

STUDIES ON ALCOXYSILANE — ALCOHOL AND PHENOXYSILANE — PHENOL BINARY SYSTEMS

By

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I. Alcoxysilane—alcohol binary systems

From the group of alkyl—alcoxysilanes mainly the mono- and difunctional alcoxysilanes are known to form azeotropic mixtures with corresponding alcohols [1]. Evidently, this can be attributed to the association of alcohols and alkyl-alcoxysilanes.

In their earlier works HOLZAPFEL [2], VORONKOV and DEITS [3, 4] treated similar questions related with the association of siloxanes, alcoxysilanes and chlorosilanes and several compounds. HOLZAPFEL [2] examined the reaction of tetra-alcoxysilanes with corresponding alcohols, by means of viscosity and conductivity tests and observed a hydrogen bond in the forming molecular compounds, without interpreting their composition, structure and stoichiometry. VORONKOV and DEITS [3, 4] determined refractivity, freezing point depression and boiling point rise in mixtures with different molarity of the examined compounds. They found that tetra-methoxy-silanes formed association with diethylamines in 1 : 2 molar ratio. Here the single electron pair of nitrogen is supposed to be co-ordinate to the formation of sp^3d^2 hybridization state in the silicon atom. According to the authors, the other examined alcoxysilanes — with different functionality — do not form complexes with amines, that can be attributed to the low sensitivity test methods.

In complex formation the dipole moment and mole polarization of the examined mixtures is known to differ from those of ideal mixtures, mole fraction-dependent curves of the mixtures show maxima or minima at concentrations corresponding to the composition of the mole compound. Since in case of association, the rule of additivity is not valid for the value of the dielectric constant either, its determination is sufficient to determine the stoichiometric composition of the formed association. This observation led GILES [5] and OEHME [6] to elaborate a very sensitive method for examining compounds able to form hydrogen — bridge bond.

Equimolar solutions made from the examined materials with indifferent solvent (CCl_4 , C_6H_{12}) mixed at different ratios lend themselves to determine

electric constants of the mixtures. If the two materials associate, then the plot of the dielectric constants vs. mole fractions of the mixtures, will not be rectilinear but curvilinear, with maximum or minimum depending on the composition.

This method was helpful in our previous tests [7] on the association of tetra-alcoxy-silanes and corresponding alcohols. Our mole polarisation, dipole moment, dielectric constant, conductivity and IR tests led to the conclusion that the tetra-alcoxy-silanes with open carbon chain always formed mole compounds of a 1 : 2 molar ratio with the corresponding alcohols, assuming a complex formation with sp^3d^2 hybridization, with co-ordination number 6.

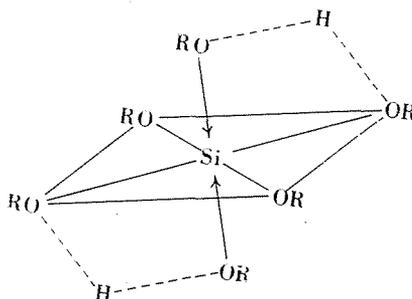


Fig. 1. Structure of the association of tetraalcoxy-silane—alcohol of 1 : 2 mole ratio

These observations induced us to association studies of mono-, di- and irifunctional alcoxy-silanes by means of dielectric constant, refractivity and IR tests. As model compounds the following alcoxy-silanes and the corresponding alcohols were chosen:

Trialkyl-mono-alcoxy-silanes:

- trimethyl-ethoxy-silane
- trimethyl-propoxy-silane

Dialkyl-dialcoxy-silanes:

- dimethyl-diethoxy-silane
- dimethyl-dipropoxy-silane
- dimethyl-dibutoxy-silane

Monoalkyl-trialcoxy-silanes:

- methyl-triethoxy-silane
- methyl-tripropoxy-silane
- methyl-tributoxy-silane

These compounds were obtained by method described previously [8]. The alcohols and cyclohexanes were absolutized as usual. All examined compounds were controlled by gas chromatography for purity using instrument

Type W. Giede 18.2. The recording was made in a 1 m column containing a chromosorb W charge wetted with 15% S. E. 30 silicone polymer.

1. Dielectric studies

From the examined alkoxy-silanes and the corresponding alcohols 2 mole cyclohexane solutions were made and the dielectric constants of these solutions and their mixtures in different mole ratios determined. The measurements were done at 25 °C ultrathermostated, at a frequency of 10.000 Hz by means

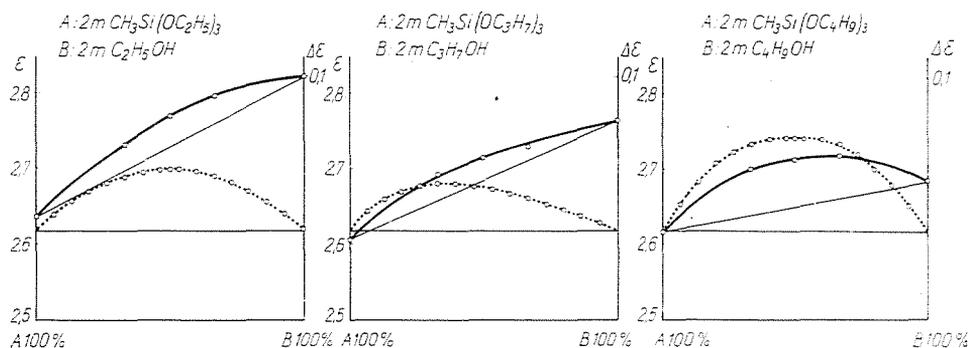


Fig. 2. Dielectric constant of alkyl-trialkoxy-silane-alcohol mixtures vs. mole fraction

of a home-made instrument [9] in a liquid condenser with a high basic capacity (300 pF).

The dielectric constants were plotted vs. mole fractions of the mixtures. As the dielectric constants of the three materials — alkoxy-silanes, alcohols and their mole compounds — may be very close, $\Delta\epsilon$ was taken as the derivation of the values for the respective composition from the line corresponding to the ideal mixture. Plotting calculated $\Delta\epsilon$ values as a function of the mole fraction, curves exhibited a peak — the mole ratio at this peak gave the composition of the association.

The methyl-triethoxy-silane-ethanol mixture shows a maximum at the composition with 2 : 1 mole ratio, and a vague maximum appears at 1 : 1 mole ratio. The methyl-tripropoxy-silane-propylalcohol mixture, however, shows a maximum only at 2 : 1 mole ratio, while the behaviour of the methyl-tributoxy-silane-butylalcohol mixture is the same as that of the ethoxy derivatives. Thus, it can be stated that complex formation is primarily possible for the composition with 2 : 1 mole ratio, but an association may form 1 : 1 mole ratio, too.

Study of mixtures of dialkyl-dialkoxy-silanes with corresponding alcohols led to the following conclusions.

Mixture of dimethyl-diethoxysilane and ethanol does not exhibit a singular point, i.e. it seems not to associate. At the same time, it associates with dimethyl-dipropoxy-silane—propylalcohol and dimethyl-dibutoxy-silane—bu-

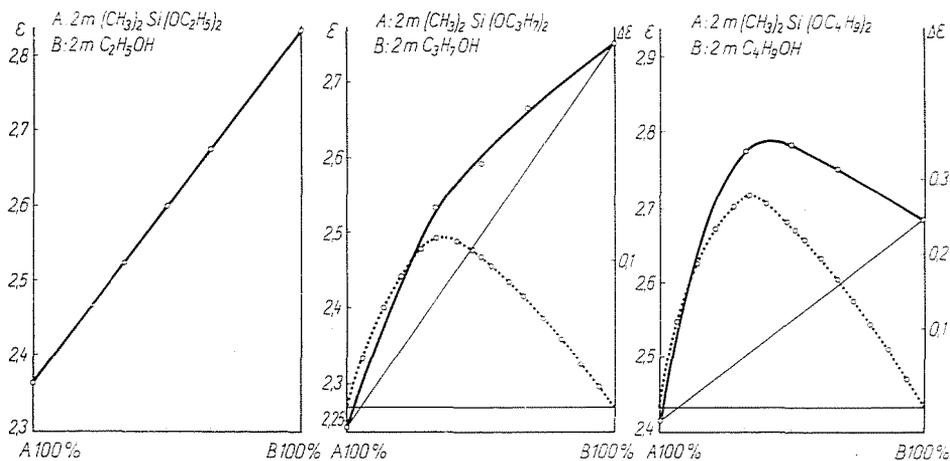


Fig. 3. Dielectric constant of dialkyl-dialcoxy-silane—alcohol mixtures vs. mole fraction

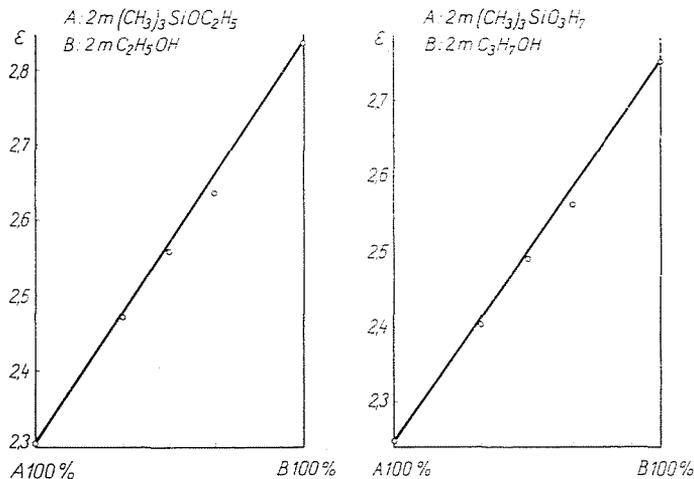


Fig. 4. Dielectric constant of trialkyl-alkoxy-silane—alcohol mixtures vs. mole fraction

tanol at the composition with 2 : 1 mole ratio. In case of monofunctional silanes, neither the trimethyl-ethoxy-silane—ethanol nor the trimethyl-propoxy-silane—propylalcohol mixtures show any maximum, the derivation from linear of the measured values does not exceed the test errors. Thus, no complex formation could be demonstrated by dielectrical tests.

These results show that the dielectric constant measured in complex formation does not much differ from that in simple mechanical physical

mixing of alkyl-alkoxy-silanes and alcohols. Among others, this may be responsible for the fact that in the difunctional line no complex formation appeared in case of dimethyl-diethoxy-silane—ethanol, while the two other difunctional silanes associated with the corresponding alcohol.

This observation leads to the supposition that the mixture of dimethyl-diethoxy-silane—ethanol of defined mole ratio forms an association, but the dielectric method is not always suitable to demonstrate it.

2. *Refractivity — composition studies*

Starting from refractometry tests by DEITS and VORONKOV [2] on the nature of the complex formation in binary systems of alkoxy-silanes and mono-substituted benzenes it seemed us interesting to perform refractivity — composition studies. Tests were made by means of a Zeiss immersion refractometer at 25 °C with T. 3. thermoprism. Refractivity values were determined at an accuracy of five decimals. In case of mixtures of monoalkyl-trialkoxy-, dialkyl-dialkoxy- and trialkyl-alkoxy-silanes with the corresponding alcohols, the refractivity — mole fraction relation was always a linear one showing that the alkyl-alkoxy-silanes formed ideal mixtures with alcohols in cyclohexane solution and therefore the association could not be demonstrated by measuring this physical property. This can be explained by the fact that in association, only the directional polarisation changes among the mole polarisation factors, but the optical member — i.e. electron and atom polarisation — does not. Hence, so-called dipole-complexes result, their formation process cannot be followed by refractivity tests but only by dielectrometry.

3. *Infrared spectrophotometry tests*

The infrared spectra were recorded by a Zeiss double-beamway spectrophotometer type UR-20, for 2 mole cyclohexane solutions of the compounds in NaCl cells of 0.02 mm layer thickness, at 25 cm⁻¹/min. exposition and 10 mm/100 cm⁻¹ paper speed. Refined evaluation concerned the OH-valence vibration range (3000 to 3800 cm⁻¹) of spectra taken at 10 cm⁻¹/min exposition and 40 mm/100 cm⁻¹ paper speed.

The spectra of ethyl- and butylalcohol vapours were taken in gas-cells with paths 100 mm long.

As it is known, in case of primary alcohols the ν OH band of the monomeric hydroxyl-groups lies in the range about 3640 cm⁻¹. The frequency of the ν OH band of the intermolecular associated hydroxyl-groups is low because of the elongation of the O—H bond taking part in the association.

Spectra of some mixtures in the range 3.000 to 3.800 cm⁻¹ are shown in Fig. 5.

The evaluation of the records is recapitulated in Table 1.

These data show that the valency vibration bands of the OH groups taking part in the association appear in the range 3510 to 3520 cm^{-1} .

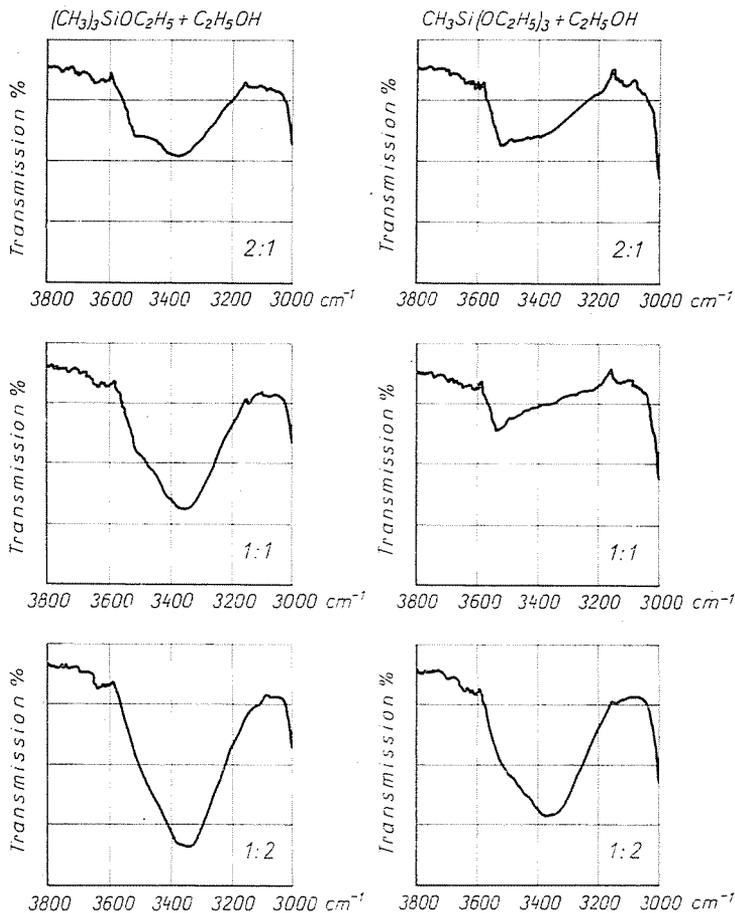


Fig. 5. IR spectra of trimethyl-ethoxy- and methyl-triethoxy-silane—ethanol mixtures with different mole ratios

Besides in case of the mixtures of $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ an ethanol in 2 : 1 mole ratio, distinct bands of the OH group of alcohol and of the OH radical entering the complex are seen, while in case of 1 : 1 mole ratio, the OH group of the complex appears only as a refracting line and in the mixture of 1 : 2 mole ratio, no presence of the complex could be shown.

For mixtures of dimethyl-diethoxy-silane—ethanol the mixture with 2 : 1 mole ratio shows the strongest complex formation as distinct absorption bands.

If there is no special mark, the exposure is that of 2 m cyclohexane solution. In IR exposures of mixtures with 1 : 1 and 1 : 2 mole ratios this appears as a refracting line.

Among the IR exposures of methyl-triethoxy-silane—ethanol mixtures, valency vibration band of the OH group of alcohol appears only for the mixture of 1 : 2 mole ratio, in exposures of the other two mixtures (2 : 1 and 1 : 1

Table I
Hydroxyl-group valency vibrations (ν OH) in the infrared spectra
of alkyl-alcoxy-silane—alcohol mixtures

Alcoxy-silane alcohol		Mole ratio	ν OH cm ⁻¹	ν' complex cm ⁻¹	Remarks
A	B	A : B			
(CH ₃) ₃ SiOC ₂ H ₅	C ₂ H ₅ OH	2 : 1	3370	3510	two distinct peaks refracting line
		1 : 1	3355	3510	
		1 : 2	3350	—	
(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₂ H ₅ OH	2 : 1	3400	3513	two distinct peaks refracting line refracting line
		1 : 1	3375	3517	
		1 : 2	3350	3515	
CH ₃ Si(OC ₂ H ₅) ₃	C ₂ H ₅ OH	2 : 1	—	3520	refracting line
		1 : 1	—	3523	
		1 : 2	3350	3520	
			C ₂ H ₅ OH vapour	3664	
	C ₂ H ₅ OH liquid	3430			
	C ₂ H ₅ OH	3340			
(CH ₃) ₂ Si(OC ₄ H ₉) ₂	C ₄ H ₉ OH	2 : 1	3350	3510	refracting line weak refracting line
		1 : 1	3350	3510	
		1 : 2	3350	—	
CH ₃ Si(OC ₄ H ₉) ₃	C ₄ H ₉ OH	2 : 1	3350	3520	two distinct peaks refracting line weak refracting line
		1 : 1	3350	3520	
		1 : 2	3350	3515	
			C ₄ H ₉ OH vapour	3674	
	C ₄ H ₉ OH liquid	3350			
	C ₄ H ₉ OH	3340			

ratios) only the band of the hydroxyl group entering the association complex appears.

The IR spectra of the dimethyl-dibutoxy-silane—butanol mixtures show mole ratio composition and very weak complex formation in case of 2 : 1 and 1 : 1 mole ratios respectively.

Methyl-tributoxy-silane—butanol mixtures exhibit two distinct hydroxyl valence vibration bands for a composition with 1 : 2 mole ratio, while for 1 : 1 and 1 : 2 mole ratios the exposures show only weak and very weak complex formations, respectively.

Comparing the results of refractivity, dielectric constant and infrared spectrophotometric test leads to the conclusion.

While no complex formation could be demonstrated by refractometry, the other two methods applied simultaneously clearly proved the formation of the associations. Accordingly, complexes of 2 : 1 mole ratio of the mixtures of tri-, di- and monofunctional silanes and suitable alcohols are likely to form. Remind that no complex formation in mixtures of monofunctional silanes and corresponding alcohols was demonstrated by dielectric tests, but by infrared spectroscopy it could be. These spectra exhibited the most intensive valence vibration at a composition of 2 : 1.

Let us see now the structure of these complexes, of given composition.

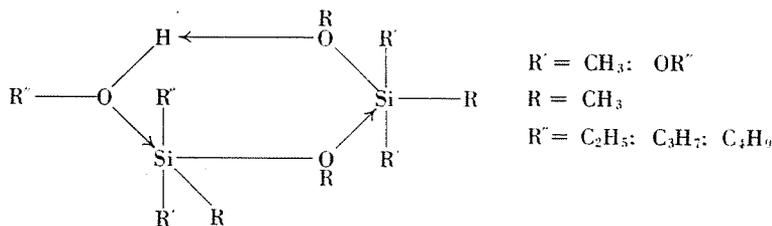


Fig. 6. Structure of the association of alkyl-alcoxy-silane—alcohol with 2 : 1 mole ratio

Earlier [7] it has been proved that the silicon atom of the tetra-alcoxy-silane acts as an acceptor and this compound forms sp^3d^2 octahedron complexes with 2 mole alcohol, similarly to the silicium-tetra-fluoride, which produces complexes of the same composition with hydrogen-fluoride (see Fig. 1).

At same time, DEITS and VORONKOV [3] found that SiCl_4 with benzene forms π -complex, where the silicium atom again acts as an acceptor.

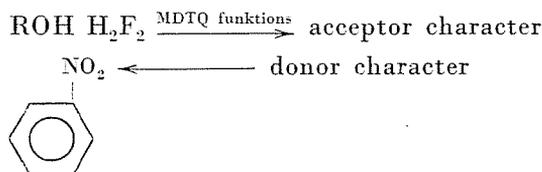
Our present investigations show that the tri-, di- and monofunctional alcoxy-silanes form complexes in 2 mole silane: 1 mole alcohol composition because the R radical probably inhibits the development of the sp^3d^2 hybridization state and so the silicium atom forms an acceptor-donor complex — probably a ring with six members — only of sp^3d (trigonal bipyramid) pentacovalent character, comprising silicium with co-ordination number 5. Its stereostructure, supposing the simplest composition is shown in Fig. 6.

It is known from the literature that the hydrogen-fluoride with trifunctional fluor-silanes still forms complexes of co-ordination no. 6., but with di- and monofunctional fluor-silanes does not. This shows that the tetra-functional silanes are complex-formers with the strongest acceptor character independently of the nature of the functional groups and with decreasing functionality their ability to form complexes diminishes as well. As the fluoride ion is stronger complex-forming ligandum that is the alcoxy radical, the hydrogen-fluoride gives complexes of co-ordinations number 6 even with methyl-trifluoride-silanes while the alcohol forms associations even with trifunctional

alcoxy-silanes with co-ordination no. 5. only. This can be attributed to of a degree depending on the sizes of fluoride ion and the alcoxy-group.

DEITS and VORONKOV [3] found that the mono-, di- and trifunctional alcoxy-silanes form complexes of donor character with mono-nitrobenzene because of the donor character of the oxygen atom in them.

They observed the strongest complex formation of donor character for monofunctional silanes. As a general rule, the ability to form complexes of acceptor character grows towards and cumulates at tetrafunction, what is proved by the complexes of co-ordination number 6 formed by hydrogen fluorides with tetra- and trifunctional fluor-silanes and by alcohol with tetra-functional alcoxy-silanes. At the same time, the ability to form complexes of donor character grows towards monofunction. This is proved also by the fact that the monofunctional silanes do not form complexes of acceptor character with hydrogen-fluoride, but enter associations of the strongest donor character with mononitrobenzene. The foregoings are shown on the following figure.



While the stability of complexes of acceptor character and of alcoxy-silanes-alcohol composition grows towards tetrafunction, the strength of the proton bridge bond inherent in the donor character of the oxygen-atom in the alcoxy-group grows towards monofunction, as proved by infrared spectrophotometry. The valence vibration of the OH group in the complex appears at 3510—2520 cm^{-1} for all mixtures, its shifting with respect to the natural vibration band refers to the proton bridge formation.

The correctness of the IR spectrophotometry results is proved also by the data in Table 2.

Table 2

Data of the calculated bond dipole moment of the homologous series $(\text{CH}_3)_n\text{Si}(\text{OCH}_3)_{4-n}$

	m_{CO}	m_{SiO}	m_{CHO}
$(\text{CH}_3)_3\text{Si}(\text{OCH}_3)$	0.96	1.26	1.13
$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$	0.86	1.16	1.14
$(\text{CH}_3)\text{Si}(\text{OCH}_3)_3$	0.77	1.07	1.15
$\text{Si}(\text{OCH}_3)_4$	0.67	0.97	1.16

It appears that the dipole moment of the Si bond and the partial charge ratio of the oxygen atom is the highest at monofunction and the donor character is linearly dependent.

The strength of the proton bridge bond calculated by BADGER and BAUER [10] from data in Table 2 is 4.29 kcal/mole, inferior to the strength of the proton bridge bond in alcohol 9.26 kcal/mole. This can be explained by the fact that the interval of the proton bridge bond is smaller in case of alcohol than in alcoxy-silanes and so the bond itself is stronger, this demonstrates the correctness of the formula in Fig. 6.

One may ask: whether not only complexes of 2 : 1 mole ratio, but a variety with different compositions and linear structure are formed and the indicated ratio is only their statistical mean. This is, however, unlikely because both alcohols and carboxylic acids exist in form of cyclic associations, moreover the latter ones form dimer conglomerates not only in vapour, but also in liquids. Thus, considered associations ought to have cyclic structures, as it is shown in Fig. 6.

II. Phenoxy-silane-phenol binary systems

Our studies were extended to some methyl-phenoxy-silanes. Trimethyl-phenoxy and dimethyl-diphenoxy-silanes, as well as phenol were chosen as model compounds. Methyl-phenoxy silanes were produced by the method described earlier [11]. Purity was controlled by gas-chromatography. The applied phenol was freshly distilled.

Dielectric studies

2 cm cyclohexane solutions of the compounds were tested similarly to the alcoxy-silanes. The resulting ϵ and $\Delta\epsilon$ values are plotted vs. mole fraction.

The dimethyl-diphenoxy-silane-phenol mixture shows a maximum at 1 : 1 mole ratio, but also at 2 : 1 mole ratio an uncertain peak appears while the trimethyl-phenoxy-silane-phenol mixture shows a single peak at 1 : 1 mole ratio.

Infrared spectrophotometry

The IR spectra of the dimethyl-diphenoxy-silane-phenol mixtures demonstrate complex formation for all three compositions. It is the weakest at 1 : 2 mole ratio, the strongest at 1 : 1 mole ratio, but even at 2 : 1 mole ratio a well defined complex formation is indicated.

Complex formation is apparent in the IR spectra of trimethyl-phenoxy-silane-phenol mixtures for all three compositions.

In the valency vibration range of the hydroxyl group more new absorption bands appear than in the phenol spectrum indicating the formation of different intermolecular associations. More detailed investigations are necessary. Location and relative size of the absorption bands proves, however, that the complex formation is the strongest at 1 : 1 mole ratio.

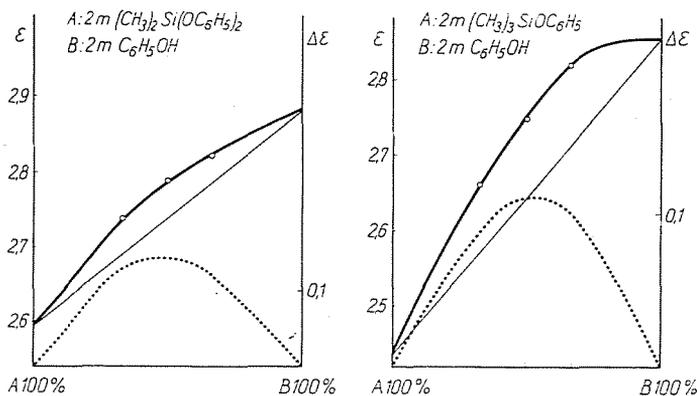


Fig. 7. Dielectric constant of dimethyl-diphenoxy-silane—phenol and trimethyl-phenoxy-silane—phenol mixtures vs. mole fraction

Table 3

Hydroxyl-group valency vibrations (ν OH) in the infrared spectra of alkyl-phenoxy-silane—phenol mixtures

Phenoxy-silane	Phenol	Mole ratio	Absorption bands in the valency vibration range of the OH-group				
A	B	A : B					
$(\text{CH}_3)_2\text{Si}(\text{OC}_6\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{OH}$	1 : 2	3380	3568	(refracting line)		3628
		1 : 1	3425	3558			3628 (refracting line)
		2 : 1	3470	3568			3628
$(\text{CH}_3)_3\text{SiOC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	1 : 2	3442 3565 3595				
			3438				
		1 : 1	3358 (refracting line)	3568	3595	3627	
		2 : 1	3358	—	3432	3568	3595 3628
	$\text{C}_6\text{H}_5\text{OH}$		3358	3628			

Referring to 2 m cyclohexane solutions.

The comparison of the results of both test methods proves that in case of methyl-phenoxy-silane—phenol mixtures the complex formation is the most probable at 1 : 1 mole ratio, as against the 2 : 1 ratio compositions of

the methyl-alcoxy-silane—alcohol complexes. This may be explained by the increased space demand of the phenoxy radical, so that a structure similar to that of the sodium-diglycoxy-methoxy-silicate and known to occur for other pentacovalent complexes of silicium is likely to exist:

IR spectrophotometry studies show that together with the compound shown in the figure above some complexes with different composition form and they are balanced.

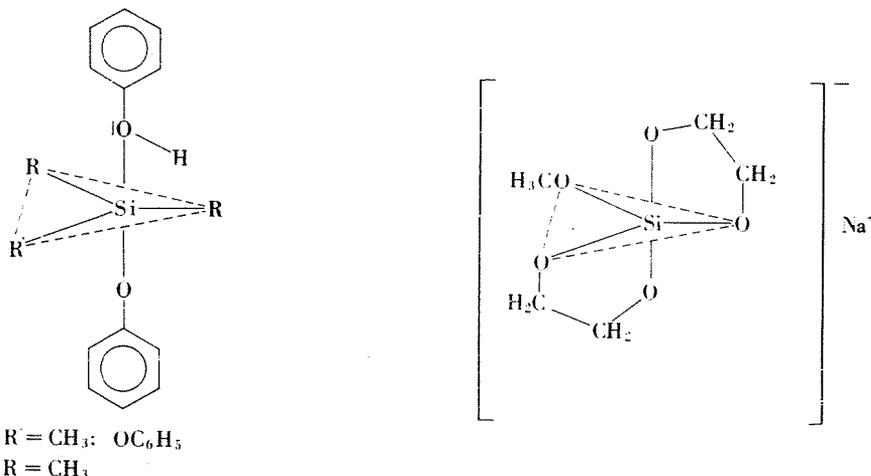


Fig. 8. Structure of the association of alkyl-phenoxo-silane—phenol with 1 : 1 mole ratio and of the sodium-diglycoxy-methoxy-silicate

Finally it can be stated that the considered associations range between physical and chemical limits, they are feebly bound dipole complexes decomposing already at boiling point and forming separate chemical units.

Summary

1. Dielectric and infrared spectrophotometry tests show complex formation in the alkyl-alcoxy-silane—alcohol mixtures mainly at 2 : 1 mole ratio composition. In the case of monofunctional silane—alcohol mixtures this could be proved only on ground of infrared spectra.
2. The shifting of the valence vibration of hydroxyl groups in the infrared absorption spectra lent itself to calculate the strength of the proton bridge bond; to be 4.29 kcal/mole.
3. Our investigations and literature data prove that the disposition to form complexes with acceptor and donor character grows towards tetrafunction and monofunction, respectively.
4. It can be supposed that in 2 : 1 associations of silane and alcohol, the silicium atom in sp³d hybridization state, with co-ordination number 5, forms the complexes of acceptor-donor character consisting of rings with six members.
5. Alkyl-phenoxo-silane—phenol mixtures exhibited the strongest complex formation at 1 : 1 mole ratio composition.

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