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Intercalation of Aliphatic Alcohol Mixtures into the Layered Lattice of Unhydrated Vanadyl Sulphate

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Abstract

The mixed intercalates of the type $VOSO_4 \cdot (2-x)C_p \cdot xC_q$ have been prepared by reaction of unhydrated layered $VOSO_4$ with liquid binary mixtures of the aliphatic alcohols. Symbols C_p and C_q mark two different unbranched primary aliphatic alcohols, p and q are numbers of carbon atoms in their molecules ($p < q$). For $q = p + 1$ the value of x changes continuously in the interval ⟨0–2⟩. For $q > p + 2$ these values range in intervals ⟨0–0.05⟩, ⟨0.9–1.1⟩ and ⟨1.75–2⟩. Relations between basal spacings of the formed layered complexes and their composition and the composition of the liquid alcohol (C_2 to C_7) mixtures were studied for fifteen systems. The schematic explanation of the arrangement of the alcohol molecules in van der Waal's gap is proposed.

Introduction

Our previous study of the intercalation of the primary aliphatic alcohols with an unbranched carbon chain into the layered lattice of unhydrated $VOSO_4$ and $VOPO_4$ led to the formulation of the stoichiometric composition for the formed layered complexes as $VOSO_4 \cdot 2C_p$ and $VOPO_4 \cdot 2C_p$ ($C_p = C_2 - C_8$) [1]. The alcohol molecules form bimolecular layers in van der Waal's gaps. The angle of their carbon chains with a plane of the layers is about 55°. This arrangement is shown schematically in Fig. 1. A similar arrangement of the aliphatic molecules is proposed for the structures of some other layered complexes [2–8].

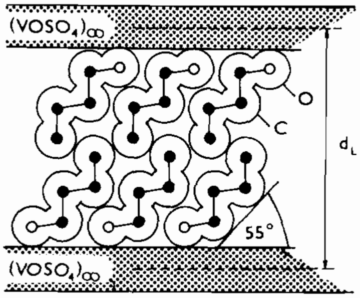

Fig. 1. Bilayer chain aggregation in $VOSO_4 \cdot 2C_4H_9OH$ [1].

This work deals with the study of the intercalation of two different unbranched aliphatic alcohols into layered tetragonal lattice $VOSO_4$. The mixed intercalates containing two types of the organic molecules have been described [2, 9–11]. Their temporary existence must be considered in all preparations of the layered complexes which are carried out by the exchange of the guest molecules [12].

Experimental

Mixed intercalates were prepared in a similar way to intercalates with only one alcohol [1]. A molar excess (1/20) of the liquid mixture of the two alcohols was added to the unhydrated $VOSO_4$ and heat treated in the temperature range of 298–360 K. The heterogeneous reaction was accompanied by a change in colour of the light grey of the solid phase to light blue. The reaction time increased with the length of the carbon chain from several hours to several days. After the intercalation reaction finished the reaction mixtures were kept at 298 K for 3 days, then the solid phases were isolated. In this way we prepared the series of samples with different molar ratios of the alcohols. Ethanol (marked only C_2 in text), n-propanol (C_3), n-butanol (C_4), n-pentanol (C_5), n-hexanol (C_6), n-heptanol (C_7) were dried and distilled prior to use.

Unhydrated $VOSO_4$ was prepared from $VOSO_4 \cdot 2H_2O$ by heating at 573 K in vacuum. $VOSO_4 \cdot 2H_2O$ was prepared by reaction of V_2O_5 with H_2SO_4 in aqueous solution and with SO_2 as reduction agent [13].

The samples for X-ray powder analysis after filtration were neither washed nor dried. Basal spacings of the layered lattice of the intercalates were calculated from the most intensive reflections (00*l*) and from reflections (*hkl*) when they were found. The method of measurement and its checking have been described in our previous work [1].

The molar ratio of the intercalated alcohols in the layered complexes was determined by gas chromatog-

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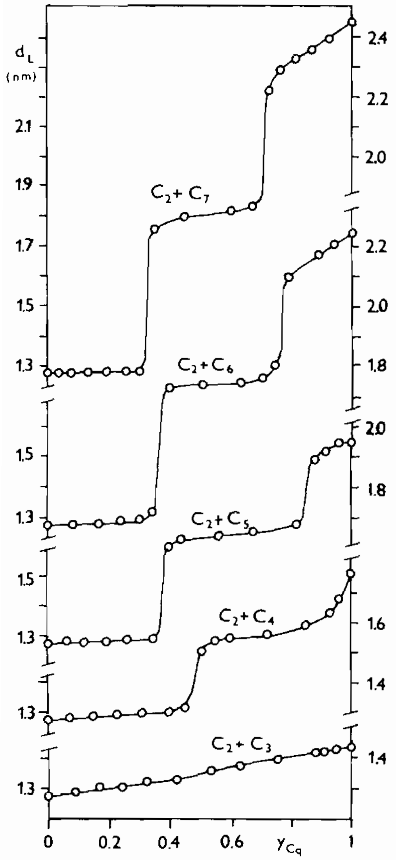


Fig. 2. Dependence of the basal spacing d_L of the prepared solid phases on the composition of the starting alcohol mixtures in the systems $VOSO_4$–C_2–C_q ($C_q = C_3, C_4, C_5, C_6$ and C_7).

raphy. Before analysis the solid samples were washed with pentane, filtered in a dry inert atmosphere and then the known amount was hydrolyzed. The obtained extract (with alcohols C_2 to C_4) was analyzed by Fractovap GV 200 apparatus (Carlo Erba, Italy) with a flame ionisation detector (Embacel AW, 10% diethyleneglycol succinate; inlet chamber 423 K, column 353 K, carrier gas N_2).

The IR spectra were measured in Nujol suspension in the region of 4000–400 cm^{-1} using a Perkin-Elmer spectrometer. Before IR analysis the samples were washed with pentane and dried in an inert atmosphere.

Results and Discussion

Curves in Figs. 2–5 show the dependence of the basal spacings of all the prepared solid phases $VOSO_4 \cdot (2-x)C_p \cdot xC_q$ on the composition of the starting alcohol mixture ($C_p + C_q$), which is given by the molar fraction y of the alcohol C_q ($p < q$).

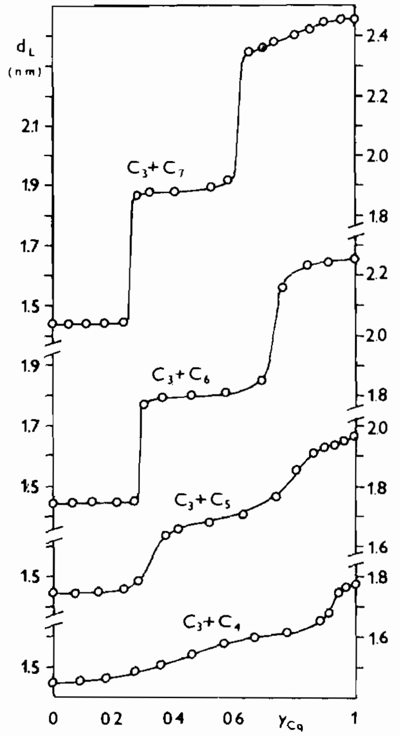


Fig. 3. Dependence of the basal spacing d_L of the prepared solid phases on the composition of the starting alcohol mixtures in the systems $VOSO_4$–C_3–C_q ($C_q = C_4, C_5, C_6$ and C_7).

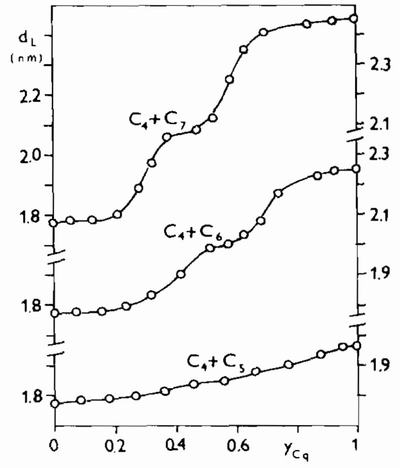


Fig. 4. Dependence of the basal spacing d_L of the prepared solid phases on the composition of the starting alcohol mixtures in the systems $VOSO_4$–C_4–C_q ($C_q = C_5, C_6$ and C_7).

The curves have the characteristic form for systems of the alcohols, the carbon chains of which differ by more than two carbon atoms. These curves can be divided into three parts (Fig. 6). The part marked R corresponds to the existence of the practically pure $VOSO_4 \cdot 2C_p$. The occurrence of the alcohol C_q is negligible ($x = 0$–0.05). The found basal

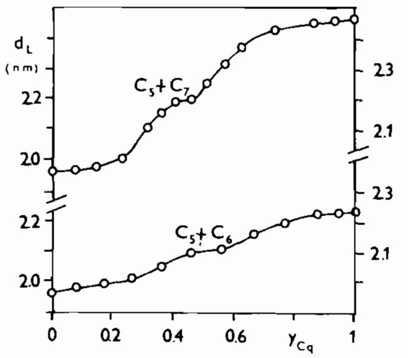


Fig. 5. Dependence of the basal spacing d_L of the prepared solid phases on the composition of the starting alcohol mixtures in the systems $VOSO_4$–C_5–C_q (C_q = C_6 and C_7).

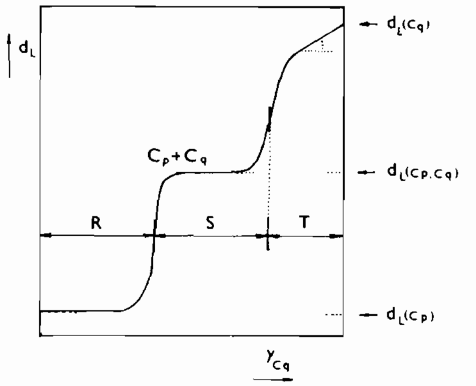
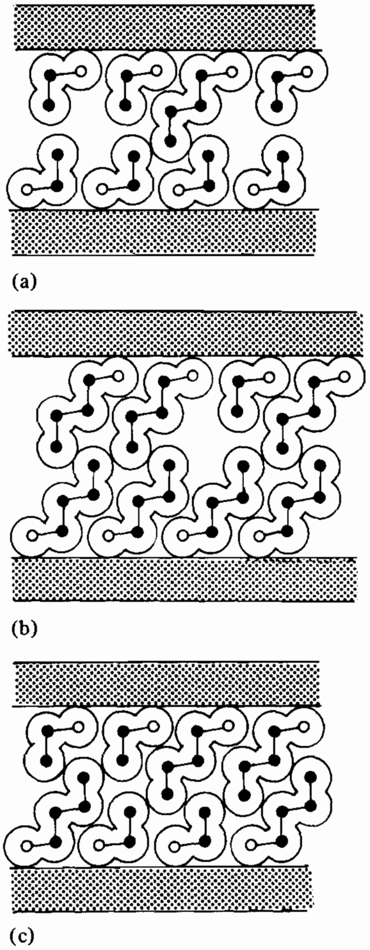


Fig. 6. A typical curve of the basal spacing dependence on the composition of the liquid binary alcohol mixture (C_p and C_q) if aliphatic chains of the alcohols differ by at least two carbon atoms. The values of the basal spacing of $VOSO_4 \cdot 2C_p$ and $VOSO_4 \cdot 2C_q$ are noted d_L (C_p) and d_L (C_q); d_L (C_p, C_q) is the basal spacing of the mixed intercalate. R, S and T are regions of the existence of these three intercalates.


(a)

(b)

(c)

Fig. 7. The arrangement of the alcohol molecules in the mixed layered complexes $VOSO_4 \cdot (2-x)C_p \cdot xC_q$ ($p < q$). (a) x ⟨0–0.05⟩, (b) x ⟨1.75–2⟩, (c) x ⟨0.9–1.1⟩.

spacings for the samples from this region are practically identical with these for $VOSO_4 \cdot 2C_p$.

The mixed intercalates formed in the region S have a value of x in the interval 0.9–1.1. The composition of these intercalates practically corresponds to the formula of $VOSO_4 \cdot C_p \cdot C_q$.

The intercalates $VOSO_4 \cdot (2-x)C_p \cdot xC_q$ (x = 1.75–2) form the solid phase in the region T. However, the content of the alcohol C_p clearly increases in the solid phase with its increasing concentration in the liquid alcohol mixture. Therefore in the region T the curve has no zero slope and its course is different from that in the region R.

Mentioned facts are assumed to be associated with the incorporation of the alcohol molecules into van der Waal's gap. The structure in Fig. 7a would correspond to the intercalate $VOSO_4 \cdot 2C_p$ in which only few short alcohol molecules C_p are replaced by the longer C_q molecules. Such a structure would be quite uncompact. This conclusion was confirmed by our X-ray analysis of the solid phases isolated from the liquid alcohol mixtures with increasing content of long chain alcohol. The solid phases contain only a low molar fraction of the alcohol C_q (x = 0–0.05) regardless of the increasing content of the long chain alcohol in the liquid alcohol mixture.

The arrangement of the guest molecules in $VOSO_4 \cdot 2C_q$ with the replacement of a small part of the longer molecules C_q by the shorter molecules C_p seems to be more probable (Fig. 7b). The solid phases in T region show a greater variability in the alcohol C_p content (x = 1.75–2) and distinct changes of the basal spacings.

The mixed intercalates are formed in the region S. A probably equimolar representation of both the alcohols in the solid phase (x = 0.9–1.1) can be explained by the fact that the width of the bimolecular alcohol layer is derived from the length of one molecule with the shorter chain and one with the longer chain. Such an arrangement is proposed in

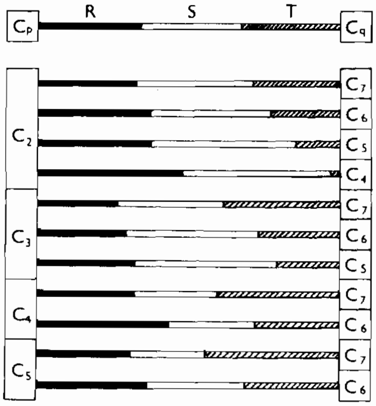


Fig. 8. Regions of existence of the intercalates $VOSO_4 \cdot 2C_p$ (region R), $VOSO_4 \cdot C_p \cdot C_q$ (S) and $VOSO_4 \cdot 2C_q$ (T) for all the studied systems containing alcohol C_2 to C_7.

Fig. 7c where it is shown that the basal spacing of the mixed intercalate must be close to the arithmetic average of the basal spacings of the unmixed layered complexes.

The dependence of the basal spacings on the composition of the alcohol mixture is insignificant if the alcohols differ only slightly in their length ($p + 1 = q$). The regions R, S and T are not distinct on these curves or cannot be distinguished. This result agrees with the suggested interpretation, because the sterical reasons lose their justification due to the small difference in the length of their carbon chains.

A comparison of the widths of the regions R and T in all the investigated systems is shown in Fig. 8. Every line on this diagram shows the situation for one system. For example, the region R of the existence of $VOSO_4 \cdot (2-x)C_2 \cdot xC_6$ ($x = 0$–0.05) is for this system larger than the R region for the alcohols C_2 and C_7. It means that in comparison with the alcohol C_6 the alcohol C_7 penetrates into the intercalate $VOSO_4 \cdot 2C_2$ more easily and in the lower concentration and changes it into the mixed intercalate. Likewise from the comparison of the T regions it follows that the alcohol C_2 more easily penetrates into $VOSO_4 \cdot 2C_6$ than into $VOSO_4 \cdot 2C_7$ (it means at lower concentration in the liquid mixture).

In this way the whole diagram in Fig. 8 can be analyzed and from this analysis we have obtained following results:

The tendency for the penetration of the longer alcohols C_q into $VOSO_4 \cdot 2C_2$ and the formation of the mixed complexes $VOSO_4 \cdot C_2 \cdot C_q$ is given by the order $C_7 > C_6 = C_5 > C_4$.

The order $C_2 > C_3 > C_4 > C_5$ expresses how easily the alcohols with the shorter carbon chain penetrate into the intercalates $VOSO_4 \cdot 2C_6$ and $VOSO_4 \cdot 2C_7$ to form the mixed complexes. Similarly for the penetration of the shorter alcohols into $VOSO_4 \cdot 2C_5$ the order is $C_2 > C_3$.

The alcohols C_6 and C_7 reduce the region of the existence of the pure intercalates $VOSO_4 \cdot 2C_5$ more than the region of the existence of the intercalates with an even number of carbon atoms, $VOSO_4 \cdot 2C_2$ and $VOSO_4 \cdot 2C_4$. Likewise the region of the existence of $VOSO_4 \cdot 2C_3$ is reduced more by the penetration of the alcohol C_5 than the region for $VOSO_4 \cdot 2C_2$.

Our results do not permit us to exactly solve the bonding of the alcohol molecules to the layers of the host lattice. Previously we found [1] that four alcohol molecules are bonded to both sides of the layer, with area $a_o^2 = 0.402$ nm^2. This part of the layer contains two vanadium atoms and ten oxygen atoms. Only two alcohol molecules can be bonded to the vanadium atoms, the remaining two molecules are probably connected by hydrogen bonding to the oxygen atoms.

This assumption does not contradict with the results of the IR spectra. The region of 4000–3000 cm^{-1} is the most important for the confirmation of the existence of the 'two types' of intercalated alcohol molecules. A greater amount of rather sharp bands appeared in this region for $VOSO_4 \cdot 2C_p$ ($C_p = C_5, C_6, C_8$), $VOSO_4 \cdot C_5 \cdot C_7$ and $VOSO_4 \cdot C_2 \cdot C_6$ compared with the spectra of the pure alcohols. The vibrations of the intercalated alcohols are influenced by the intercalation with the host lattice, but they can be influenced by the mutual interaction of the alcohol molecules, as well.

Only very weak bands in the region 3645–3640 cm^{-1} were found in all the measured intercalates. These bands are assigned to the stretching vibration of the free OH group [14]. Weak and medium intense bands were found in the regions of 3558–3530 cm^{-1} and 3410–3300 cm^{-1}. The first of these regions can be assigned to the mutual interaction of the alcohols [15], the second would characterize the interaction of the OH group with the vanadium atom. Broad intense bands in the region of 3180–3165 cm^{-1} belong most probably to the interaction of the alcohol with the host lattice resulting in the hydrogen bonding between oxygen atoms of the host lattice and hydrogen atoms from OH groups of the alcohol molecules.

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