171. C.L. Markert and F. Miller, Proc. Nat. Acad. Sci. U.S.A., 45, 753 (1959).
172. M.E. Carsten and J.G. Pierce, J. Biol. Chem., 235, 78 (1960).
173. R. Richterich *et al.*, Biochim. Biophys. Acta, 56, 240 (1962).
174. K.A. Trayser and S.P. Colowick, Arch. Biochem. Biophys., 94, 177 (1961).
175. S.R. Mardashev and Wang Shao-hua, Dokl. Akad. Nauk SSSR, 142, 709 (1962).
176. D. Rogers and F.J. Reithel, Arch. Biochem. Biophys., 89, 97 (1960).
177. E. Heilbronn, Biochim. Biophys. Acta, 58, 222 (1962).
178. R.D. Gaines and K.J. Goering, Biochem. J., 96, 13 (1962).
179. E.M. Press *et al.*, Biochem. J., 74, 501 (1960).
180. J.S. McGuire and G.M. Tomkins, J. Biol. Chem., 235, 1634 (1960).
181. M. Ottesen and A. Spector, Compt. rend. Trav. Lab. Carlsberg, 32, 63 (1960).
182. C. Tanford, in "Symposium on Protein Structure" (Edited by A. Neuberger), New York, 1958 p. 35.
183. S.R. Dickman *et al.*, J. Biol. Chem., 235, 169 (1960).
184. L. Kh. Eidus and G.K. Otarova, Biokhimiya, 24, 982 (1959).
185. A.A. Yunis *et al.*, J. Biol. Chem., 235, 3163 (1960).
186. M.J. Spiro, J. Biol. Chem., 236, 2901 (1961).
187. J. Brahms, J. Amer. Chem. Soc., 81, 4997 (1959).
188. S.E. Shnol', Voprosy Med. Khim., 4, 443 (1958).
189. J.A. Christiansen, Acta Chem. Scand., 14, 107 (1960).
190. S.E. Shnol' *et al.*, Voprosy Med. Khim., 5, 259 (1959).
191. T. Wieland *et al.*, Biochem. Z., 331, 103 (1959).
192. T. Wieland *et al.*, Z. Naturforsch., 15b, 434 (1960).
193. J. Paul and P. Fottrell, Biochem. J., 78, 418 (1961).
194. M.U. Tsao, Arch. Biochem. Biophys., 90, 234 (1960).
195. A.A. Pokrovskii, Voprosy Med. Khim., 6, 228 (1960).
196. J.L. Faney *et al.*, J. Clin. Invest., 36, 272 (1958).
197. M.D. Prager *et al.*, J. Lab. Clin. Med., 54, 694 (1959).
198. M.D. Prager and I.C. Atkins, Biochim. Biophys. Acta, 54, 495 (1961).
199. B. Hess and S.J. Walter, Klin. Wochenchr., 39, 213 (1961).
200. A. Albert and P. Yohnson, Biochem. J., 81, 218 (1961).
201. C. Baglioni, J. Biol. Chem., 237, 69 (1962).
202. R.L. Speer *et al.*, J. Lab. Clin. Med., 54, 685 (1959).
203. J.H. Humphrey and R.R. Paster, Lancet, 1, 196 (1957).
204. C.C. Curtain, J. Histochem. Cytochem., 9, 484 (1961).
205. A. Saha, J. Chromatog., 7, 155 (1962).
206. A. Saha, J. Chromatog., 7, 165 (1962).

Laboratory for the Biochemistry of the
Nitrogen Metabolism of Microorganisms,
Institute of Biological and Medical Chemistry,
Academy of Medical Sciences of the USSR

U. D. C. 547.245:546.287

ORGANIC DERIVATIVES OF LAMINAR SILICATES

E. V. Kukharskaya and A. D. Fedoseev

CONTENTS

1. Introduction 490
2. Production of organic derivatives of laminar silicates by replacement of OH or OM groups attached to silicon 491
3. Production of organic derivatives of laminar silicates by addition of organic radicals to broken Si–O–Si and Si–O–Al bonds 492
4. Production of synthetic silicates containing organic radicals. 493

1. INTRODUCTION

Organic derivatives of silicates are an extremely interesting group of compounds. Rather more than 20 years ago Berger first reported[1] the preparation of methoxylated montmorillonite; this was the first of a series of intensive investigations of organic derivatives of laminar silicates, and attracted the attention of investigators studying the surface structure of various clays.

An accurate knowledge of the surface structure of clays is necessary for understanding many of their properties, such as their acidity, adsorption and exchange capacity, thixotropy, and so on, which are due to the presence of a negative charge on their particles.

Disperse crystals of clays are known to possess structural irregularities and defects, because of the inclusion of foreign atoms and groups in the lattice, the presence of difficultly removable impurities and of holes, etc. These deviations from the ideal structure in the smallest clay microcrystallites are often used in theories of the negative charge on their surface. The best known hypothesis is that of Marshall and Van der Meulen[2,3], which ascribes the negative charge to the replacement of multiply charged cations in the crystal lattice by less highly charged cations: for instance, Si^{4+} is replaced by Al^{3+} in a tetrahedral layer such as is typical of vermiculite, or Al^{3+} is replaced by Mg^{2+} or Fe^{2+} in an octahedral layer, which often occurs in montmorillonite. The theory of isomorphous substitution, while explaining the existence of wide differences in the chemical composition of similar clays, has its weak points. Calculations show[4] that if their acidity is considered to arise solely as a result of isomorphism, clays should be strong acids in the H-form, but their acidity is known to be constant between pH 3 and pH 5–5.6.

Edelman and Favejee[5] explained the negative charge on clay particles in terms of the acidity due to the presence of acidic Si–OH groups on the surface. Although several years ago the existence of Si–OH groups in laminar silicates was considered to be improbable, more recent studies[6-9], especially of infrared absorption spectra of certain hydrosilicates[10-13], demonstrate their presence in various silicate formations.

Definite proof of their presence is not easy, however. One possibility is the production of organic derivatives of the hydrosilicates by replacing the hydroxy-groups attached to silicon by organic radicals.

The organic derivatives are not merely of interest for investigating the surface structure of laminar silicates, since they have their own practical significance for the sterilisation and stabilisation of soils, the deactivation of poisons, the preparation of hydrophobic silicate materials, and so on. Organic derivatives of laminar silicates will undoubtedly also find practical application as fillers for various types of rubber and as selective adsorbents.

The experience gained in more than a century's study of the chemistry of organosilicon compounds has been applied

to the production and investigation of the organic derivatives of laminar silicates. Three methods are at present known for their production: the replacement by organic radicals of the active surface OH or OM groups attached to silicon, the addition of organic radicals to broken Si–O–Si or Si–O–Al bonds in silicates, and the production of synthetic silicates containing organic radicals.

2. PRODUCTION OF ORGANIC DERIVATIVES OF LAMINAR SILICATES BY REPLACEMENT OF OH OR OM GROUPS ATTACHED TO SILICON

The Si–OH groups on the surface of clays are chemically similar in behaviour to the Si–OH groups in silanols. The acidic hydroxy-groups attached to silicon in H-montmorillonite were first replaced by methoxy-groups by the action of diazomethane in ether solution[1]:

$$\equiv Si-OH + CH_2N_2 \longrightarrow \equiv Si-OCH_3 + N_2 .$$

Analysis of the product for methoxy-groups[14] has shown that not all the hydroxy-groups of the clay can be methylated. Further study of this reaction[15–17] led to the disuse of ether as the solvent and concentration on the drying of the samples, since hydrolysis of diazomethane produces methanol:

$$CH_2N_2 \xrightarrow{H_2O} CH_3OH + N_2,$$

and the presence of methanol and ether interferes in the determination of methoxy-groups.

In hydrogen montmorillonite dried at 300° only 10% of the exchangeable hydrogen ions react with diazomethane. The prolonged action of gaseous diazomethane replaces a further 10% of the H^+ ions.

The hydroxy-groups of silica gel could be partially replaced by methoxy-groups by the action of diazomethane[1,18,19].

Most work on the production of organic derivatives of silicates has been carried out with montmorillonite, and, to a lesser extent, with kaolinite, pyrophyllite, halloysite, attapulgite, amorphous aluminosilicate, and certain other minerals. Montmorillonite has attracted most attention because of its high content of surface-active hydroxy-groups. A fairly large number of three-layer plates, made up of two outer silicon–oxygen tetrahedral layers and an intermediate aluminium–oxygen octahedral lattice, are known to be held in the montmorillonite crystal by relatively weak van der Waals' forces; montmorillonite thus has a planar laminar lattice, able to swell, and with an extended available internal surface. It has been studied in the acid (hydrogen montmorillonite) and alkaline (potassium and sodium montmorillonite) forms.

Bart and Gusman[20,21] investigated the reaction of sodium and potassium montmorillonite with methyl, ethyl, and allyl iodide, and concluded that etherification and not alkali exchange, occurs:

$$\equiv Si-O^-M^+ + RI \longrightarrow \equiv Si-OR + MI,$$

where R = CH_3, C_2H_5, or $CH_2{=}CHCH_2$ and M = K or Na. Deuel[22] later repeated these experiments, and also obtained methoxylated and ethoxylated montmorillonite.

The reaction between sodium montmorillonite and di-(β-chloroethyl) sulphide (Yperite, mustard gas)[22,23] proceeds analogously; Yperite has a bifunctional molecule and can form the mono- or di-ether:

$$2 \equiv Si-ONa + ClCH_2CH_2SCH_2CH_2Cl \rightarrow \equiv Si-O-CH_2CH_2SCH_2CH_2-O-Si\equiv + 2NaCl.$$

The reaction proceeds readily in aqueous medium at room temperature, with substitution of more than 80% of the acid groups. Alkoxy-derivatives of this type are fairly stable to the action of water, but dilute alkali produces rapid hydrolysis, with the formation of the original sodium montmorillonite.

Alkoxylated clays are more stable to hydrolysis the larger the organic radical present. Montmorillonite hydroxypropyl ether, obtained by the action of propylene oxide on an aqueous suspension of hydrogen montmorillonite[23]:

$$\equiv Si-OH + CH_2-CH-CH_3 \longrightarrow \equiv Si-OCH\begin{matrix}CH_3\\CH_2OH\end{matrix}$$

(O)

or $\equiv Si-OCH_2CH-CH_3$ (OH),

is also relatively stable to the action of water. The ether was produced at room temperature, in a maximum yield of 89%.

The practical value of these reactions of clays with Yperite and propylene oxide is evident. The former shows that clays can deactivate poisons, and the reaction with propylene oxide can be used for the sterilisation of clay soils and humus.

The reaction of clays with alkylchlorosilanes[4]:

$$\equiv Si-OH + ClSi(CH_3)_3 \longrightarrow \equiv Si-O-Si(CH_3)_3 + HCl ,$$

is also of practical interest, but unfortunately the resulting hydrophobic materials were not sufficiently well characterised.

The Si–OH groups of silanols and laminar silicates behave very similarly in acylation reactions. Acetic anhydride and acetyl chloride have been investigated as acylating agents, and have been used for the preparation of acyloxysilanes from silanols[24–26]. Heating hydrogen montmorillonite with acetyl chloride or acetic anhydride replaces the OH groups by acetoxy-groups[27,28]:

$$\equiv Si-OH + (CH_3CO)_2O \longrightarrow \equiv Si-OCOCH_3 + CH_3COOH,$$
$$\equiv Si-OH + CH_3COCl \longrightarrow \equiv Si-OCOCH_3 + HCl .$$

Acetic anhydride acetylates montmorillonite to a considerably greater extent than does acetyl chloride; the explanation given for this by Spencer and Gieseking[28] is that the reaction temperature is higher with acetic anhydride, the reaction being carried out at boiling point.

Benzoyl chloride evidently reacts with hydrogen montmorillonite in the same way as acetyl chloride, but Slabaugh, who carried out this reaction[29], did not consider the possibility of hydrolysis of the acyloxy-derivatives of the montmorillonite, and treated the reaction products with 80% ethanol.

Acetylated montmorillonite is a hydrophobic powder which adsorbs organic liquids to a greater extent than does hydrogen montmorillonite[28]. Hydrolysis of the acyloxy-derivative gives a product having the hydrophilic properties of the original hydrogen montmorillonite:

$$\equiv Si-OCOR \xrightarrow{H_2O} \equiv Si-OH + RCOOH,$$

where R = CH_3 or C_6H_5.

The most systematic studies of the organic derivatives of laminar silicates and their preparation were conducted by Deuel and his coworkers[23,30-34], who used Wyoming bentonite, which is almost pure montmorillonite.

Thionyl chloride replaces the hydroxy-groups of sodium or hydrogen montmorillonite attached to silicon by chlorine:

$$\equiv SiOH\,(M) + SOCl_2 \longrightarrow \equiv Si{-}Cl + SO_2 + H\,(M)\,Cl\,.$$

Preliminary studies have shown that gibbsite $Al_2O_3.H_2O$ does not react with thionyl chloride[30], *i.e.* OH groups attached to aluminium in clays are not replaced by chlorine under these conditions.

The production of reactive Si–Cl bonds in laminar silicates offered wide possibilities for the preparation of varied types of organic derivatives. Chemically the Si–Cl bond in the chloro-derivatives of laminar silicates is very like the Si–Cl bond in chlorosilanes. Montmorillonite chloride, like chlorosilanes, is readily hydrolysed by water[23]. Alcohols (methanol, ethanol, propanol, butanol, phenol, D-glucose) gives the alkoxy-derivatives of the alkoxy-type, more than 80% of the acidic groups of the montmorillonite being replaced[23,30]:

$$\equiv Si{-}Cl + HOR \longrightarrow \equiv Si{-}OR + HCl.$$

The reaction of montmorillonite chloride with ethylenediamine gives the amino-derivative[23]:

$$\equiv Si{-}Cl + H_2NCH_2CH_2NH_2 \longrightarrow \equiv Si{-}NHCH_2CH_2NH_2 + HCl\,,$$

and the second amino-group may also react, to give the diamino-derivative of montmorillonite:

$$\equiv Si{-}NHCH_2CH_2NH{-}Si\equiv\,.$$

Of particular interest is the reaction of montmorillonite chloride with organomagnesium and organolithium compounds, producing derivatives containing the Si–C bond, which is stable towards hydrolysing agents. Ethylmagnesium chloride and phenylmagnesium bromide or phenyllithium have given ethyl- and phenyl-montmorillonite respectively by reaction with montmorillonite chloride[28,30]:

$$\equiv Si{-}Cl + RMgX \longrightarrow \equiv Si{-}R + ClMgX,$$

where R = C_2H_5 or C_6H_5 and X = Cl or Br.

The reaction between methylmagnesium halides and hydrogen montmorillonite can be used for the determination of active hydrogen by the Tserevitinov (Zerewitinoff) method[30].

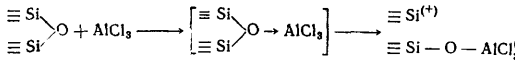
Phenylmontmorillonite has also been obtained by the Friedel–Crafts reaction between montmorillonite chloride and benzene in the presence of aluminium chloride[30,33]:

$$\equiv Si{-}Cl + C_6H_6 \xrightarrow{AlCl_3} \equiv Si{-}C_6H_5 + HCl.$$

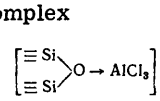
A high degree of substitution is produced in this reaction, because of two processes simultaneously taking place, the reaction at the Si–Cl bond, and the splitting of Si–O–Si bonds by the aluminium chloride.

3. PRODUCTION OF ORGANIC DERIVATIVES OF LAMINAR SILICATES BY ADDITION OF ORGANIC RADICALS TO BROKEN Si–O–Si and Si–O–Al BONDS

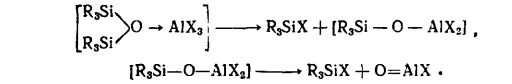
There are few studies on organic derivatives of laminar silicates prepared in this way. As mentioned above, there is rupture of Si–O–Si bonds in the reaction between montmorillonite chloride and benzene in the presence of aluminium chloride. Deuel and Huber[30] represent this process as follows:



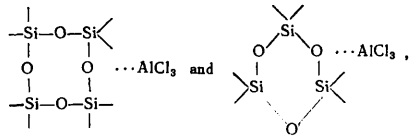
Voronkov *et al.*[35] also indicated the possible formation of the intermediate complex



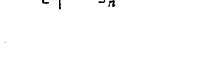
in their study of the decomposition of hexaalkyldisiloxanes by aluminium halides to produce halogenosilanes:



It has recently been shown that aluminium chloride can coordinate an oxygen atom in cyclic poly(dialkylsiloxanes)[36]; the resulting complexes

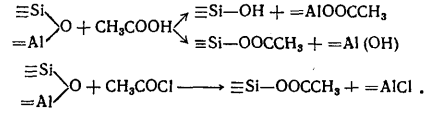


give chlorine-containing aluminoxypolysiloxanes when the ring is subsequently opened:



where n = 3 or 4.

The use of methods such as infrared spectroscopy[36] and differential thermal analysis for studying the final products of the acylation of amorphous aluminosilicate by acetyl chloride and acetic anhydride has shown that, as well as the normal replacement of hydroxy-groups on the surface of the aluminosilicate by acyloxy-groups, there is rupture of Si–O–Al bonds[37,38]. The final reaction products obtained with acetic acid are different from those obtained with acetyl chloride:

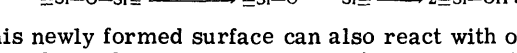


Controlled hydrolysis of the acylation products with water also confirms the suggested mechanism involving rupture of an Si–O–Al bond[37].

It has been suggested that thionyl chloride reacts with laminar silicates in the same way as aluminium chloride, by breaking siloxane and aluminosiloxane bonds[39].

The production of organic derivatives by tribochemical methods is also doubtless a reaction of this type.

Weyl[40] has suggested that the mechanical rupture of Si–O–Si bonds leads to the formation on the surface of active electrically charged areas which react readily with water:



This newly formed surface can also react with other compounds used as milling media. A patent specification[41] has described the comminution of silica gel and quartz in

the presence of alkenes, and specifically styrene, to produce a stable Si–C bond. These processes have been studied in more detail only with silica[42,43]. By pulverising silica in an atmosphere of helium, it was shown that the active areas produced by rupture of Si–O–Si bonds have a lifetime of up to 260 h.

Styrene produces a compound $\equiv O_3Si-CH_2CHC_6H_5$,[43] which can react with more styrene to produce a polymeric product:

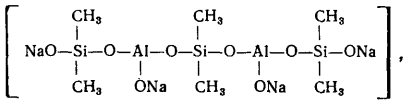
$$\equiv O_3Si\,(CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_n CH_2CHC_6H_5 \cdot$$

Many other organic reagents have since been used. Silica has been milled in the presence of methanol, butanol, benzene, ether, and 2-methyl-5-vinylpyridine. The comminution is accompanied by a considerable rise in temperature, reaching 1000° in places within a short time. Benson and Castle[43] have suggested that a thermo-ionic process takes place during the milling.

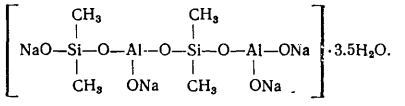
The mechanical method for the production of derivatives with stable non-hydrolysable bonds will undoubtedly find wide application both for the preparation of organic derivatives of silicates and for the production of technically valuable materials based on them.

4. PRODUCTION OF SYNTHETIC SILICATES CONTAINING ORGANIC RADICALS

Kreshkov and coworkers[44-48] have reported the formation of organoaluminosilicates from alkylalkoxysilanes and aqueous alkaline aluminate solutions[44]. The products obtained depend on the molar ratio of Al to Si in the initial mixture. With Al : Si = 1 : 1 the product is:

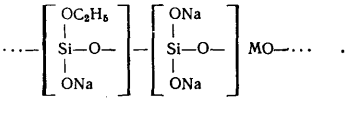


and with Al : Si = 2 : 1 it is:



X-Ray structural and crystalloscopic analysis of the products showed them to be organohydroalumino- and organoalumino-silicates of similar structure to alkali metal hydroalumino- and alumino-silicates such as kaolinite, albite, and anorthoclase.

Organic derivatives with an Si–O–C bond are formed in reactions of tetraalkoxysilanes with certain metal hydroxides, particularly with calcium and aluminium hydroxides. Microscopic investigation of these derivatives has shown them to be definitely similar to the calcium and aluminium hydrosilicates pyrophyllite and okenite[45,46]. Later Kreshkov *et al.*[44] reported that tetraethoxysilane reacts with aqueous alkaline stannate and plumbate solutions to produce compounds of the general formula



Alkylalkoxysilanes react with potassium, magnesium, zinc, calcium, and other acetates in alcoholic solution to form the corresponding organosilicates[47,48]. The properties of these products varied greatly with the number and nature of the alkyl radicals in the initial alkylalkoxysilane; dialkyldialkoxysilanes generally gave resinous film-forming compounds with physical properties like those of organosilicon polymers.

The production of artificial silicates by Kreshkov's method is of great interest, since an accurate determination of the structure of the resulting compounds would be a direct proof of the possible existence of a covalent bond in the mineral–organic radical system.

---o0o---

The main difficulty met with in the chemistry of organic derivatives of silicates is the pronounced tendency of laminar silicates towards adsorption and exchange reactions. Many non-ionic organic molecules are dipoles. When in contact with liquids, solutions, or suspensions containing polar substances, clays, which are also polar, attract the oppositely charged centres of the surrounding polar particles. Stable association with molecules which are not dipoles is also met with, for example by the formation of a hydrogen bond between aliphatic chains and oxygen on the surface of the clay particles. Studies in desorption[49] have shown that the desorption processes are very complex and depend on the nature of the minerals and the adsorbed materials. In most cases complete desorption is attained only with great difficulty, and sometimes residual adsorbed organic compounds cannot be completely removed even at 200°–300°. At lower temperatures adsorbed products may remain in spaces within the mineral for 2–10 months.

Furthermore, clays retain water molecules very readily on the surface and between the layers, and it is very difficult to remove this water and obtain the mineral completely dry. This very considerably complicates the investigation of organic derivatives of silicates, since the presence of water cannot be tolerated in the production of hydrolysable derivatives such as alkoxy-, acyloxy-, and halogeno-compounds.

It is also known that uncompensated charges in clays are generally neutralised by adsorbed cations which lie mainly on the basal cleavage surface; these adsorbed cations can be replaced by organic cations such as substituted ammonium ions. The views of those investigators who reject the possibility of formation of organic derivatives of clays are based on such adsorption and ion-exchange processes[50,51], but some do accept that Si–OH groups can exist on the surface of clays[51].

It must also be borne in mind that Greenland, Russell, Brown, and coworkers[50,51] generally worked with readily hydrolysable organic derivatives of the laminar silicates (the halogeno-, acyloxy-, and alkoxy-derivatives), and some hydrolysis products may have been adsorbed if the starting mineral and the reaction apparatus were insufficiently dry or if insufficient precautions had been taken to avoid all contact of the reactants and reaction products with atmospheric moisture. However, a complete analogy in the behaviour of products adsorbed on the initial and the modified clays could clearly not be expected under desorption conditions. This is confirmed by Soviet studies of the adsorption properties of modified silica gels[18,19,52-55].

The existence of organic derivatives of laminar silicates and particularly of derivatives containing the Si–C bond (which is stable to hydrolysis) has been decisively demonstrated by differential thermal analysis[38,56,62], infrared spectroscopy[32,38,63], and X-ray structure analysis[28].

The Institute of Silicate Chemistry of the Academy of Sciences of the USSR has recently undertaken studies on the production of organic derivatives of Chinese kaolin, which according to its chemical composition is almost pure kaolinite[59,61]. This mineral was chosen mainly because kaolinite does not undergo ion exchange with organic ions[57]. Because of its low cation-exchange capacity the amount of organic cations adsorbed by it is very low. Organic molecules cannot penetrate between the elementary layers of kaolinite, and adsorption takes place only at the boundaries and on the outer surface of the mineral[58]. This considerably reduces the difficulties of distinguishing between the effects of adsorption and exchange reactions on the one hand, and reactions leading to the formation of an organic derivative on the other.

The kaolin was ultrasonically comminuted in organic compounds such as biphenyl and diphenylmethane and in poly(alkylsiloxane) liquids. In all cases organic derivatives of the kaolin were produced, which were hydrophobic powders containing 0.1–0.3% of carbon by weight. The organic residues, which were evidently covalently bound to the mineral particles as alkyl-, alkoxy-, and siloxy-groups, could not be removed by repeated extraction with organic solvents.

The differential thermal analysis curves obtained with the organic kaolin derivatives exhibited exothermic peaks, because of the combustion of the organic components, at temperatures of the order of 450°–650° (depending on the nature of the organic groups)[56]. The initial kaolin does not give an exothermic effect in this temperature range[60].

The rupture of Si–O–Si bonds when laminar silicates are comminuted is confirmed by our investigation of chrysotile asbestos: ultrasonic pulverisation of Bazhenov chrysotile asbestos in an aqueous medium leads to an increase in the number of hydroxy-groups attached to silicon[61]. The active hydrogen of the Si–OH groups was determined by the Terent'ev micromodification of the Tserevitinov (Zerewitinoff) method[64], which gives sufficient reproducibility[61].

The organic derivatives of mineral polymers can be expected to find wide practical application in the near future, because of their valuable physicochemical properties such as water-repellency and selective adsorption.

1. G. Berger, Chem. Weekblad, 38, 42 (1941).
2. C. E. Marshall, Z. Krist., 91A, 433 (1935).
3. J. B. Van der Meulen, Rec. Trav. chim., 54, 107 (1935).
4. H. Deuel, Ber. deut. keram. Ges., 31, 1 (1954).
5. C. H. Edelman and J. C. L. Favejee, Z. Krist., 102, 417 (1940).
6. R. H. McConnel, Amer. Min., 35, 166 (1950).
7. E. Thilo, H. Funk, and E. M. Wichman, in "Fizicheskaya Khimiya Silikatov" (Physical Chemistry of Silicates), Collected Papers, Inostr. Lit., Moscow, 1956, p. 5.
8. H. Scheler, Z. anorg. Chem., 314, 298 (1962).
9. H. Funk and H. Stade, Z. anorg. Chem., 315, 79 (1962).
10. Ya. I. Ryskin, Optika i Spektrosk., 7, 278 (1959).
11. Ya. I. Ryskin, G. P. Stavitskaya, and N. A. Toropov, Zhur. Neorg. Khim., 5, 2727 (1960) [Russ. J. Inorg. Chem., 1315 (1960)].
12. Ya. I. Ryskin and G. P. Stavitskaya, Optika i Spektrosk., 8, 606 (1960).
13. Ya. I. Ryskin, Optika i Spektrosk., 12, 518 (1962).
14. F. Vieböck and C. Brecher, Ber., 63, 2818 (1930).
15. L. M. Vivaldi and S. B. Hendricks, Anales Edafol. Fisiol. Vegetal. (Madrid), 2, 601 (1952).
16. J. J. Fripiat, M. C. Gastuche, and C. R. Van Compernolle, 5e Congr. Internat. Sci. Soc. Leopoldville, II, 401 (1954).
17. J. J. Fripiat and Ekka, Pedologie, 7, 51 (1957).
18. K. D. Shcherbakova and K. I. Slovetskaya, Dokl. Akad. Nauk SSSR, 111, 855 (1956).
19. V. M. Chertov, R. Yu. Sheinfain, N. S. Kruglikova, and I. E. Neimark, Ukrain. Khim. Zhur., 27, 190 (1961).
20. R. Bart, S. Gusman, and S. B. Thesis, Massachusetts Inst. of Technol., Cambridge, 1946.
21. R. Bart and S. Gusman, Colloid Chem., 7, 431 (1950).
22. H. Deuel, Kolloid Z., 124, 164 (1951).
23. H. Deuel, G. Huber, and R. Iberg, Helv. Chim. Acta, 33, 1229 (1950).
24. A. Ladenburg, Ber., 40, 2274 (1907).
25. G. Martin and F. S. Kipping, J. Chem. Soc., 95, 302 (1919).
26. I. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, J. Amer. Chem. Soc., 68, 2282 (1946).
27. J. E. Gieseking, Advances in Agronomy, 1, **159** (1949).
28. W. F. Spencer and J. E. Gieseking, J. Phys. Chem., 56, 751 (1952).
29. W. H. Slabaugh, J. Phys. Chem., 56, 748 (1952).
30. H. Deuel and G. Huber, Helv. Chim. Acta, 34, 1697 (1951).
31. H. Deuel, Kolloid Z., 124, 164 (1951).
32. H. Deuel, G. Huber, and H. H. Günthard, Helv. Chim. Acta, 35, 1799 (1952).
33. H. Deuel and R. Iberg, Helv. Chim. Acta, 36, 808 (1953).
34. H. Deuel, Ber. deut. keram. Ges., 31, 1 (1954).
35. M. G. Voronkov, B. N. Dolgov, and N. A. Dmitrieva, Dokl. Akad. Nauk SSSR, 84, 959 (1952).
36. A. A. Zhdanov, K. A. Andrianov, and A. A. Bogdanova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1261 (1961).
37. J. Uytterhoeven, J. J. Fripiat, and L. Dock, Compt. rend. Acad. roy. Belgique, [5], 45, 611 (1959).
38. J. Uytterhoeven, Silicates industriels, 25, 403 (1960).
39. J. Wartman and H. Deuel, Helv. Chim. Acta, 42, 1166 (1959).
40. W. A. Weyl, J. Amer. Ceram. Soc., 32, 367 (1949); Trans. Soc. Glass Technol., 32, 247 (1948).
41. L. M. Arnett, M. F. Bechtold, and R. E. Benson, U. S. P. 2728732 (1955); Chem. Abs., 50, 5950 (1956).
42. H. Deuel, Helv. Chim. Acta, 39, 1586 (1956).
43. R. E. Benson and J. E. Castle, J. Phys. Chem., 62, 840 (1958).
44. A. P. Kreshkov, L. V. Myshlyaeva, and A. M. Khananashvili, Trudy Moskov. Khim.-Tekhnol. Inst. Mendeleeva, 24, 333 (1957).
45. A. P. Kreshkov and L. V. Myshlyaeva, Trudy Moskov. Khim.-Tekhnol. Inst. Mendeleeva, 13, 38 (1948).
46. A. P. Kreshkov, A. N. Chivikova, G. D. Nessonova, V. A. Matveev, and M. L. Darshkevich, Trudy Moskov. Khim.-Tekhnol. Inst. Mendeleeva, 17, 15 (1952).
47. A. P. Kreshkov and A. N. Chivikova, Zhur. Prikl. Khim., 27, 1128 (1954).
48. A. P. Kreshkov and M. L. Darashkevich, Trudy Moskov.-Tekhnol. Inst. Mendeleeva, 24, 327 (1957).
49. R. Glaeser, Compt. rend., 232, 1496 (1951).
50. G. Brown, R. Green-Kelly, and K. Norrisch, Nature, 169, 756 (1952).
51. D. J. Greenland and E. W. Russell, Trans. Faraday Soc., 51, 1300 (1955).
52. A. V. Kiselev, N. V. Kovaleva, A. L. Korolev, and K. D. Shcher-

bakova, Dokl. Akad. Nauk SSSR, 124, 617 (1959).
53. R. Yu. Sheinfain and I. E. Neimark, "Trudy Nauch.-Tekh. Konf. po Voprosam Struktury i Svoistv Sorbentov" (Reports of the Scientific and Technical Conference on the Structure and Properties of Sorbents), Goskhimizdat, 1959, p. 136.
54. I. E. Neimark and I. B. Slinyakova, Ukrain. Khim. Zhur., 27, 196 (1961).
55. I. B. Slinyakova and I. E. Neimark, Kolloid. Zhur., 24, 220 (1962).
56. H. Deuel and R. Iberg, Helv. Chim. Acta, 36, 808 (1953).
57. R. E. Grim, W. H. Allaway, and F. L. Cuthbert, J. Amer. Chem. Soc., 30, 137 (1947).
58. F. W. Bradley, J. Amer. Chem. Soc., 67, 975 (1945).
59. E. V. Kukharskaya, Yu. I. Skorik, and N. G. Boiko, Dokl. Akad. Nauk SSSR, 147, 350 (1963).
60. Fu Su-jên, Candidate's Thesis (Ph. D. Equivalent), Institute of Silicate Chemistry of the USSR Academy of Sciences, 1961.
61. Yu. I. Skorik, A. D. Fedoseev, E. V. Kukharskaya, and K. G. Gileva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 932 (1963).
62. J. H. Fripiat, J. Uytterhoeven, U. Schobinger, and H. Deuel, Helv. Chim. Acta, 43, 176 (1960).
63. R. Gentili and H. Deuel, Helv. Chim. Acta, 40, 106 (1957).
64. A. P. Terent'ev and A. I. Kireeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 172 (1951).

Institute of Silicate Chemistry,
Academy of Sciences of the USSR

U. D. C. 532.783

CHEMICAL CHARACTERISTICS, STRUCTURE, AND PROPERTIES OF LIQUID CRYSTAL

V. A. Usol'tseva and I. G. Chistyakov

1. Introduction 495
2. Chemical characteristics of molecules 497
3. X-Ray diffraction by liquid crystals 502
4. Some properties of liquid crystals 505

1. INTRODUCTION

Some organic compounds, heated below their melting point, can form a structure whose properties are intermediate between those of true solid crystals and those of true liquids [1,2]. Liquid crystals combine properties of liquids (fluidity, drop formation, etc.) with properties of solid crystalline materials (anisotropy, electrical, optical, and other properties).

Heating is not the only method of preparing liquid crystals: dissolution of solid crystals of certain substances in specific solvents can also give rise to liquid crystals.

The nature of liquid crystals has been the object of many investigations. The problem has been reviewed by Vul'f [3], Lehmann [4], Friedel [5], Mauguin [6], Vorländer [7], Tsvetkov [8], Weygand [9], Brown and Shaw [10], and Chistyakov [11]. The most comprehensive survey, by Brown and Shaw, cites 475 original papers. The properties of liquid crystals have been discussed at symposia in Germany [12], held in 1931, and in England [13,14], held in 1933 and in 1958.

The last few years have witnessed a renewal of interest in liquid crystals, due above all to their practical importance [15]. Liquid crystals play an important part in the metabolism of living organisms [16-19], and their study is of interest in medicine and biology. Because many wetting agents and detergents, dyes, and polymers can form liquid crystals, their study is of great importance to chemical technology. Shubnikov has pointed out [15] that the remarkable properties of liquid crystals (very large specific rotation of the plane of polarisation, strong pleochroism, electrical and magnetic properties) can be utilised by preparing these materials in a glassy form.

Lehmann [4] distinguished two types of liquid crystals, of widely different viscosities, which he called, respectively, liquid crystals ["Flüssige Kristalle" (Ed. of Translation)] (viscosity of the order of 10^{-2} P) and flowing crystals ["Fliessende Kristalle" (Ed. of Translation)] (viscosity approximately 10 times higher).

Friedel [5] showed that the most essential characteristic of liquid crystals is not their viscosity, but their internal structure, which is intermediate between the three-dimensional lattice of solid crystals and the structureless, amorphous liquid state. Friedel introduced the concept of a mesomorphic state, and distinguished two types of mesomorphs, the nematic and the smectic, corresponding respectively to Lehmann's liquid and flowing crystals.

States of matter can be classified as follows from the point of view of their internal structure:

1. Amorphous state. This is characterised by a completely disordered distribution of molecular position and motions. Molecular rotation is possible about three mutually perpendicular axes.

2. Nematic state. The centres of gravity of the chain-like molecules of which the liquid crystal is composed are randomly distributed, but the chains themselves are oriented along a strictly defined direction. The centres of gravity of the molecules can move in all three dimensions, and molecular rotation is possible about the long axis (Fig. 1*a*).

Compounds which form nematic liquid crystals include *p*-azoxyanisole (t_1 = 116°, t_2 = 133°) and anisaldazine (t_1 = 160°, t_2 = 180°). Throughout the present article, t_1 is used for the melting point of the solid crystal to the liquid-crystalline state and t_2 for the melting point of the liquid crystal to the isotropic liquid state.

3. Smectic state. The centres of gravity (and the chain ends) of the molecules are located on equidistant planes. The centres of gravity can move in two directions (on their plane); molecular rotation is possible about one axis (Fig. 1*b*).

Smectic liquid crystals are formed, for example, by ammonium oleate (at room temperature) and by ethyl *p*-azoxybenzoate (t_1 = 114°, t_2 = 120°).