

OSCILLOPOLAROGRAPHIC EXAMINATION OF SOME ORTHOSILICIC ACID DERIVATES

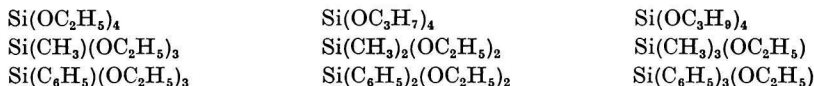
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Je popsán kapacitní účinek některých ethoxylových derivátů ortokřemičité kyseliny. Adsorptivita je úměrná počtu ethoxylových skupin a je závislá na dipolovém momentu.

Organo-silicon compounds are of interest not only from a theoretical point of view, but also as important starting materials of various silicone products. Such silicones can be advantageously produced using substituted orthosilicic acid esters as raw materials, as proposed by J. Proszk, J. Nagy and I. Lipovetz [1]. A study of the — as yet unknown — polarographic behaviour of these compounds seems to be worth while, on account of their practical importance.

The present work deals with three homologous series of orthosilicic acid derivatives; these are the following:



Since these compounds do not contain any polarographically reducible groups, the oscillopolarographic investigation of their capacitive action was employed.

Experimental Part

A „Very Low Frequency Oscilloscope“ EMG Type 1538 was used, together with a polarising and derivating circuit, that was essentially the same as that described by J. Heyrovský and R. Kalvoda [2].

The compounds studied had been prepared by a solventless Grignard reaction [3, 4].

A molar solution of potassium chloride was used as supporting electrolyte throughout the work; solutions other than neutral were out of question because of the danger of

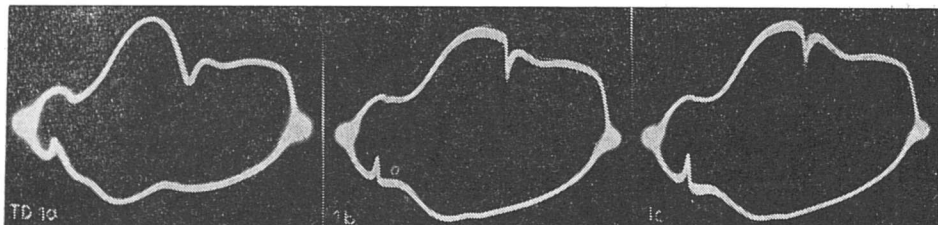


Fig. 1. $dE/dt = f_1(E)$ curves of tetraalkoxysilanes in 1 M-KCl.
a) tetraethoxysilane; b) tetrapropoxysilane; c) tetrabutoxysilane.

hydrolysis. The compounds examined were dissolved in methyl alcohol, and this solution was added to the supporting electrolyte. Steady oscillograms could be obtained only by the use of a streaming mercury electrode [5].

The oscillograms of the *tetraalkoxysilanes* (Fig. 1) are all similar: there is a characteristic cathodic incision at a potential corresponding to a Q value of 0,5 to 0,6 ($-0,97$ to $-1,17$ V vs. SCE), and a further, smaller anodic one at a Q value of about 0,1. The Q value of the cathodic incision is independent of the concentration with the propoxy- and butoxy-compounds (0,60 and 0,57, respectively), while in case of the ethoxy-ester the value of Q is constant only above a certain limiting value of concentration (curve A, Fig. 7). The depth of the incisions is a function of concentration; the larger cathodic

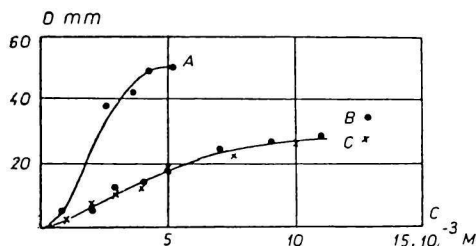


Fig. 2. Depth of incision (D , mm) plotted against molar concentration (C).

A. tetraethoxysilane; B. tetrapropoxysilane; C. tetrabutoxysilane.

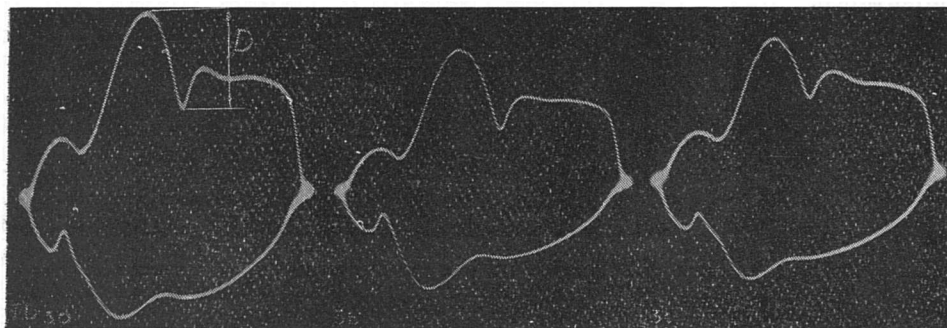


Fig. 3. $dE/dt = f_1(E)$ curves of methylethoxysilanes in 1 M-KCl.
a) methyltriethoxysilane; b) dimethyldiethoxysilane; c) trimethylethoxysilane.

incision can be evaluated better. (The depths were measured as shown on Fig. 4/A.) The oscillographic activity of the ethoxy-compound was largest, whereas the propoxy- and butoxy-compounds showed equal activity (Fig. 2).

Methylethoxysilanes show a pattern practically identical to that of the alkoxy-silanes (Fig. 3), but the Q values are markedly dependent on the concentration (curves B, C and D, Fig. 7). The depth of the incision is a function of the concentration (Fig. 4).

The oscillographic curves of the *phenylethoxysilanes* are markedly different, compared with the above, with one new cathodic incision in case of the mono- and disubstituted compounds, and a further

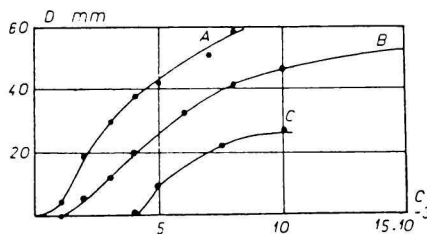


Fig. 4. Depth of incision (D , mm), plotted against molar concentration (C).

A. methyltriethoxysilane; B. dimethyldiethoxysilane; C. trimethylethoxysilane.

(fourth) anodic one in case of the trisubstituted derivative (Fig. 5). The Q values of the cathodic incision are 0,62; 0,59 and 0,57, respectively; all are quite independent of concentration. The depth of the incision depends on the concentration, as shown on Fig. 6.

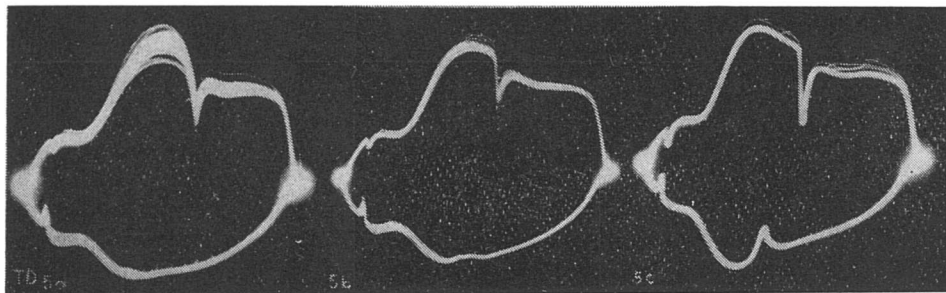


Fig. 5. $dE/dt = f_1(E)$ curves of phenylethoxysilanes in 1 M-KCl. a) phenyltriethoxysilane; b) diphenyldiethoxysilane; c) triphenylethoxysilane.

A „cutting off“ of the curves at higher concentrations does not occur, showing the incision to be of the capacitive type.

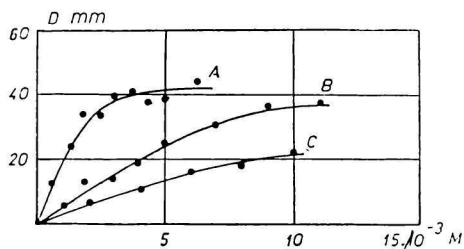


Fig. 6. Depth of incision (D , mm), plotted against molar concentration (C). A. phenyltriethoxysilane; B. diphenyldiethoxysilane; C. triphenylethoxysilane.

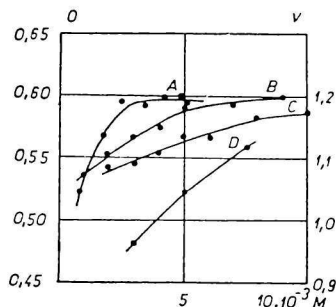


Fig. 7. Dependence of Q values on concentration. A. tetraethoxysilane; B. methyltriethoxysilane; C. dimethylethoxysilane; D. trimethylethoxysilane.

Discussion

Characteristic of the oscillopolarograms of all the compounds investigated is a cathodic desorption incision at a Q value of 0,5—0,6. In case of the methylethoxysilanes the Q value is dependent on the concentration, in case of the tetraethoxy-compound such a dependence exists only until an upper limiting concentration is not reached, while with all other compounds the value of Q is quite independent of the concentration (Fig. 7). A regular tendency can be detected, if the compounds are listed according to the order of their increasing molecular weights (Table 1).

As we see the energy necessary for the adsorption-desorption procedures is above a critical molecular size (molecular weight) no longer a function of concentration.

Table 1
Concentration-dependence of Q values

| Derivatives | MW | Q |
|------------------------|-----|-----------------------------------|
| trimethylethoxysilane | 120 | greatly dependent |
| dimethyldiethoxysilane | 148 | dependent |
| methyltriethoxysilane | 178 | dependent |
| tetraethoxysilane | 208 | dependent in dilute solution only |
| phenyltriethoxysilane | 240 | independent |
| tetrapropoxysilane | 264 | independent |
| diphenyldiethoxysilane | 272 | independent |
| triphenylethoxysilane | 304 | independent |
| tetrabutoxysilane | 320 | independent |

A striking regularity can be detected as regards the depth of the incisions: the depths corresponding to a given concentration seem to be proportional to the number of ethoxy-groups in the molecule (Table 2).

Table 2
Depths of incision with the various compounds
($C = 6 \cdot 10^{-3} M$)

| Derivatives | D, mm | μ |
|------------------------|-------|-------|
| trimethylethoxysilane | 16,5 | 1,146 |
| dimethyldiethoxysilane | 32,0 | 1,358 |
| methyltriethoxysilane | 48,0 | 1,678 |
| triphenylethoxysilane | 15,5 | 1,250 |
| diphenylethoxysilane | 28,0 | — |
| phenyltriethoxysilane | 43,0 | 1,538 |

These results could suggest the idea, that it is the ethoxy-groups, which are responsible for the oscillopolarographic activity. However, ethyl acetate, that ought to be of great activity, is poorly active; hexamethyldisiloxane on the other hand, which contains the $\equiv Si-O-$ group also characteristic of the compounds investigated, is quite inactive. Accordingly assignment of the activity to one particular group does not seem to be justified.

Similarly it is impossible to explain the above phenomenon by the well known dependence of capacitive activity on solubility [6]: the more soluble phenyl-compounds show — quite unexpectedly — greater activity. Relative solubilities were estimated by adding the compounds to the supporting electrolyte and noting the first appearance of haziness [7]. The methyl-compounds are readily soluble, nevertheless the above mentioned proportionality holds for these as well.

This interesting behaviour can be explained by the fact that adsorption in case of a metallic adsorbent surface is the stronger, the more polar the adsorbed molecules are. Comparison of the dipole moments of the compounds (row 2, Table 2) [8] with the specific

activities shows a parallelism between these two properties. This indicates the oscillopolarographic activity of the compounds studied to be in close connection to their molecular structure.

The above results make it possible to analyse the compounds investigated; beside the analytical uses these data yield new possibilities for the physicochemical essay of these orthosilicic acid derivatives based on oscillopolarographic indication or determination [9].

The autor is indebted to Dr. J. Proszk, Dr. R. Kalvoda and J. Nagy for their valuable advice, further to J. Nagy and his co-workers for having kindly made available the materials to be tested.

Summary

Oscillopolarographic behaviour of alkoxyasilanes, further methyl- and phenyl-substituted ethoxyasilanes was investigated. Specific activities were found roughly proportional to the number of ethoxy groups in the molecule; a correspondence was found between activity and dipole moment.

ОСЦИЛЛОПОЛЯРОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ НЕКОТОРЫХ ПРОИЗВОДНЫХ ОРТОКРЕМНИЕВОЙ КИСЛОТЫ

ТАМАШ ДАМОКОШ

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Описан емкостный эффект некоторых этоксиловых производных ортокремниевой кислоты. Адсорбционная способность пропорциональна числу этоксиловых групп и зависит от дипольного момента.

LITERATURE

1. Proszk J., Lipovetz I., Nagy J., Magyar Kém. Lapja 11—12 (1952). — 2. Heyrovský J., Kalvoda R., *Oszillographische Polarographie mit Wechselstrom*, Berlin 1960, 30. — 3. Nagy J., Periodica Polytechnica 2, 241 (1958). — 4. Proszk J., Lipovetz I., Nagy J., Magyar Szab. PO-126-668 (1952); PO-146-825 (1954). — 5. Györbiró K., Poós L., Proszk J., Acta Chim. Acad. Sci. Hung. 9, 27 (1956). — 6. Kalvoda R., Collection 25, 3071 (1960). — 7. For the Idea of This Simple Solubility Test the Author is Indebted to Dr. R. Kalvoda. — 8. Nagy J., Cand. diss. university Budapest 1961. — 9. Molnár L., Lecture Held at the International Analytical Chemistry Congress, Budapest 1961.

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