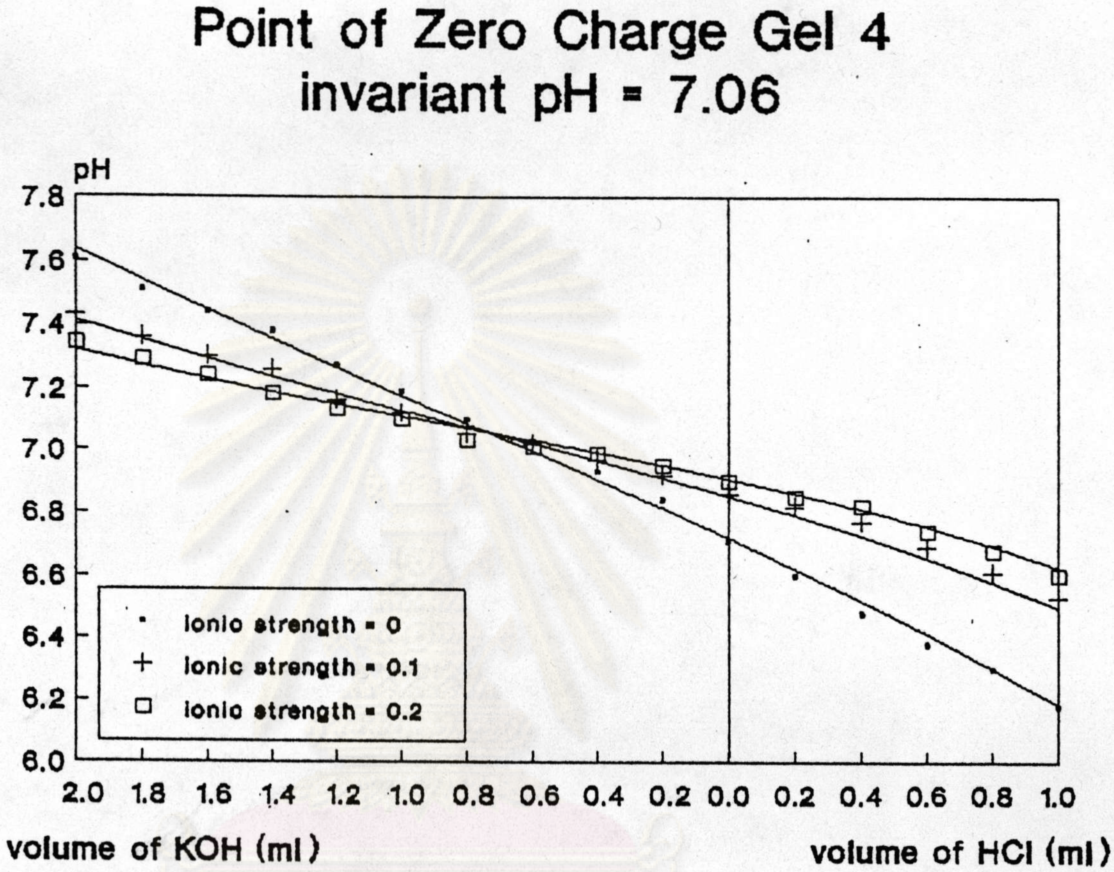

Figure 41 Determination of the Point of Zero Charge (PZC) of Gel 4 at initial condition

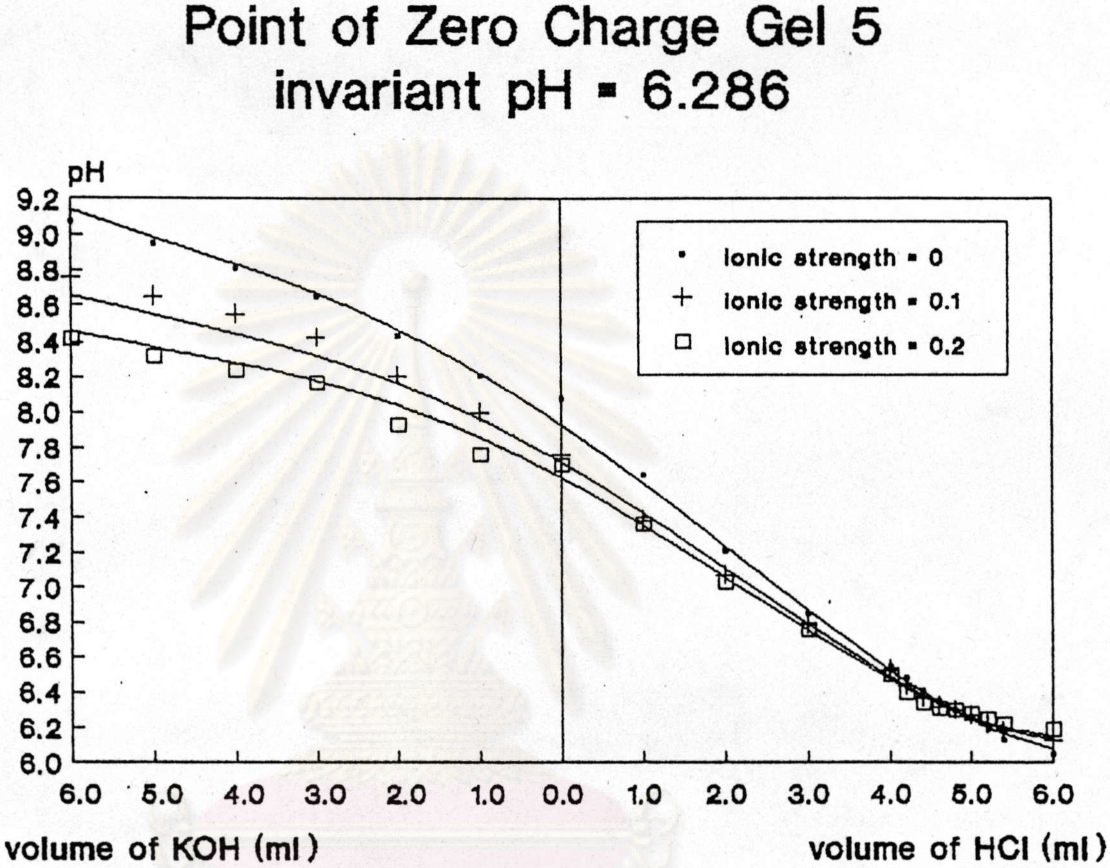

Figure 42 Determination of the Point of Zero Charge (PZC) of Gel 5 at initial condition

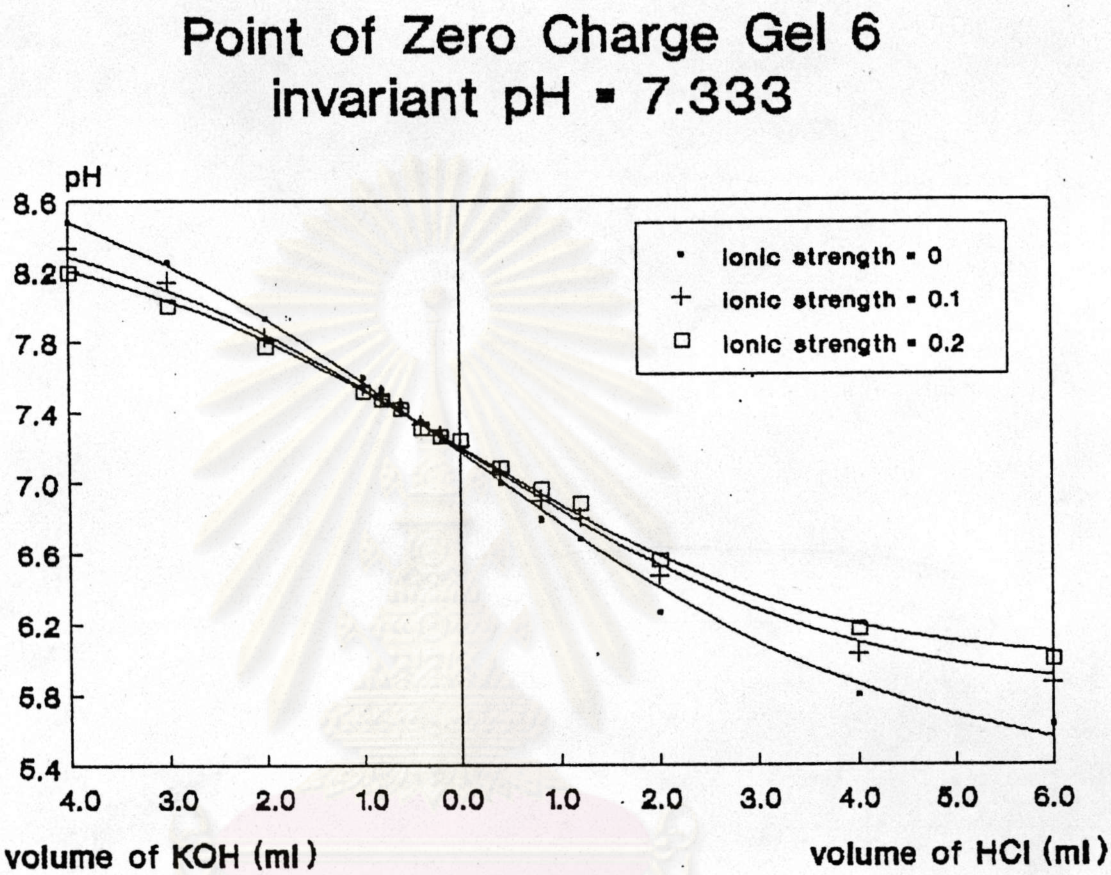

Figure 43 Determination of the Point of Zero Charge (PZC) of Gel 6 at initial condition

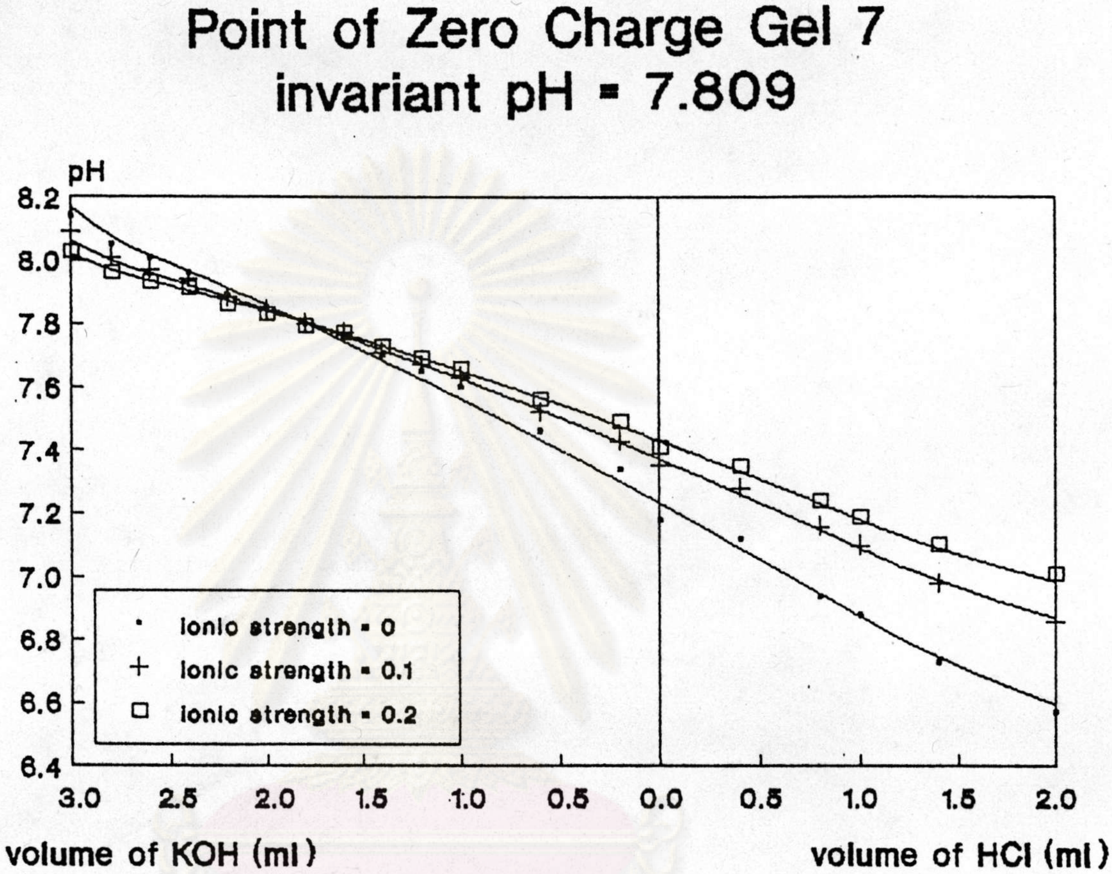

Figure 44 Determination of the Point of Zero Charge (PZC) of Gel 7 at initial condition

Table 15

Point of Zero Charge of aluminum hydroxide gel from various sources during aging at ambient temperature

SAMPLE	Point of Zero Charge after storage at AT* for (months)		
	0	3	6
GEL 1	6.512	6.552	6.628
GEL 2	6.808	6.929	6.957
GEL 3	6.981	7.262	7.464
GEL 4	7.060	7.482	7.407
GEL 5	6.286	6.584	7.073
GEL 6	7.333	7.580	7.665
GEL 7	7.809	7.840	8.030

* ambient temperature

Effect of Sorbitol on the Stability of Aluminum Hydroxide Gel

The use of polyols such as sorbitol to improve the stability of aluminum hydroxide gel have been studied by many authors (Nail et al., 1976 d; Shah et al., 1981). In the present study, the effect of sorbitol on the aging of aluminum hydroxide gel after storage at 45°C, was determined by following : pH, preliminary antacid test, acid neutralizing capacity test, reaction velocity test and hydroxide to aluminum ratio. It was found that of the acid neutralizing capacity, gels containing sorbitol loss less than an identical gels without sorbitol (Tables 8, 10, Figure 46). In addition, the pH value and hydroxide to aluminum ratio of the gels containing sorbitol still remained constant (Tables 4, 14, Figures 45, 47).

The increase in hydroxide to aluminum ratio indicated that further polymerization occurred during aging (Nail et al., 1976c). Sorbitol apparently inhibited the secondary polymerization. Inhibition of this reaction retarded particle growth and the subsequent development of crystalline forms of aluminum hydroxide. The mechanism of interaction between polyols and aluminum hydroxide gel was investigated by Shah et al. (1981). They showed that the hydrogen bonding between sorbitol and aluminum hydroxide gel corresponding to the decrease of the rate constant (Table 10). The comparisons of hydroxide to aluminum

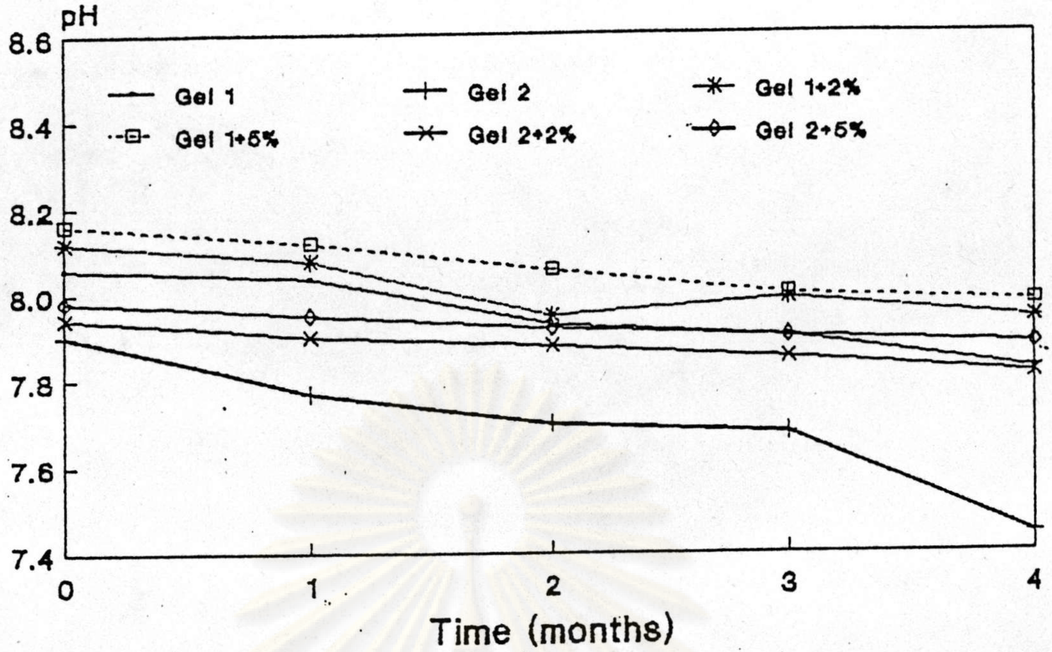

Figure 45 Effect of sorbitol on the change in pH values of aluminum hydroxide gel during aging at 45°c

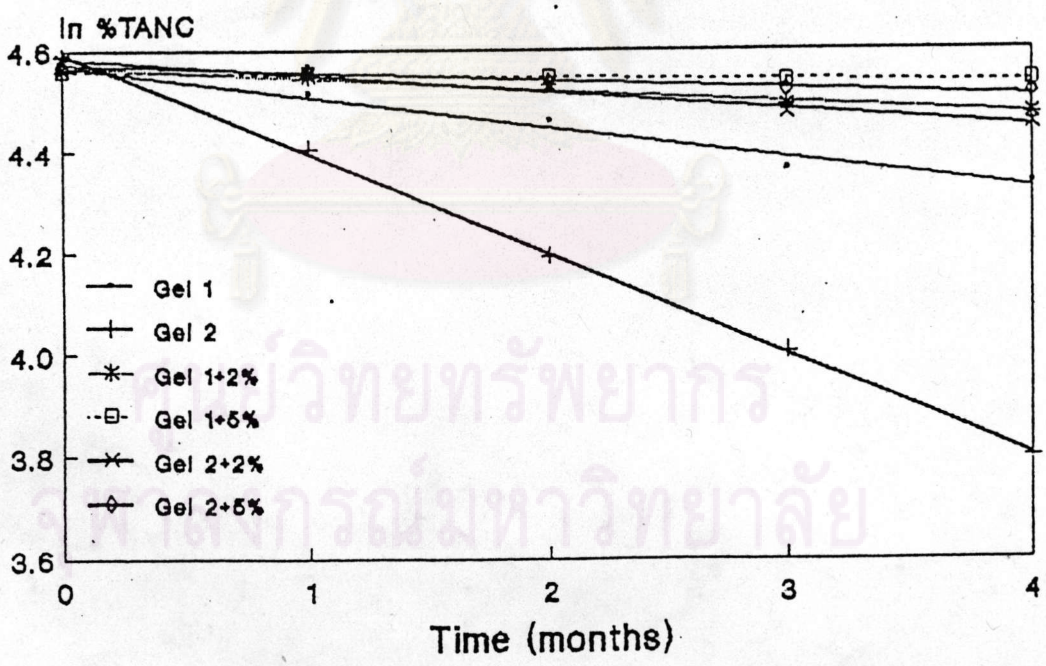

Figure 46 Effect of sorbitol on the change in Acid Neutralizing Capacity of aluminum hydroxide gel during aging at 45°c

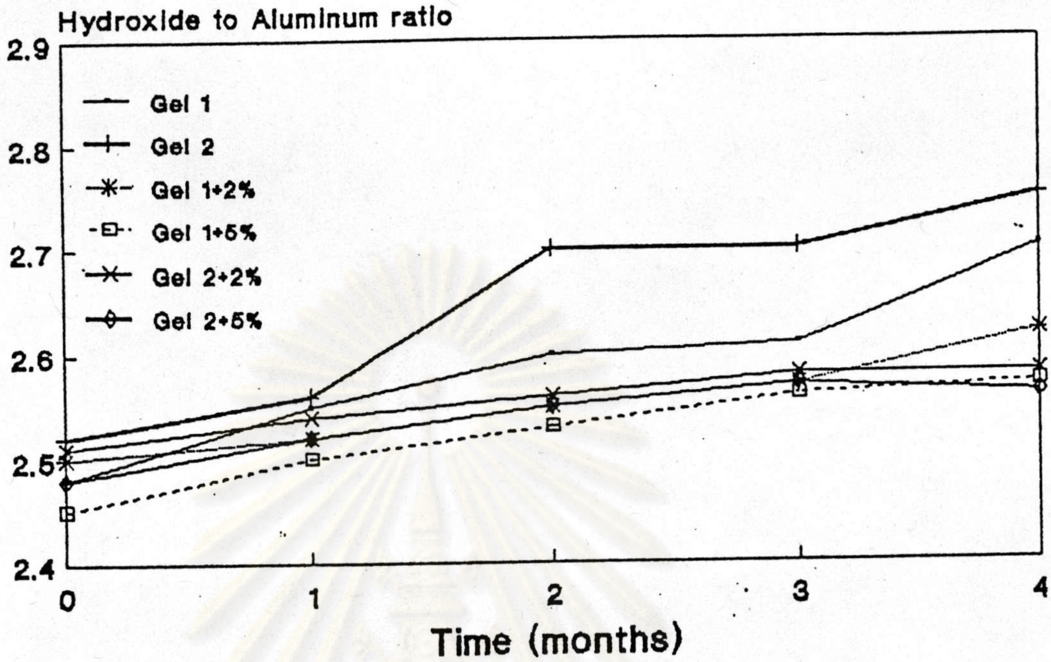

Figure 47 Effect of sorbitol on the change in Hydroxide to Aluminum ratio of aluminum hydroxide gel during aging at 45°c

ratio are shown in Figure 47. It may be observed that the hydroxide to aluminum ratio of gels with sorbitol increased less than gels without sorbitol during aging at 45°C.

The Surface Adsorption of Preservatives by Aluminum Hydroxide Gel

The effect of pH on the adsorption of methyl paraben, propyl paraben, butyl paraben and chlorhexidine gluconate on aluminum hydroxide (Gel 1 and Gel 2) are illustrated (Figures 48-55). The results showed that the adsorption of various esters of parabens decreased with increasing pH (Tables 16-21). The same plot was also prepared for chlorhexidine gluconate, but the different result occured. It was shown that the adsorption of chlorhexidine gluconate increased as pH was increased. (Tables 22, 23).

A major influence of pH is on the degree of ionization of the esters of parabens, with pKa values of 8.4 (Martin, 1983). Therefore, the equilibrium concentration was calculated as the concentration of unionized compound, and Langmuirian constants were calculated from these data (Tables 24-26). The correlation coefficient indicated that the adsorption was Langmuirian. In addition, the Langmuirian constants of chlorhexidine gluconate is shown in Table 27.

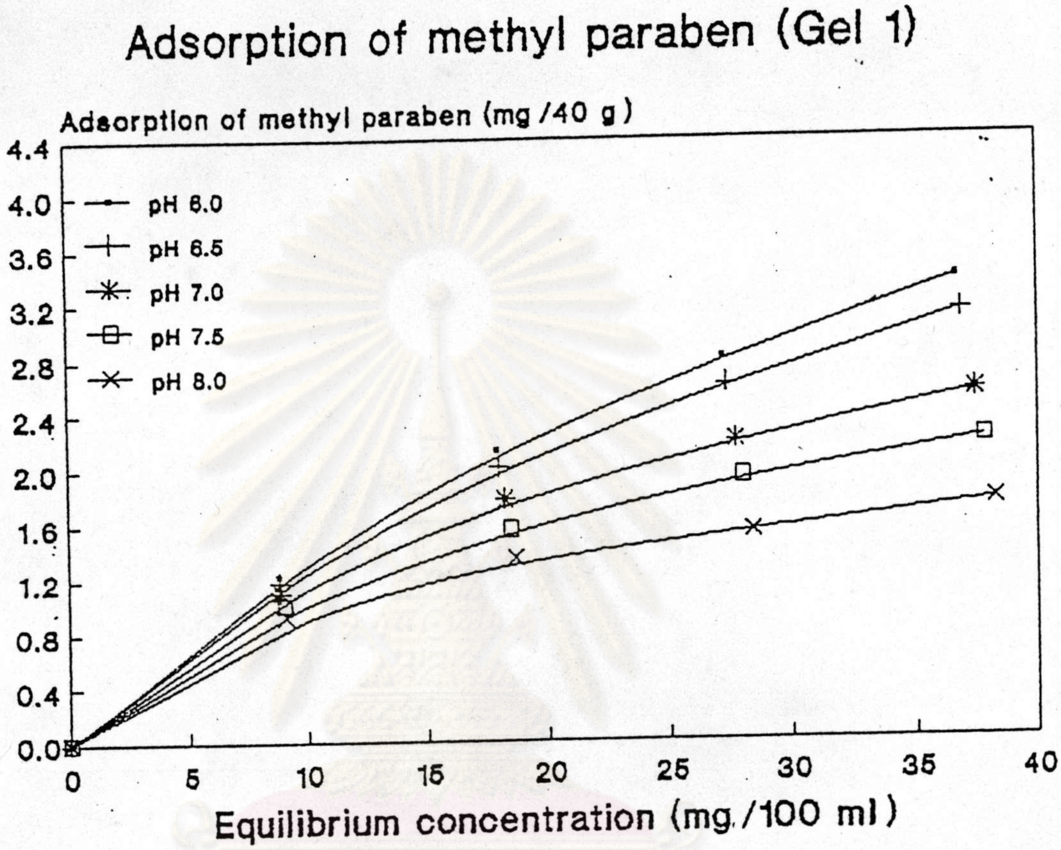

Figure 48 Adsorption isotherms for the adsorption of methyl paraben to Gel 1 at various pH values

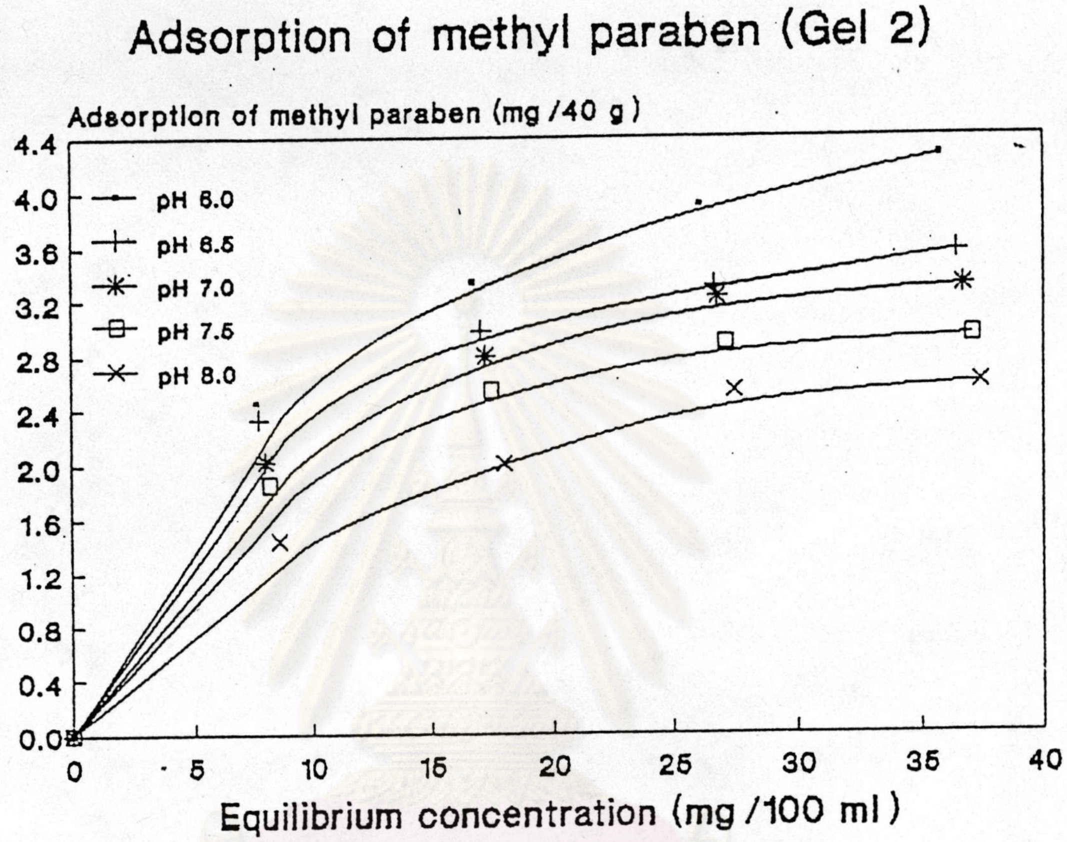

Figure 49 Adsorption isotherms for the adsorption of methyl paraben to Gel 2 at various pH values

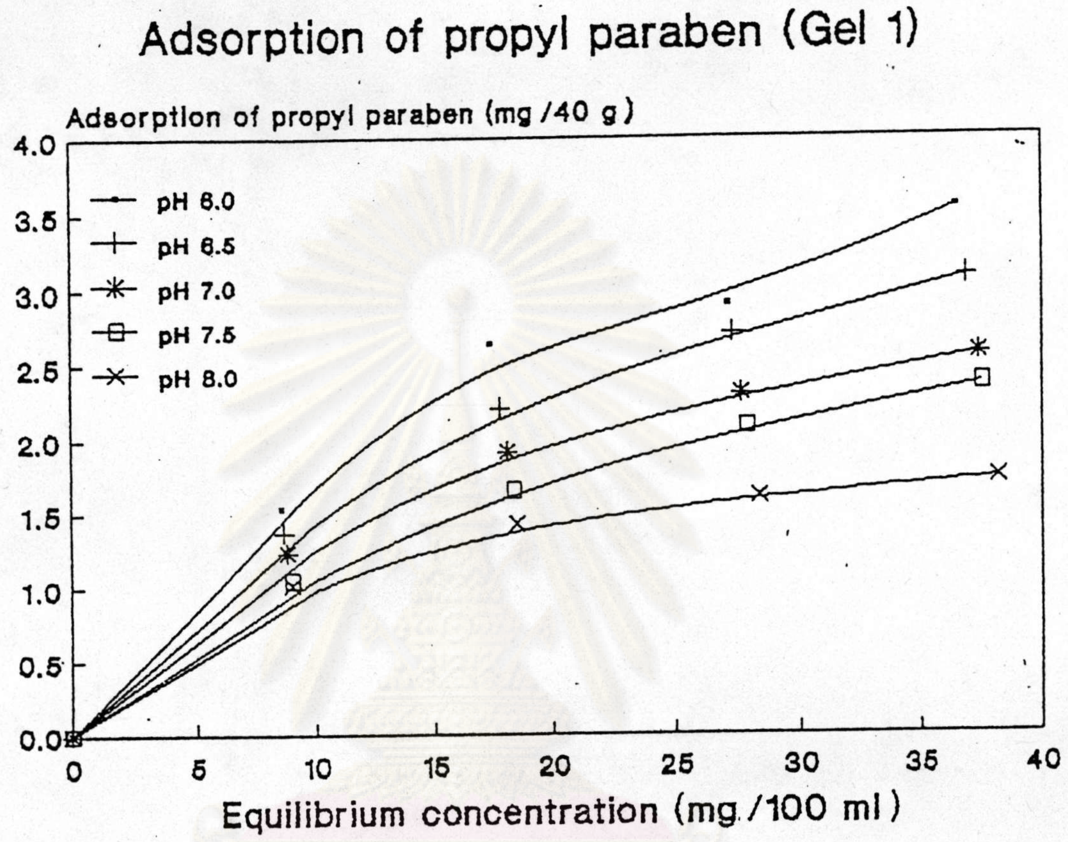

Figure 50 Adsorption isotherms for the adsorption of propyl paraben to Gel 1 at various pH values

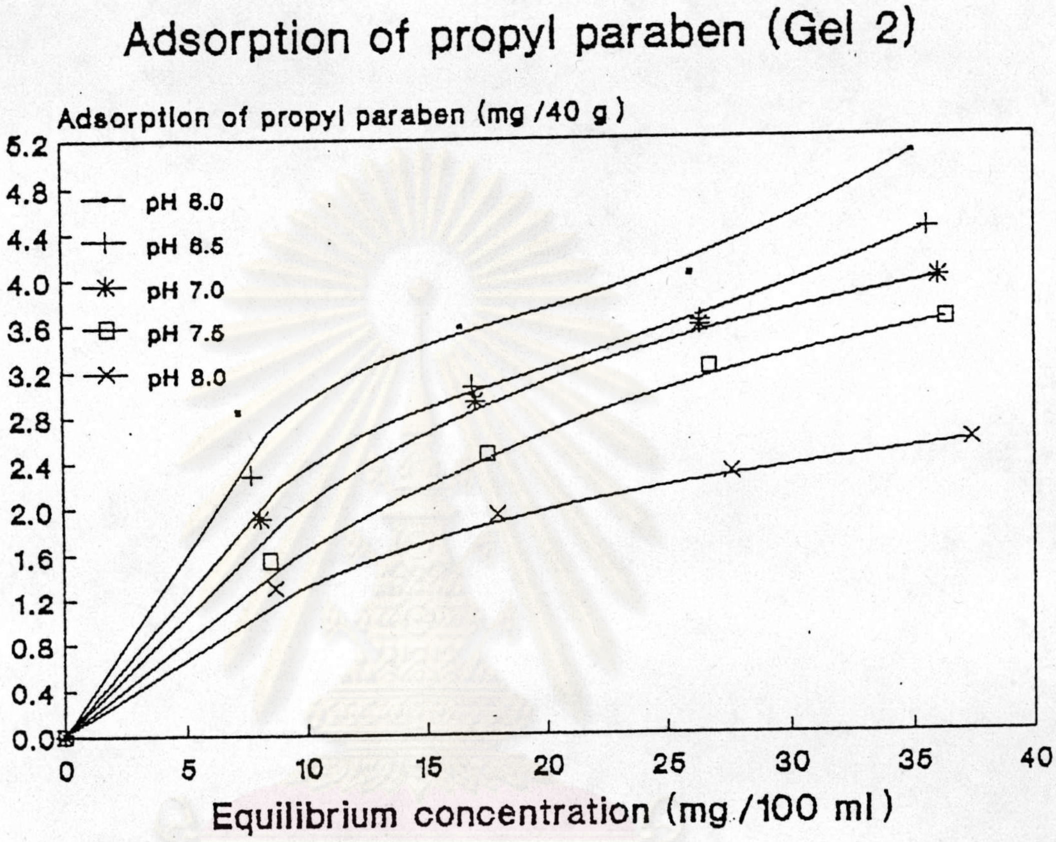

Figure 51 Adsorption isotherms for the adsorption of propyl paraben to Gel 2 at various pH values

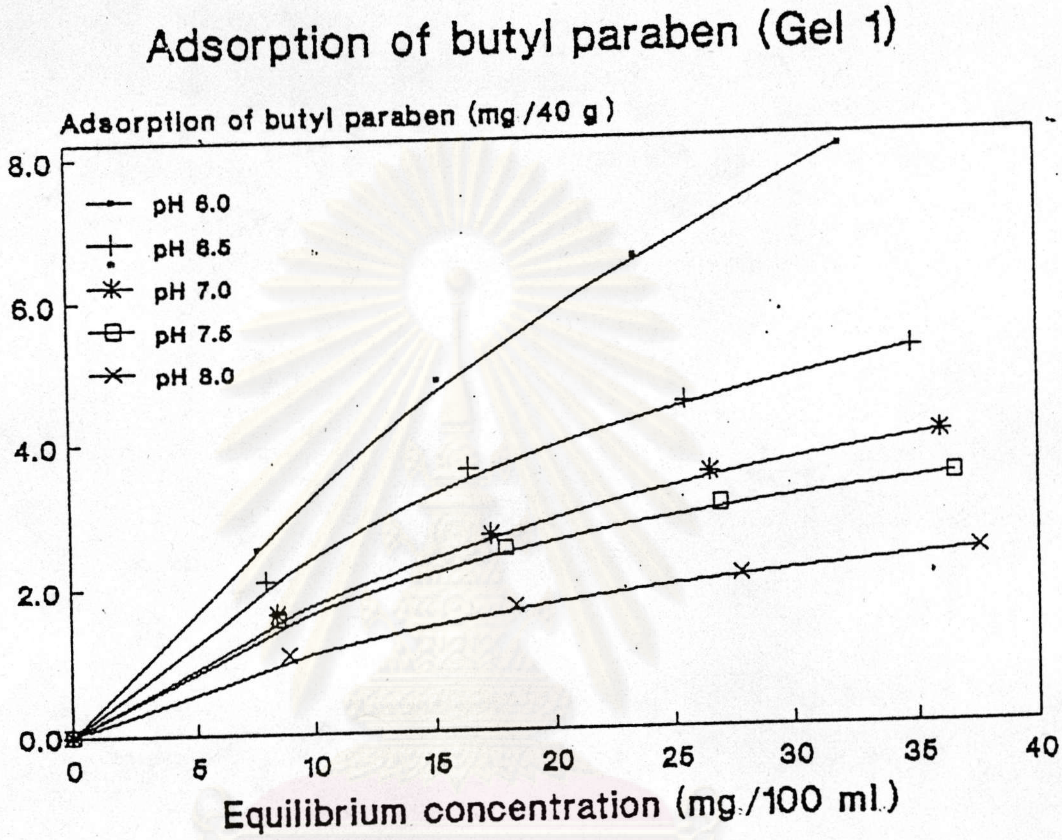

Figure 52 Adsorption isotherms for the adsorption of butyl paraben to Gel 1 at various pH values

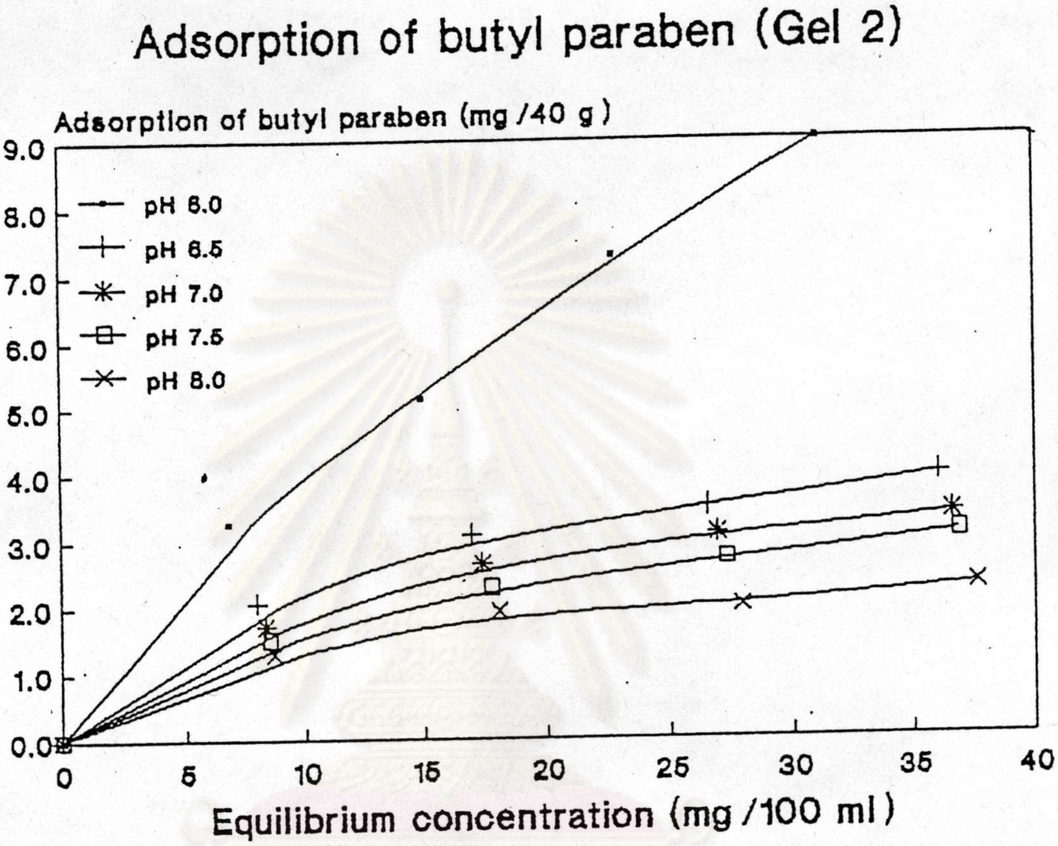

Figure 53 Adsorption isotherms for the adsorption of butyl paraben to Gel 2 at various pH values

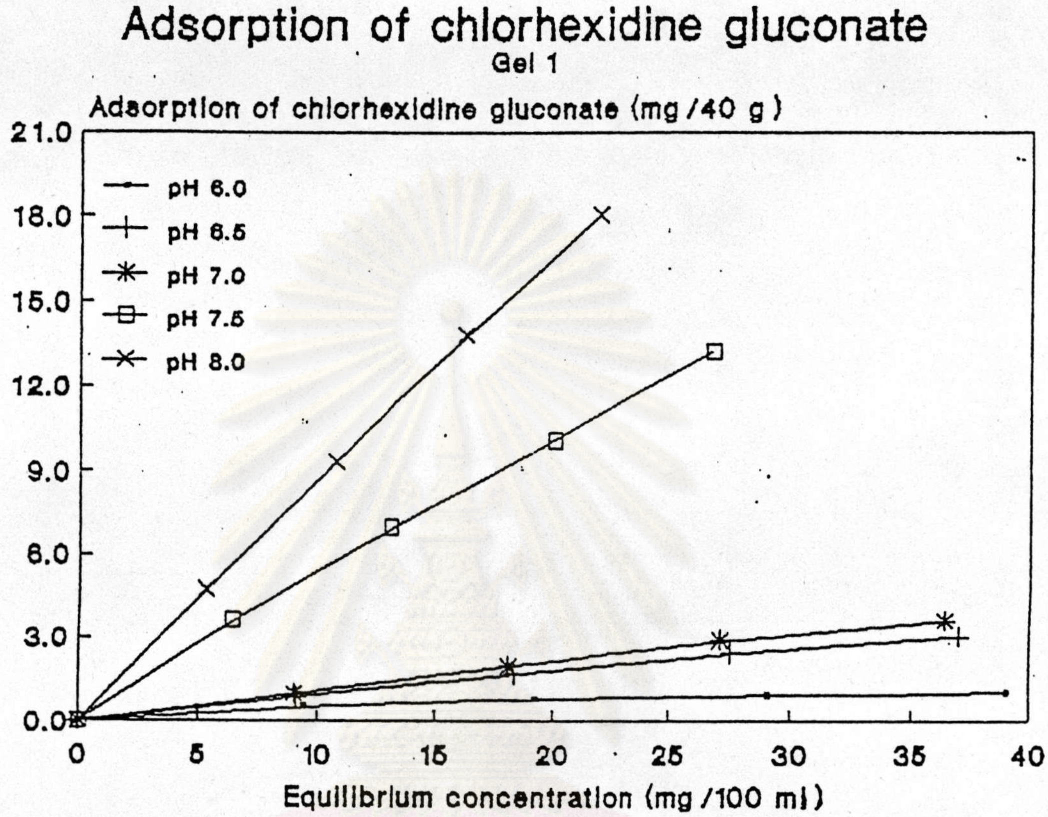

Figure 54 Adsorption isotherms for the adsorption of chlorhexidine gluconate to Gel 1 at various pH values

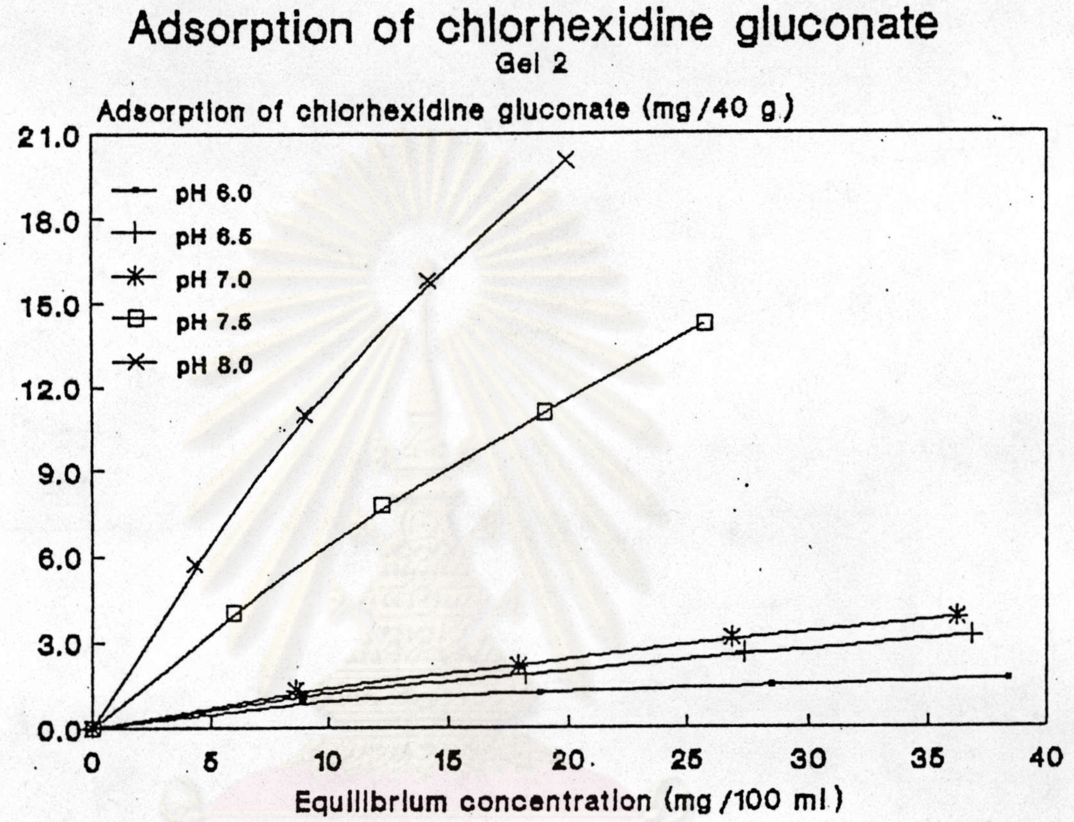

Figure 55 Adsorption isotherms for the adsorption of chlorhexidine gluconate to Gel 2 at various pH values

Table 16

Adsorption of methyl paraben to Gel 1 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	8.78[a]	1.22
	17.85[b]	2.13
	27.25[c]	2.79
	36.65[d]	3.36
6.50	8.82[a]	1.18
	17.97[b]	2.01
	27.39[c]	2.60
	36.89[d]	3.12
7.00	8.90[a]	1.10
	18.21[b]	1.77
	27.80[c]	2.19
	37.47[d]	2.54
7.50	9.00[a]	1.00
	18.42[b]	1.56
	28.06[c]	1.93
	37.81[d]	2.20
8.00	9.08[a]	0.92
	18.63[b]	1.35
	28.46[c]	1.53
	38.27[d]	1.74

a = initial concentration 10 mg /100 ml
b = initial concentration 20 mg /100 ml
c = initial concentration 30 mg /100 ml
d = initial concentration 40 mg /100 ml

Table 17

Adsorption of methyl paraben to Gel 2 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	7.55 [a]	2.45
	16.64 [b]	3.34
	26.06 [c]	3.90
	35.75 [d]	4.26
6.50	7.67 [a]	2.33
	17.00 [b]	2.98
	26.68 [c]	3.31
	36.45 [d]	3.56
7.00	7.98 [a]	2.02
	17.19 [b]	2.79
	26.77 [c]	3.22
	36.71 [d]	3.30
7.50	8.14 [a]	1.85
	17.44 [b]	2.54
	27.11 [c]	2.88
	37.08 [d]	2.93
8.00	8.56 [a]	1.44
	17.98 [b]	2.00
	27.46 [c]	2.53
	37.43 [d]	2.58

a = initial concentration 10 mg /100 ml
b = initial concentration 20 mg /100 ml
c = initial concentration 30 mg /100 ml
d = initial concentration 40 mg /100 ml

Table 18

Adsorption of propyl paraben to Gel 1 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	8.48 [a]	1.53
	17.35 [b]	2.64
	27.09 [c]	2.90
	36.49 [d]	3.53
6.50	8.64 [a]	1.37
	17.80 [b]	2.20
	27.30 [c]	2.71
	36.93 [d]	3.07
7.00	8.74 [a]	1.23
	18.08 [b]	1.91
	27.66 [c]	2.30
	37.45 [d]	2.56
7.50	8.94 [a]	1.04
	18.33 [b]	1.65
	27.88 [c]	2.08
	37.58 [d]	2.36
8.00	8.95 [a]	1.01
	18.47 [b]	1.42
	28.38 [c]	1.60
	38.23 [d]	1.72

a = initial concentration 10 mg/100ml
b = initial concentration 20 mg/100ml
c = initial concentration 30 mg/100ml
d = initial concentration 40 mg/100ml

Table 19

Adsorption of propyl paraben to Gel 2 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	7.17 [a]	2.84
	16.42 [b]	3.57
	25.97 [c]	4.02
	34.97 [d]	5.05
6.50	7.72 [a]	2.29
	16.95 [b]	3.05
	26.41 [c]	3.60
	35.60 [d]	4.40
7.00	8.06 [a]	1.91
	17.07 [b]	2.92
	26.39 [c]	3.57
	36.04 [d]	3.97
7.50	8.43 [a]	1.54
	17.52 [b]	2.46
	26.76 [c]	3.20
	36.33 [d]	3.61
8.00	8.67 [a]	1.29
	17.96 [b]	1.93
	27.67 [c]	2.29
	37.40 [d]	2.55

a = initial concentration 10 mg/100 ml
b = initial concentration 20 mg/100 ml
c = initial concentration 30 mg/100 ml
d = initial concentration 40 mg/100 ml

Table 20

Adsorption of butyl paraben to Gel 1 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	7.48 [a]	2.52
	15.17 [b]	4.85
	23.45 [c]	6.55
	32.02 [d]	8.02
6.50	7.91 [a]	2.09
	16.40 [b]	3.60
	25.52 [c]	4.48
	34.80 [d]	5.21
7.00	8.39 [a]	1.62
	17.31 [b]	2.68
	26.51 [c]	3.49
	35.96 [d]	4.01
7.50	8.42 [a]	1.56
	17.89 [b]	2.49
	26.93 [c]	3.05
	36.52 [d]	3.42
8.00	8.87 [a]	1.07
	18.29 [b]	1.68
	27.90 [c]	2.08
	37.58 [d]	2.38

a = initial concentration 10 mg/100 ml
b = initial concentration 20 mg/100 ml
c = initial concentration 30 mg/100 ml
d = initial concentration 40 mg/100 ml

Table 21

Adsorption of butyl paraben to Gel 2 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	6.80 [a]	3.20
	14.90 [b]	5.12
	22.73 [c]	7.27
	31.04 [d]	9.00
6.50	7.95 [a]	2.05
	16.94 [b]	3.06
	26.54 [c]	3.46
	36.08 [d]	3.93
7.00	8.31 [a]	1.70
	17.37 [b]	2.62
	26.94 [c]	3.06
	36.63 [d]	3.34
7.50	8.47 [a]	1.51
	17.73 [b]	2.26
	27.29 [c]	2.69
	36.88 [d]	3.06
8.00	8.66 [a]	1.28
	18.06 [b]	1.91
	28.01 [c]	1.97
	37.69 [d]	2.27

a = initial concentration 10 mg/100 ml
b = initial concentration 20 mg/100 ml
c = initial concentration 30 mg/100 ml
d = initial concentration 40 mg/100 ml

Table 22

Adsorption of chlorhexidine gluconate to Gel 1 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	9.42 [a]	0.58
	19.22 [b]	0.78
	29.06 [c]	0.92
	39.04 [d]	1.01
6.50	9.12 [a]	0.89
	18.36 [b]	1.66
	27.59 [c]	2.41
	37.01 [d]	3.00
7.00	9.00 [a]	0.99
	18.08 [b]	1.95
	27.16 [c]	2.85
	36.42 [d]	3.58
7.50	6.38 [a]	3.62
	13.05 [b]	6.95
	20.00 [c]	10.02
	26.80 [d]	13.21
8.00	5.28 [a]	4.71
	10.69 [b]	9.30
	16.20 [c]	13.79
	21.96 [d]	18.04

a = initial concentration 10 mg/100 ml
b = initial concentration 20 mg/100 ml
c = initial concentration 30 mg/100 ml
d = initial concentration 40 mg/100 ml

Table 23

Adsorption of chlorhexidine gluconate to Gel 2 at various pH values

pH	Equilibrium concentration C(mg /100 ml)	Adsorption x(mg /40 g)
6.00	8.99 [a]	1.01
	18.78 [b]	1.22
	28.52 [c]	1.46
	38.36 [d]	1.69
6.50	8.81 [a]	1.20
	18.18 [b]	1.84
	27.43 [c]	2.57
	36.83 [d]	3.18
7.00	8.66 [a]	1.33
	17.88 [b]	2.15
	26.90 [c]	3.11
	36.18 [d]	3.82
7.50	5.98 [a]	4.02
	12.25 [b]	7.75
	18.98 [c]	11.04
	25.77 [d]	14.24
8.00	4.28 [a]	5.71
	9.01 [b]	10.98
	14.18 [c]	15.81
	19.93 [d]	20.07

a = initial concentration 10 mg/100 ml
b = initial concentration 20 mg/100 ml
c = initial concentration 30 mg/100 ml
d = initial concentration 40 mg/100 ml

Table 24

The Langmuirian constants* for the adsorption of methyl paraben to aluminum hydroxide gel at various pH values

pH	Methyl paraben (Gel 1)			Methyl paraben (Gel 2)		
	r^2	a	b	r^2	a	b
6.0	0.9987	0.0225	0.1857	0.9983	0.1075	0.1333
6.5	0.9980	0.0258	0.1599	0.9989	0.1612	0.1035
7.0	0.9990	0.0408	0.1062	0.9975	0.1367	0.1009
7.5	0.9995	0.0502	0.0875	0.9974	0.1675	0.0878
8.0	0.9960	0.1028	0.0585	0.9881	0.1255	0.0856

* Equilibrium concentration calculated as the unionized species

Table 25

The Langmuirian constants* for the adsorption of propyl paraben to aluminum hydroxide gel at various pH values

pH	Propyl paraben (Gel 1)			Propyl paraben (Gel 2)		
	r^2	a	b	r^2	a	b
6.0	0.9644	0.0479	0.1363	0.9718	0.0963	0.1539
6.5	0.9998	0.0456	0.1230	0.9605	0.0733	0.1458
7.0	0.9998	0.0577	0.0950	0.9998	0.0639	0.1442
7.5	0.9987	0.0511	0.0909	0.9969	0.0527	0.1425
8.0	0.9998	0.1458	0.0540	0.9997	0.0975	0.0885

* Equilibrium concentration calculated as the unionized species

Table 26

The Langmuirian constants* for the adsorption of butyl paraben to aluminum hydroxide gel at various pH values

pH	Butyl paraben (Gel 1)			Butyl paraben (Gel 2)		
	r^2	a	b	r^2	a	b
6.0	0.9740	0.0169	0.5781	0.9199	0.0272	0.4804
6.5	0.9970	0.0389	0.2280	0.9961	0.0824	0.1302
7.0	0.9990	0.0353	0.1832	0.9987	0.0757	0.1155
7.5	0.9998	0.0582	0.1316	0.9978	0.0706	0.1088
8.0	0.9992	0.0650	0.0939	0.9855	0.1492	0.0698

* Equilibrium concentration calculated as the unionized species

Table 27

The Langmuirian constants* for the adsorption of chlorhexidine gluconate to aluminum hydroxide gel at various pH values

pH	Chlorhexidine gluconate (Gel 1)			Chlorhexidine gluconate (Gel 2)		
	r^2	a	b	r^2	a	b
6.0	0.9976	0.0782	0.0333	0.9728	0.0828	0.0537
6.5	0.9812	0.0074	0.3488	0.9163	0.0221	0.1726
7.0	0.9160	0.0044	0.6506	0.9085	0.0168	0.2483
7.5	0.9520	0.0079	1.8601	0.9933	0.0121	1.4948
8.0	0.9889	0.0052	4.4170	0.9991	0.0228	1.6126