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Résumé

Nous avons étudié l'adsorption négative des anions $I^*O_3^-$ et $Cr^*O_4^{--}$ à différents bentonites en fonction d'électrolytes additionnés. Pour les électrolytes NaCl et Na_2SO_4 les résultats sont en bon accord avec ceux de SCHOFIELD et MATTSON; nous avons étudié aussi l'effet de l'addition de solutions de $CaCl_2$; celles-ci produisent le même effet à des dilutions 20 fois plus grandes que les solutions de NaCl. Comme ceci ne peut pas être expliqué sur la base de la théorie de DEBYE-HÜCKEL, nous avons appliqué la théorie exacte de la couche double; le facteur 20 mentionné plus haut mène à une valeur de $\zeta = -75$ mV. En introduisant cette valeur de ξ, une représentation graphique $s\delta - 1/\sqrt{c}$ pour les résultats des expériences au Na-bentonite + solutions de NaCl, donne une surface spécifique de 1110 m²/g.

The Structure of Schmidt's Aluminium Hydroxide Gel

Aluminum hydroxide gels are used as adsorbents for proteins, enzymes, and viruses, particularly for preparing vaccines against foot-and-mouth disease[1]. The gel first used for this purpose was WILLSTÄTTER's C-gamma gel, which was the final product of aging in aqueous solution of the C-alpha gel, which is amorphous aluminum hydroxide, through an intermediary C-beta gel, which is the aluminum oxide monohydrate, Boehmite[2]. These transformations are slow, taking months for completion into the C-gamma gel. SCHMIDT[3] modified WILLSTÄTTER's procedure by autoclaving the C-alpha gel at 120°C in order to obtain a stable product in a shorter time. The gel thus obtained is considered similar to WILLSTÄTTER's C-gamma gel[4]. The purpose of this communication is to show, by X-ray diffraction and electron microscopy, that SCHMIDT's gel is made up of particles which are different in crystalline structure, morphology, and dimensions from WILLSTÄTTER's C-gamma gel, but similar to WILLSTÄTTER's C-beta gel.

SCHMIDT's gel was prepared according to the original paper[3], or obtained as sold by Aktieselskabet Kemisk Industri from Kopenhagen[1]. WILLSTÄTTER's C-gamma gel was prepared by the original procedure[5], or by KRAUT's procedure[6] from ammonium alum. The gels were prepared for and examined by X-ray diffraction and electron microscopy as described previously[7]. The data from X-ray diffraction powder photographs are listed in the Table along with data on well crystallized Boehmite[8]. Figures 1 and 2 are electron micrographs of SCHMIDT's gel. Figure 3*A* is of WILLSTÄTTER's gel and Figure 3*B* is of KRAUT's C-gamma gel.

Fig. 1.—Electron micrograph, ×20000 of SCHMIDT's aluminum hydroxide gel dried on Formvar from aqueous suspension and shadow cast with chromium at arctan 0·32.

From the Table it is evident that both samples of SCHMIDT's gels have the most characteristic lines of Boehmite[9] and that the lines are different from those of the C-gamma gel which are composed of a mixture of aluminum oxide trihydrates, Bayerite and Gibbsite[10]. Figures 1 and 2 are of SCHMIDT's gel, dried on a Formvar substrate and shadow cast with chromium at arctan 0·32 showing typical aggregates of fine particles (*X*) and fibrils (*Y*) at low magnification (×20 000) in Figure 1 and at higher magnification (×62 000) in Figure 2. The fibrils range in diameter from about 50 to 100 A.U., Figure 2*A*. Although they appear to be relatively short (lengths average about 400 to 1000 A.U.), and no long, extended fibrils are observed, they can measure as long as about 0·25 μ. While the major portion of the material appears to be fibrous, there are also crystalline particulates in a wide distribution of diameters as large as 0·5 μ and as small as 200 A.U., Figure 2*B*. Both Figures 1 and 2 contain material which is similar to that observed in C-beta gels formed by aging of C-alpha gels at room temperature[11] in pH's greater than 7·4, or to that observed in C-beta gels formed by boiling concentrated aqueous suspensions of amorphous aluminum hydroxides[12] precipitated from aluminum chloride (or nitrate) by ammonium hydroxide solution.

C-gamma gels are composed of particles of a completely different morphology from SCHMIDT's gels. This is demon-

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Fig. 2.—Electron micrograph, × 62000 of SCHMIDT's gel dried on Formvar from aqueous suspension, shadow cast with chromium at arctan 0·32.
(*A*) To show the predominant fibrous fraction.
(*B*) To show the crystalline, particulate fraction.

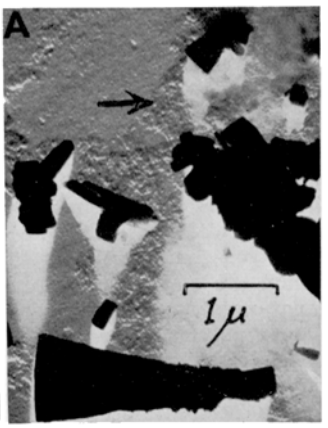

Fig. 3.—Electron Micrographs of C-gamma gel of aluminum hydroxide, × 12000, dried on Formvar film and shadow cast with chromium at arctan 0·32.
(*A*) of WILLSTÄTTER's gel.
(*B*) of KRAUT's gel.

Comparison between the X-Ray Powder Patterns of well Crystallized Boehmite with SCHMIDT's and *C*-Gamma Gels

No.	Standard Boehmite		SCHMIDT's gel		SCHMIDT's gel Akt. Kemisk		C-gamma gel WILLSTÄTTER's		C-gamma gel KRAUT's	
	d(A. U.)	I/I_0	*d*(A. U.)	I/I_0	*d*(A. U.)	I/I_0	*d*(A. U.)	I/I_0	*d*(A. U.)	I/I_0
1	6·11	1·00	13·00	1·00	4·42	1·00	5·23	0·20	5·29	0·20
2	3·164	0·65	5·59	0·38	3·12	0·20	4·85	0·50	4·80	1·00
3	2·346	0·53	4·35	0·56	2·31	0·40	4·72	1·00	4·33	0·90
4	1·980	0·06	4·10	0·03	1·85	0·53	4·36	0·80	4·18	0·30
5	1·860	0·32	3·88	0·38	1·43	0·30	4·19	0·10	3·89	0·40
6	1·850	0·27	3·17	0·56	1·31	0·13	3·90	0·10	3·61	0·40
7	1·770	0·06	3·09	0·56	1·12	0·20	3·55	0·10	3·43	0·20
8	1·662	0·13	2·37	0·38			3·31	0·10	3·21	0·60
9	1·527	0·06	1·85	0·75			3·21	0·60	3·03	0·20
10	1·453	0·16	1·44	0·38			2·71	0·30	2·84	0·10
11	1·434	0·09	1·32	0·03			2·47	0·40	2·73	0·20
12	1·412	0·01	1·13	0·06			2·40	0·20	2·48	0·50
13	1·396	0·02					2·37	0·30	2·41	0·70
14	1·383	0·06					2·29	0·10	2·27	0·60
15	1·369	0·02					2.23	0·90	2·23	0·80
16	1·312	0·15					2·17	0·30	2·16	0·10
17	1·303	0·03					2·08	0·30	2·08	0·10
18	1·224	0·01					2·05	0·10	2·02	0·60
19	1·209	0·02					1·99	0·40	1·98	0·10
20	1·1782	0·03					1·92	0·20	1·91	0·60
21	1·1711	0·01					1·84	0·20	1·79	0·50
22	1·1609	0·03					1·81	0·10	1·73	0·70
23	1·1337	0·05					1·73	0·70	1·68	0·10
24	1·1152	0·02					1·69	0·10	1·64	0·20
25	1·0917	0·01					1·65	0·20	1·60	0·40
26	1·0459	0·02					1·60	0·40	1·57	0·10
27	1·0281	0·01					1·58	0·10	1·55	0·20
28							1·56	0·40	1·52	0·20
29							1·49	0·10	1·48	0·20
30							1·46	0·50	1·46	0·30
31							1·45	0·30	1·44	0·50
32							1·40	0·30	1·39	0·30
33							1·38	0·20	1·36	0·10
34							1·36	0·10	1·34	0·50
35							1·34	0·50	1·30	0·10
36							1·28	0·20	1·28	0·10
37							1·26	0·10	1·25	0·20
38							1·23	0·10	1·23	0·10
39							1·22	0·50	1·21	0·40
40							1·18	0·30	1·20	0·10
41							1·17	0·10	1·18	0·10
42							1·14	0·20	1·16	0·10
43							1·12	0·30	1·14	0·10
44							1·07	0·20	1·12	0·10
45									1·11	0·30
46									1·01	0·10

strated in Figure 3, where the dried C-gamma gels are seen to contain the hexagonal platelets and prisms of the trihydrate Gibbsite and the triangular or hour-glass shaped somatoids of the trihydrate Bayerite[10]. In addition, in these samples, a fine dispersion of background particles (arrow, Fig. 3*A*), is observed with diameters about 200 A.U.

These results show that the particles which constitute the solid phase of SCHMIDT's gels are different from those of the WILLSTÄTTER's C-gamma gels, but are similar to those of the C-beta gels, which are also composed of fibrils, having a Boehmite structure, shown in a previous paper[11], formed by condensation polymerization of the amorphous aluminum hydroxide molecules of the C-alpha gel[13]. Their X-ray diffraction data do not coincide exactly with the data of well crystallized Boehmite because the fibrils are exceedingly small and friable and are neither completely polymerized nor oriented[14]. After autoclaving, SCHMIDT's gels do not change spontaneously into Bayerite and Gibbsite which constitute the C-gamma gels, and from this point of view they are different from the C-beta gel[11]. This stability of crystalline structure, of particle size, and of shape in SCHMIDT's gels make them superior to WILLSTÄTTER's C-beta or C-gamma gels for preparation of adsorbents. In addition to the ammonium alum, other aluminum salts, like the chloride, the nitrate, or the acetate, can be used for preparing gels composed of Boehmite fibrils[12], but the fibrils in these are thicker in diameter[13] and have therefore a small surface area than those from SCHMIDT's gel.

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Résumé

Les auteurs démontrent que le gel d'hydroxyde d'aluminium (gel de SCHMIDT) soumis aux rayons X diffractés et examiné au microscope électronique se révèle formé de particules différant par leur structure, leur morphologie et leur dimensions de celles du gel C-gamma de WILLSTÄTTER, mais semblables à celles du gel C-béta du même nom.

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Crystalline Acetates from 'Croton Resin'

The local irritant and laxative actions of Croton oil (ex. *Croton tiglium*) have been known for a very long time, and to these effects have later been added those of cocarcinogenic action[1], leucocyte migration promotion[2] and 'cord factor'[3] activity. The teams led by CHERBULIEZ[4] and FLASCHENTRÄGER[5] carried out separations some 25 years ago, and further separations have been recently attempted chromatographically[6].

Prompted by the results of MEIER and SCHÄR[2] the oil was worked up as described by CHERBULIEZ for the preparation of the 'Croton resin' ('principe vésicant'), in our case using a continuous countercurrent distribution apparatus[7] for partition between heptane and methanol. This resin was now subjected to chromatography on alumina using eluents graded from benzene through ether-chloroform-methanol, thus yielding about 80 non-crystalline fractions, all with very similar I.R. spectra, and of which the most active in the leucocyte migration test were eluted with benzene-ether (1 : 5) and fitted closely with CHERBULIEZ's description of the original 'principe vésicant'.

[Found for this fraction (3 determinations):
C 68·98; H 8·81; $(CO)CH_3$ 4·73%; M.W. 608; 688[8]; $[\alpha]_D^{20°}$: + 56 ($c = 1·0$ in $CHCl_3$)].

Calculated for $C_{37}H_{56}O_9$:
C 68·91; H 8·75; CH_3 (one) 2·33%; M.W. 644·8

Hydrolysis of the 'Croton resin' using methanolic barium hydroxide[9] or a strongly basic ion-exchange resin (Amberlite IRA-120 in basic form) and subsequent working up by partition between ether and water gave from the aqueous phase a resin that, after crystallization from ethanol, yielded a small amount of crystalline material (m.p. 240–245°, decomp.) of formula $C_{21}H_{32}O_7$.

[Found (8 determinations):
C 64·05; H 8.20%;
(3 determinations):
O 28·66; $(C)CH_3$ 10·44; $(CO)CH_3$ 2·81; $(C)CH_3$ 10·71%.
$C_{21}H_{32}O_7$ requires C 63·61; H 8·14; O 28·25; CH_3 3·78%.]
This was probably identical with the 'Alkohol Phorbol' of FLASCHENTRÄGER[9].

Acetylation in pyridine of the crude water-soluble fraction from the hydrolysis and chromatography on magnesolcelite[10] or alumina gave three crystalline acetates (*A*, *B*, and *C*).

The separation was followed by paper chromatography of alternate fractions (Zaffaroni system formamide-cyclohexane-benzene) and the acetates were recrystallized to paper chromatographic purity from ether or ether-petroleum. The properties of the acetates are summarized in the table. The results from acetate determinations (hydrolysis) were not satisfactory. Further acetylation of

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