STABILITY AND STRUCTURAL PROPERTIES OF ORGANOSUSPENSIONS. II

Stability of Organophilic Bentonite Suspensions in Mixtures of Apolar and Polar Liquids

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The sedimentation rates and sediment volumes of suspensions of "Bentone 34" were investigated in mixtures of benzene with methanol, ethanol, propanol and butanol, further with nitrobenzene. The sedimentation rates proved to change with alcohol concentrations according to a curve of minimum-maximum type. In the first and particularly in the third extreme points the formation of almost thixotropic systems was experienced. At maximum sedimentation rates a diffuse sedimentation takes place. Changes in sediment volume and sedimentation rate are always of opposite sense. The thixotropic trend diminishes with the rise of the number of carbon atoms in the alcohol. This was interpreted by the WO. OSTWALD—BUZÁGH principle of continuity. The formation of a structure sedimenting with a sharp boundary was experienced also in mixtures of benzene and nitrobenzene, up to certain limits of concentration. However, owing to specific solvation effect of nitrobenzene, the structure decomposes already over relatively low concentrations of nitrobenzene, and a stable sol forms.

On this basis, the sedimentation and the structural properties of organophilic bentonite suspensions were interpreted by the disintegration of the particles and by the formation of a card skeleton structure of the evolved lamellae. On increasing the solvation, first a disintegration-adhesion (coherent), then an incoherent section follows. Subsequently, in the case of alcohols coagulation and structure formation (second coherent section), and lastly a structureless coarse coagulation take place.

Introduction. In our experiments with pure organic liquids described in our previous communication [1] we established that the card skeleton theory of HOFMANN [2] can also be applied to organophilic clay minerals, and that the stability and sediment volume are determined by the disintegration of the particles and the adhesion forces existing between the lamellae [3]. In order to study more thoroughly the role of solvation conditions, measurements of sedimentation rate and sediment volume were carried out also in mixtures of apolar and polar organic solvents such as benzene and methanol, benzene and ethanol, benzene and propanol, benzene and butanol, further benzene and nitrobenzene.

The applied technique was identical in every respect with that used in our earlier experiments [1], "*Dutch Boy Bentone 34*" serving as basic substance. The investigations were carried out with 0,2 g samples in 20 ml test tubes with 0,1 ml scale, in a thermostat at a temperature of $25 \pm 0{,}1$ °C.

Experimental results

In *mixtures of benzene and ethanol* of various composition, just as in various pure organic solvents, sedimentation with a diffuse and sharp boundary surface

Table I

Sedimentation rate and sediment volume vs. concentration by volume of methanol

Methanol volume proc.	Methanol mol/l.	Dielectric. const. at 25°C	Sedimentation rate cm/sec.	Sediment volume ml
0,00	0,00	2,29	0,0057	4,10
0,50	0,09	2,32	0,0038	5,40
1,00	0,17	2,35	0,0024	5,50
1,75	0,30	2,41	0,0010	7,00
2,50	0,43	2,47	0,0014	6,20
5,00	0,85	2,66	0,0031	5,00
7,50	1,28	2,88	0,0111	3,40
10,00	1,70	3,16	0,0145	2,60
12,50	2,13	3,36	0,0160	2,40
15,00	2,56	3,83	0,0135	2,70
20,00	3,41	4,47	0,0050	4,80
25,00	4,26	5,73	0,0044	5,10
30,00	5,11	6,84	0,0042	4,10
45,00	7,67	10,70	0,0086	2,80
60,00	10,22	14,92	0,0144	2,15
100,00	17,04	25,49	0,0434	1.20

Table II

Sedimentation rate and sediment volume vs. concentration by volume of ethanol

Ethanol volume proc.	Ethanol mol/l.	Dielectric. const. at 25 °C.	Sedimentation rate cm/sec.	Sediment volume ml
0,00	0,00	2,29	0,0057	4,10
0,25	0,06	2,36	0,0042	5,60
0,50	0,12	2,44	0,0003	7,80
1,00	0,25	2,48	0,0003	8,00
2,50	0,61	2,66	0,0011	7,20
5,00	1,23	3,00	0,0031	3,20
7,50	1,83	3,36	0,0082	2,90
10,00	2,46	3,82	0,00006	9,50
15,00	3,68	5,01	0,00003	10,10
20,00	4,91	6,30	0,00004	7,10
30,00	7,37	9,56	0,0022	4,30
45,00	11,05	14,70	0,0191	2,50
60,00	14,73	20,22	0,0580	1,70
100,00	24,55	33,56	0,1190	0,85

Table III

Sedimentation rate and sediment volume vs. concentration by volume of propanol

Propanol volume proc.	Propanol mol/l.	Dielectric const. at 25 °C	Sedimentation rate cm/sec.	Sediment volume ml
0,00	0,00	2,29	0,0057	4,10
0,50	0,07	2,32	0,0045	4,80
1,00	0,13	2,35	0,0036	5,00
2,50	0,33	2,46	0,0033	5,60
5,00	0,67	2,57	0,0042	4,90
7,50	1,00	2,73	0,0057	4,10
10,00	1,33	2,90	0,0111	3,40
15,00	2,00	3,33	0,0187	2,60
20,00	2,66	3,82	0,0134	3,10
22,00	2,93	4,11	0,0120	3,20
25,00	3,33	4,55	0,0104	3,25
30,00	4,00	5,33	0,0104	3,30
40,00	5,32	7,28	0,0072	4,00
45,00	5,99	8,22	0,0055	4,10
50,00	6,66	9,36	0,0058	3,30
60,00	7,99	12,81	0,0084	2,30
80,00	10,65	16,64	0,0138	1,50
100,00	13,31	21,08	0,0162	1,00

Table IV

Sedimentation rate and sediment volume vs. concentration by volume of butanol

Butanol volume proc.	Butanol mol/l.	Dielectric const. at 25 °C	Sedimentation rate cm/sec.	Sediment volume ml
0,00	0,00	2,29	0,0057	4,10
1,00	0,11	2,35	0,0058	4,80
2,00	0,22	2,40	0,0067	4,40
3,00	0,33	2,45	0,0083	3,70
6,00	0,63	2,60	diffuse	3,20
10,00	1,09	2,85	,,	2,40
15,00	1,63	3,15	,,	2,30
20,00	2,16	3,56	,,	2,10
30,00	3,27	4,54	,,	2,10
40,00	4,35	5,94	,,	2,10
50,00	5,44	7,72	,,	1,80
65,00	7,07	10,76	,,	1,60
80,00	8,70	14,01	,,	1,20
100,00	10,87	17,85	,,	0,70

was experienced. The values of sedimentation rate and sediment volume measured in various mixtures are given in Tables I—IV. It must be noted that, according to our measurements, the differences due to changes in the density and inner friction of liquids proved to be negligible in respect to the experienced effects. The sedimentation rates and sediment volumes plotted against concentrations by volume of the alcohols are shown in Figures 1—4 while the sedimentation rates plotted against the molar concentrations of alcohols in Fig. 5.

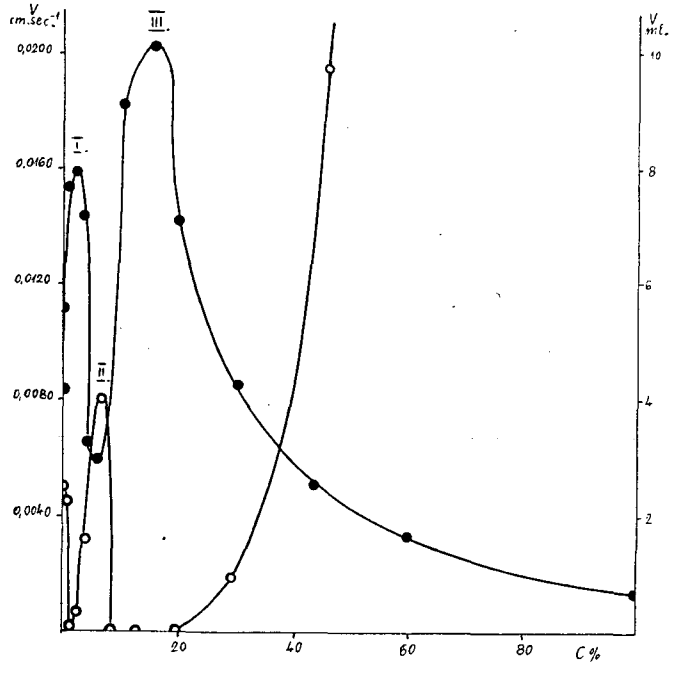

Fig. 1. Sedimentation rate and sediment volume *vs.* concentration by volume of methanol.
o sedimentation rate
● sediment volume

It can be seen from the data of the tables and from the figures that three extreme points appear in the changes of sedimentation rate and sediment volume in the mixtures of benzene with methanol, ethanol and propanol. Changes in sedimentation rate and sediment volume always proved to be opposite to each other.

Up to the first extreme point (*cf.* point I in the figures) the capability of structure formation of the suspensions gradually increased (first coherent section). Accordingly, the sedimentation rates diminished while at the same time the sediment volumes increased. The "quasi-thixotropic" character and apparent stability, respectively, attained their maximum values in the first critical point.

In the next section of the curve (between critical points I and II) the capability of structure formation decreased (incoherent section). The sedimenting suspension

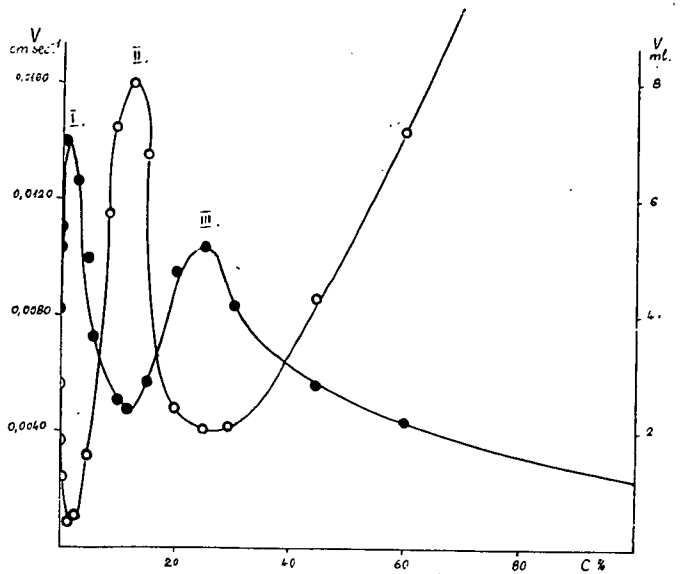

Fig. 2. Sedimentation rate and sediment volume *vs.* concentration by volume of ethanol.
o sedimentation rate ● sediment volume

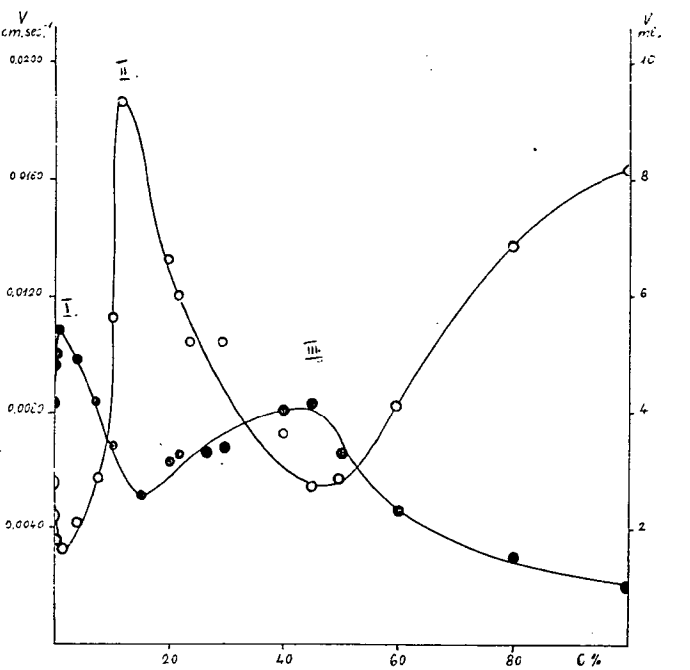

Fig. 3. Sedimentation rate and sediment volume *vs.* concentration by volume of propanol.
o sedimentation rate ● sediment volume

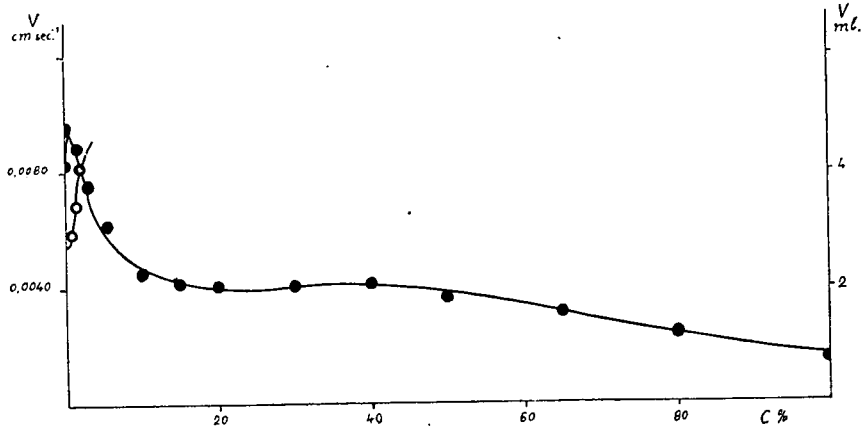

Fig. 4. Sedimentation rate and sediment volume *vs.* concentration by volume of butanol.
o sedimentation rate
● sediment volume

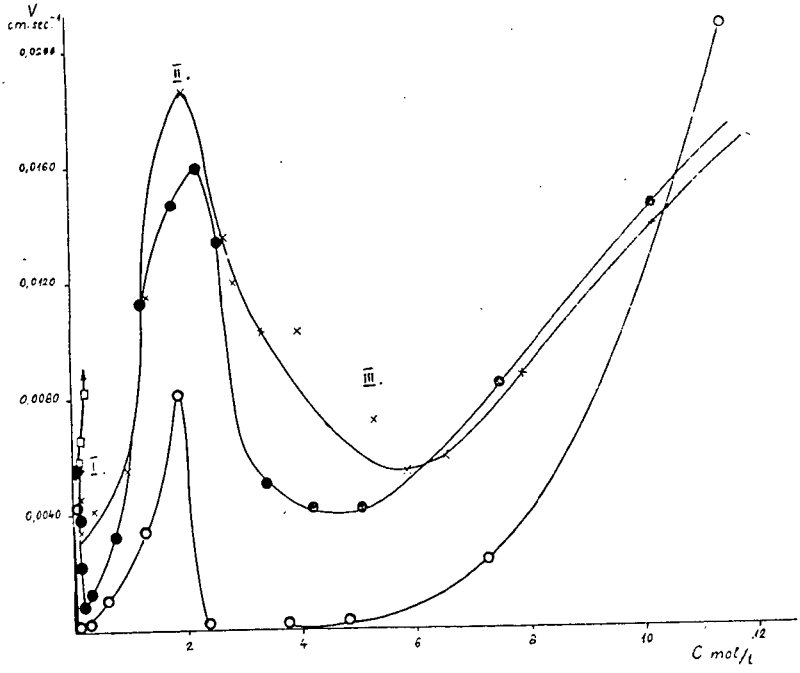

Fig. 5. Sedimentation rates *vs.* the molar concentrations of alcohols.
o methanol
● ethanol
× propanol
□ butanol

becomes to be of a more diffuse distribution when the concentration of alcohols rises, and the particles sediment more or less independently of each other. Accordingly, the sedimentation rate increases and the sediment volume diminishes. Minimum values of the quasi thixotropic character and of apparent stability appear in critical point II (cf. points II in the figures). Subsequently, the trend to thixotropy again increases (second coherent section). Thus, sedimentation takes place with a sharp boundary surface and at gradually decreasing rates. Sediment volumes again rise. Quasi thixotropic character and apparent stability attain their second maxima in point III. At this second maximum, the sedimentation rate is much lower than at the first maximum. Moreover, the systems proved to be almost thixotropic.

Above the third critical concentration (coagulation section), coarse aggregates can be observed already at the preparation of the suspensions. The sedimentation is of a diffuse character, sedimentation rates rapidly rise while sediment volumes decrease on raising the concentration of alcohol.

The above described qualitative observations in respect to the behaviour of suspensions are summarised in Table V.

Table V

Behaviour of suspensions in various sections of the curves sedimentation rate vs. alcohol concentration

Sections	Interaction with medium	Character of sedimentation	Character of sediment
up to point I	Increase of swelling, disintegration. Peptised particles form a coherent, loose structure.	with a sharp boundary	Transparent, swollen, loose, easily suspendable
between points I and II	Strong swelling, peptisation. Adhesion forces diminish with increasing alcohol concentrations.	diffuse	Compact, transparent jelly With the increase of alcohol concentration its suspendability gradually decreases. Low sediment volumes.
betwen points II and III	Aggregation of peptised particles increases with increasing alcohol concentrations.	With increasing alcohol concentrations boundary surfaces become sharper.	Opaque, loose, readily suspendable. High sediment volumes.
beyond point III	Strong coagulation already on preparing the suspension.	diffuse	Readily suspendable. Sediment volume low.

On comparing the curves of sedimentation rates in mixtures containing alcohols with various numbers of carbon atom, it appears that the quasi thixotropic character of systems corresponding to critical concentrations I and III is affected to a great extent by the number of carbon atoms of the applied alcohol, in that this character becomes weaker with the rise of the number of carbon atoms. The increase of the diffuse character with the rise of the number of carbon atoms is readily observable qualitatively in the section between critical concentrations I and II (incoherent section).

In mixtures of benzene and butanol, up to a butanol content of 3%, sedimentation takes place with a sharp boundary surface. At butanol concentrations over 3%, however, owing to the strong peptising effect of butanol, a solvent with a relatively high number of carbon atoms, sedimentation is rather diffuse. Therefore, it was not possible to quantitatively investigate sedimentation rates with the method applied by us. However, it has been qualitatively established that at high concentrations of alcohol (over 80%) the coagulating effect of alcohols also prevails in this case, though to a smaller extent than in the case of alcohols with a lower number of carbon atoms.

In the case of mixtures containing methanol, ethanol and propanol, also the *dieletric constants* where determined in media of various composition (cf. Fig. 6).

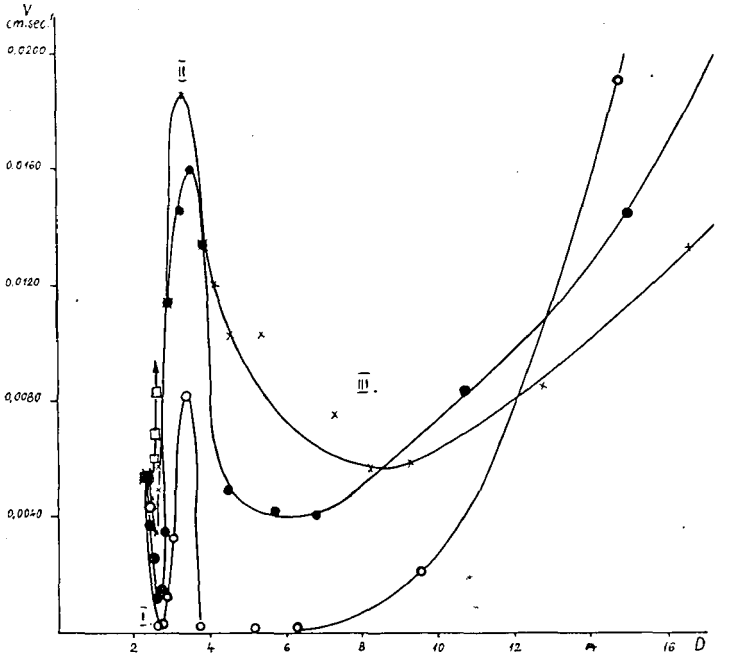

Fig. 6. Sedimentation rates *vs.* dielectric constant of the mixtures.
o methanol
● ethanol
× propanol
□ butanol

On comparing the measured dielectric constants of mixtures of critical composition (*cf.* Table VI) it can be observed that the first and second critical points of the curves appear practically at the same dielectric constants in the case of all the three types of alcohols tested. The critical point III, in turn, occurs in the case of alcohols with a rising number of carbon atoms at increasing values of dielectric constant.

Table VI
Dielectric constants at the critical points

	I	II	III
Methanol	2,48	3,36	5,01
Ethanol	2,41	3,36	5,73
Propanol	2,46	3,33	8,22

In *mixtures of benzene and nitrobenzene*, sedimentation rates could only be measured up to a nitrobenzene content of 30%. In mixtures containing more than 30% of nitrobenzene, suspensions were obtained which sedimented in a diffuse manner, and thus it was impossible to quantitatively establish sedimentation rates with the applied method. The measured values of sedimentation rate and sediment volume are shown in Table VII and Fig. 7, respectively.

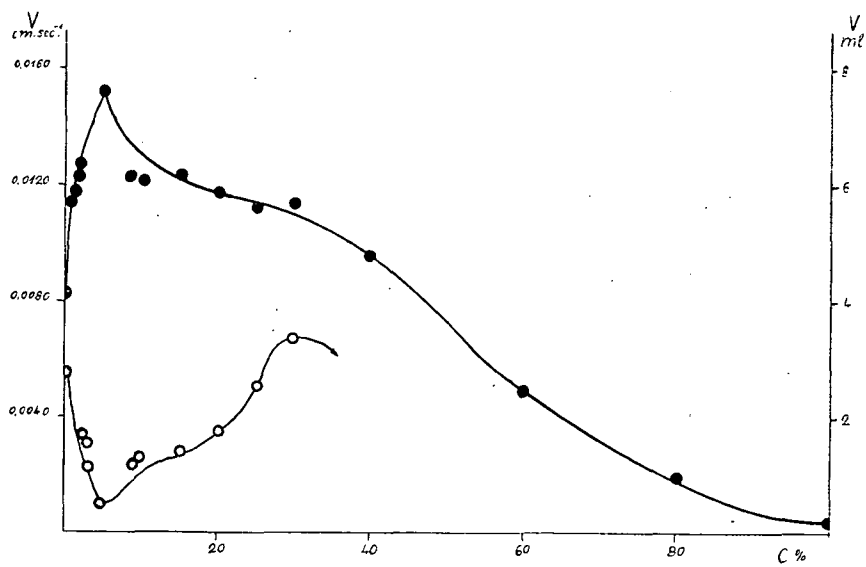

Fig. 7. Sedimentation rate and sediment volume *vs.* concentration by volume of nitrobenzene.
o sedimentation rate
● sediment volume

On increasing the quantity of nitrobenzene, similarly a system of quasi thixotropic character formed in these mixtures, up to certain limit of concentration (coherent section). Accordingly, sedimentation took place with a sharp boundary surface, sedimentation rates decreased while sediment volumes increased. Over this concentration limit, the structure decomposed, gradually increasing proportions of the substance peptised and sediment volumes diminished (stable incoherent system).

Table VII

Sedimentation rate and sediment volume vs concentration by volume of nitrobenzene

Nitrobenzene volume proc.	Dielectric const. at 25 °C	Sedimentation rate cm/sec.	Sediment volume ml
0,00	2,29	0,0057	4,10
0,25	2,46	0,0033	5,60
0,50	2,47	0,0029	5,70
1,00	2,77	0,0026	6,20
2,50	2,94	0,0022	6,30
5,00	3,53	0,0010	7,60
7,50	3,93	0,0022	6,20
10,00	4,48	0,0024	6,10
15,00	5,70	0,0027	6,20
20,00	6,93	0,0035	5,70
25,00	8,17	0,0051	5,50
30,00	9,54	0,0067	5,60
40,00	12,29	diffuse	4,70
60,00	15,97	,,	2,50
80,00	25,67	,,	1,00
100,00	34,82	,,	0,30

Evaluation of experimental results

Our earlier statements concerning pure liquids [1] were supported by the experimental data obtained with liquid mixtures.

In benzene, the particles of the organophilic bentonite powder disintegrate, due to fair swelling. In this way, the coarse isodimensional particles convert into a greater number of lamellar units. Since however the polar portions of surfaces (4) are poorly solvated by benzene, relatively great adhesive forces form between these. Thus, the card skeleton structure develops from the lamellae, resulting in a relatively slow sedimentation with a sharp boundary surface.

On the effect of the small amounts of *alcohol* added to benzene, owing to the orientated adsorption of the alcohol molecules, the particles are disintegrated to a gradually increasing extent (*cf.* JORDAN [4]). However, the possibility of adhesive linkages still exists between the polar portions of surface not coated by alcohol molecules. Moreover, the capability of structure formation becomes stronger up to critical point I, due to the increase of the number of particles (first coherent section). Accordingly, the sedimentation rates decrease while, just owing to the increase of the number of particles, sediment volumes increase at the same time.

In the section after critical point I, the linkages between particles decompose, due to the now already complete solvation of the polar portions of surface (incoherent section). Sedimentation takes up a diffuse character, just due to the decomposition of structure, and thus the sedimentation rates increase up to critical point II. From systems sedimentating in this manner, a sediment consisting of swollen particles but of compact nature is deposited.

On further raising the quantities of alcohol added, the polar character of the medium becomes predominant. Consequently, the continuous transition (continuity) between the organophilic bentonite particles of apolar surface and the medium

decreases, and thus the system coagulates (*cf.* the Wo. OSTWALD—BUZÁGH principle of continuity [5]). Accordingly, the particles again form a structure (second coherent section), a quasi thixotropic character evolves, and sedimentation rates decrease. The sediment again takes up a looser aggregational state, while the sediment volumes increase. This becomes gradually more pregnant up to critical point III where sedimentation rates disclose again a minimum, and sediment volumes a maximum value. On further raising the concentration of alcohol, the medium becomes polar to such an extent that the powder is a priori not disintegrated. In this section, when the alcohol concentration is increased, gradually a more coarse coagulation takes place, without any structure formation. The sedimentation rate increases and the sediment volume decreases with the rise of alcohol concentration (coagulation section).

On investigating the role of the *dielectric constant* of the mixtures, the following statements can be made.

As it was mentioned earlier, in the case of all the three alcohols tested, both first critical points appear at the same dielectric constant while the site of critical point III shifts to mixtures of higher dielectric constants when the number of carbon atoms of the alcohol increases. This is interpreted as follows. The sites of critical points I and II are closely correlated with the orientated adsorption of alcohol molecules, and thus with the surface properties of the solvatated substance, being practically independent of the number of carbon atoms of the alcohol present. Namely, from the aspect of the orientated adsorption of alcohols apparently only the relative quantities of polar portions of surface play significant role. The site of critical point III, in turn, is determined by the coagulating effect of alcohol, and thus it depends also on the number of carbon atoms of the alcohol. With the increase of the number of carbon atoms, the continuity between the apolar particle and the medium improves, and thus the coagulation effect becomes weaker [5].

Also the effect of alcohols with various numbers of carbon atom on the quasi thixotropic character can be explained by presuming that, with the increase of the number of carbon atoms, continuity improves and adhesion diminishes. Consequently, in the case of alcohols with higher numbers of carbon atoms a less rigid card skeleton structure evolve. Accordingly, with the increase of the number of carbon atoms, the height of the maximum of sediment volumes decreases.

In *mixtures of benzene and nitrobenzene*, when the content of nitrobenzene is raised, the solvation of particles and the continuity throughout increase because the organophilic bentonite is particularly well solvated by nitrobenzene [1, 4]. Up to a nitrobenzene content of 5%, linkages form between the lamellae, due to the adhesion of non completely solvated sites, and thus a card skeleton structure evolves. Accordingly, in this interval (coherent section) an increase of the number of particles and the formation of a quasi thixotropic character may be expected. At a nitrobenzene content of over 5%, the card skeleton structure already decomposes (*e. g.* beyond critical point I of the curve of alcohol), while the quantity of peptised portion increases, sedimentation becomes to be diffuse, and sediment volume diminishes. At nitrobenzene contents over 30% this solvation attains such an extent that a completely stable organophilic bentonite sol forms. Here the coagulating effect does not appear. Thus, the particular solvation-stabilisation effect of nitrobenzene manifests itself also in this case, and it cannot be explained by the polar

nature of nitrobenzene [4], because in the case of the similarly polar alcohols, coagulation takes place at the same dielectric constant. This also proves the correctness of our earlier presumption concerning specific adsorption [1].

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