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ORIGINAL CONTRIBUTION

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# Colloidal stability of electrostatically stabilized sol particles.

## Part II: The role of hydration and the concentration of potential-determining ions in coagulation and peptization of ferric hydroxide sols

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**Abstract** The colloid stability of ferric hydroxide sol has been investigated at three different HCl concentrations. The total HCl concentration in the sols was A > B > C, the amount of HCl adsorbed was A = B > C. The parameters which characterize the stability (flocculation value, gelation concentration, repeptizability) are related to the amount of adsorbed HCl, because this property governs the hydrophility of the sols. In contrast, the peptizability of powders after drying the sols depends on the total concentration of HCl in the system. The hydrochloric acid impedes the condensation of surface groups to $\rangle$Fe–O–Fe$\langle$ bonds.

From water vapor adsorption and heat of immersion data the hydration potential barrier is constructed which is comparable to the barrier according to the DLVO theory The differences and anomalies in the stability of sols are interpreted as differences in the hydrophility of samples.

**Key words** Electrostatic barrier – hydration barrier – flocculation – gelation – peptization

## Introduction

In the previous paper [1] the properties of powders prepared from ferric hydroxide sol were investigated. The powders were prepared by drying at different relative vapor pressures. Peptizability of the powders dried at high relative vapor pressure was found to be fairly high, presumably because the adsorbed water prevented the formation of close contacts between the sol particles. Thus, two potential barriers may form; one is related to the high adsorption energy of water, the other is due to repulsive electrostatic interaction. The electrostatic barrier regulates the rate of flocculation and the "hydration barrier" (at closer separation) regulates the rate of particles coalescence or sintering.

The aim of our present investigation was to establish the role of concentration of potential determining ions in the coagulation process. Is it sufficient to take into account the two potential barriers for processes (flocculation, gelation, sintering or particle coalescence...) which are commonly refered to as coagulation [1].

From the two consecutive processes, i.e., flocculation and "sintering," the interpretation of the second process is more complicated and also more important in many cases. According to Schukin and Amelina [2], cohesion forces appearing on the contact between particles determine the rheological properties of concentrated dispersions. According to Derjaguin et al. [3, 4], adhesion deforms the particles on the surface and this promotes the sintering. Derjaguin and Churaev [5, 6] discussed the interactions between surfaces and particles on the basis of the disjoining pressure. Among the forces which create the disjoining pressure, we believe that the structural forces caused by adsorbed water molecules are important [7].

## Experimental

### Ferric hydroxide sol

The sol was prepared according to Graham's method [1]. Three samples were prepared from this sol by adding different amounts of HCl (Table 1). The acid content of the medium and sol (titrated with NaOH up to the isoelectric point) differs widely. Thus, the greater part of HCl is bound to the surface of the ferric hydroxide particles by chemisorption.

The sols were dried over concentrated sulfuric acid. The ignition losses at 800 °C were 0.188–0.197 g/g. The composition of dried powder without bound HCl was $FeO(OH) \cdot 0.25\ H_2O$. The specific surface of the powders calculated from water vapor adsorption according to the BET isotherm was $156 \pm 7\ m^2 g^{-1}$. The equivalent hydrodynamic radius of the particles calculated from the sedimentation coefficient (measured by ultracentrifuge) was $3.8 \pm 0.3$ nm.

The age of sols used in the present investigations was 1–2 years while the sol investigated earlier was 22 years old. The other data including the electronmicrographs were reported earlier [1]. Also, the methods (peptization, adsorption, immersion) are described in [1].

The yield value was measured as follows. A copper cylinder (diameter $d = 2$ mm) was immersed into the sol which was then concentrated slowly at room temperature up to gelation. That force, $F$, was measured which was needed to pull out the cylinder from the gel. The yield value is defined as $\tau = F/\pi dl$, where $l$ is the length of cylinder immersed into the gel. The bottom of the gel was on a sieve so that the air could penetrate into the hole left after the cylinder was pulled out.

The electrokinetic potential was measured in dilute suspensions of the powders dried at 120 °C (these powders peptize very slowly), using a Standard Zeta-Meter microelectrophoresis apparatus (Zeta-meter Inc. New York). The dispersion media were acidified by HCl so that the concentration were the same as in the dispersion media of sols A, B and C (Table 1).

**Table 1** Analytical data of the investigated ferric hydroxide sols

| Sample | $HCl\ (mmol\ dm^{-3})$ in sol | in medium | $FeO/OH/0.25\ H_2O$ % w/w |
|---|---|---|---|
| A | 229 | 65.3 | 10.4 |
| B | 175 | 11.9 | 10.3 |
| C | 115 | 1.7 | 10.1 |

## Results

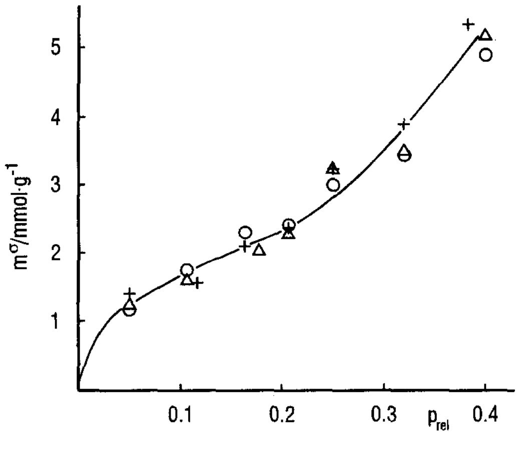
### Water vapor adsorption and peptization of powders prepared from sols

The amount of adsorbed water vapor has been determined by desorption from the air-dried powders obtained from the sols. The amounts adsorbed are the same for all three sols, in spite of different amounts of chemisorbed HCl (Fig. 1). The linearized BET equation gives a straight line for $p_{rel} = p/p_0 = 0.05 - 0.3$; the correlation index is 0.99. The heat of adsorption derived from the BET equation is $6.4\ kJ\ mol^{-1}$ higher than the condensation heat of water (20 °C: $44.2\ kJ\ mol^{-1}$). The heat of adsorption of the polymolecular layers can be calculated using the BET equation modified by Toth [8]. The heat of adsorption for the first and the second layer are both larger than the heat of condensation (9.3 and $1.58\ kJ\ mol^{-1}$). These data show that the affinity of $FeO(OH) \cdot 0.25\ H_2O$ particles to water vapor is very strong.

For the characterization of the bonding strength of water molecules to the oxide, immersion heats $|q_w|$ were measured at different presorbed amounts of water $m^\sigma$ (Fig. 2). The amounts of water needed for one and two absorbed layers are indicated. (The value 7–8 $J\ g^{-1}$ in Fig. 2 indicates the heat of solution of adsorbed HCl).

The derivates of the function $q_w = f(m^\sigma)$, with some approximation, give the differential molar heat of adsorption which is characteristic of the bonding strength. The approximation means that the measured heat effect is not

**Fig. 1** Amount of water, $m^\sigma$, adsorbed on ferric hydroxide sol particles as function of relative vapor pressure ($p_{rel} = p/p_0$) of the drying atmosphere. sol A: △; sol B: +; sol C: □



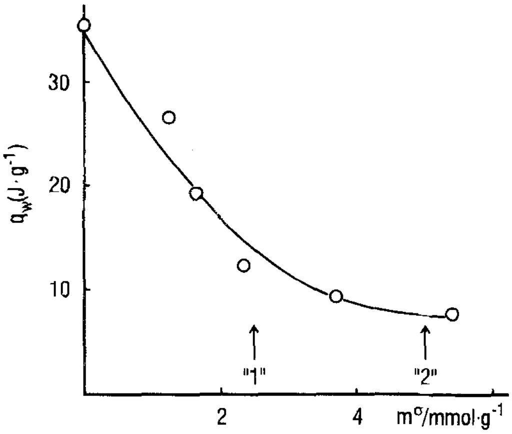


**Fig. 2** Immersion enthalpy, $q_w$, as a function of amount, $m^\sigma$, of water adsorbed, sol B as adsorbed amount

**Table 2** Peptizability of ferric hydroxide in 0.002 M and 0.02 M HCl solution (dried at different relative vapor pressures).

| $p/p_0$ | Peptized amount (% w/w) in 0.002 M | 0.02 M |
|---|---|---|
| | HCl solutions | |
| Sol A | | |
| 0.0 | 90 | 100 |
| 0.3 | 100 | 100 |
| 0.5 | 100 | 100 |
| Sol B | | |
| 0.0 | 0 | 90 |
| 0.3 | 0 | 100 |
| 0.5 | 100 | 100 |
| Sol C | | |
| 0.0 | 0 | 0 |
| 0.3 | 0 | 55 |
| 0.5 | 0 | 75 |

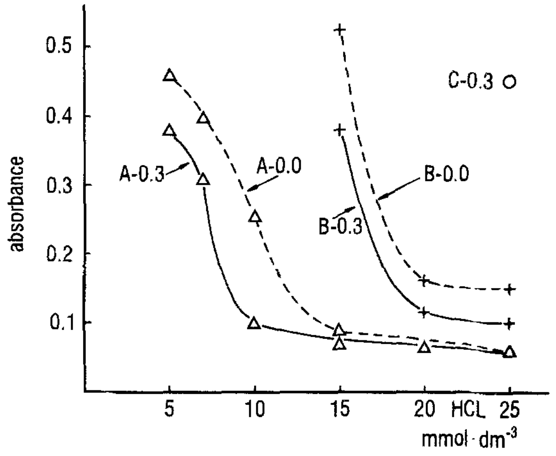


**Fig. 3** Absorbance of the sols, adjusted to mass content of 0.2 w/w% as a function of the concentration of peptizer (HCl). The sols were prepared by peptization of the dried powders from sols A, B and C. Relative water vapor pressure at drying 0.0 and 0.3. (Absorbance = lg($I_0$/I), cell length 1 cm)

only the heat of water molecules attached to the surface, but also contains the heat of solution of HCl. These secondary effects should be the same for the samples presorbed with different amounts of water, because a considerable dilution takes place during immersion. The amount of water is 1000 fold higher than the maximum amount presorbed (5 mmol g$^{-1}$). For this reason the heat of immersion was only measured for sample B.

From $q_w$ (Fig. 2) it follows that the average value of $\Delta q_w/\Delta m^\sigma$ is 8.4 kJ mol$^{-1}$ up to the first water layer, and 2.4 kJ mol$^{-1}$ from the first to second layer. These values are very similar to the heat of adsorption calculated from the absorption isotherm by Toth's equation [8]. The solid/vapor interfacial energy decreases up to the development of the bimolecular adsorption layer (Fig. 2).

Peptizability of powders prepared from A, B and C sols was determined after drying them at three different vapor pressures. Peptizability is measured as percentage (w/w) of particles $< 1$ μm to be dispersed. The peptized amounts were measured at two different concentrations of the peptizing agent HCl. The results are in agreement with our previous paper [1] (Table 2). The peptized amount increases with the vapor pressure at drying and also with the concentration of hydrochloric acid. The HCl content of the original sol plays an important role, too. For example, sol C dried at $p/p_0 = 0.0$ was not, but sol A was fully peptizable in 0.02 mol dm$^{-3}$ HCl.

The peptizability was also characterized by the absorbance of peptized sols. The diameter of sol particles was less than 1 μm. Figure 3. illustrates the absorbance as a function of peptizing agent concentration. Sample C dried at $p/p_0 = 0.3$ can only be poorly repeptized at the highest peptizing agent, whereas the powders of sol A are fully peptizable (absorbance $< 0.1$) when the acid concentration is higher than 20 mmol dm$^{-3}$. The absorbance of the original sols was 0.06. The peptizability of powders is: A > B > C.

## Coagulation of sols at high water content and the peptization of coagulums

The electrochemical data of the sols, calculated from Table 1, are shown in Table 3. The flocculation values were determined by measurement of flocculation rate of the 0.1% sols. The three original sols were diluted with

**Table 3** Electrical double layer data of the ferric hydroxide sols

| Sample | Debye–Huckel parameter $10^{-8}(m^{-1})$ | Surface charge density $(C m^{-2})$ | Surface potential (mV) | Flocculation value, $KNO_3$ $(mmol\ dm^{-3})$ |
|---|---|---|---|---|
| A | 8.41 | 0.91 | 211 | 320 |
| B | 3.59 | 0.91 | 255 | 320 |
| C | 1.36 | 0.65 | 287 | 120 |

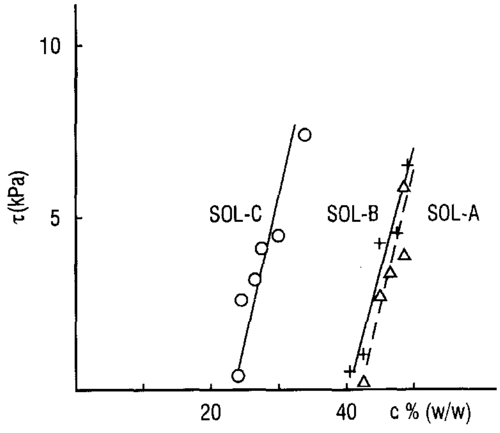


**Fig. 4** Dependence of yield value, τ, on the concentration of ferric hydroxide gels prepared from sols A, B, and C

**Table 4** Absorbance of repeptized ferric hydroxide sols. The sols were coagulated with $MgCl_2$ repeptized after 1 week with HCl solution. A week later the absorbance of the sols (0.2% w/w) was again measured. Aging of the flocs at $MgCl_2$ concentrations as in the table and at a HCl concentration as in the medium of the sols (Table 1). Repeptization at 0.05 mol $dm^{-3}$ $MgCl_2$ and 0.002 mol $dm^{-3}$ HCl

| $MgCl_2$ mol $dm^{-3}$ | Absorbancy A | B | C |
|---|---|---|---|
| 0.2 | 0.37 | 0.30 ± 0.01 | 1.02 ± 0.05 |
| 0.98 | 0.27 | 0.42 | 0.65 |
| 2.45 | 0.30 | 0.44 | 0.42 |
| 4.08 | 0.42 | 0.85 ± 0.05 | 0.36 ± 0.02 |

HCl solution of the same concentration as in the medium (Table 1). Evidently, the sols do not behave as hydrophobic colloids because the flocculation value of sol C is smallest in spite of the largest surface potential and the smallest concentration of HCl. Overbeek [9] wrote about these contradictory facts: "Now, where do structural forces effect this picture essentially? Only in repeptization? Or is their range comparable to the Debye–Hückel length at coagulation, so that they have a direct influence on some of the c.c.c.?"

For gelation of sol C a solid mass content of 25% w/w is needed for sol A and B 40–42% w/w (Fig. 4). The relative gel points of the three sols correspond to the changes of the flocculation values. As the solid content at the gel point and, therefore, the number of contact points is lower for sol C, the attractive force at the contact points must be larger than for sols A and B. "Contact" does not mean a direct solid/solid contact because slight dilution causes rapid and complete peptization.

In further experiments the sols were coagulated with $MgCl_2$. The flocs were aged for 1 week, diluted with HCl solutions, and waiting another week the absorbance was measured (Table 4). Coagulation is not completely reversible because the absorbance remains larger than 0.06. In the case of the lowest $MgCl_2$ concentration the absorbances of sols A and B are very close to each other. The larger absorbance of sol C indicates a stronger attractive force between the particles. The peptizability of sol C increases with increasing $MgCl_2$ concentration. However, the absorbance decreases with increasing $MgCl_2$ concentration, which indicates that within a week of aging the bonding energy between primary particles in the flocculate is smaller. This statement is true only at the same package of flocs. For this reason, the sols were flocculated with 0.2 mol $dm^{-3}$ $MgCl_2$ solution and, after settling, the concentrations were increased, as shown in Table 4.

The effect of increasing concentration of electrolytes on the repulsion forces between mica surfaces [10] and increasing stability of dispersions is known [11, 12]. According to Pashley [13] and Israelachvili [14]: "exponentially repulsive hydration forces between surfaces occur only once a hydrated ionic species in the electrolyte solution binds to the surfaces." This statement was also confirmed by newer results [15].

Furthermore, "there are no hydration forces in acid solution even when the surfaces are fully covered with bound $H_3O^+$ ions." In our investigations, the $MgCl_2$ only increases the hydration of sol C, which has the lowest HCl concentration.

## Discussion

Two fundamental conclusions concern the colloidal stability of sols (Table 5). Data related to flocculation of samples

**Table 5** Summary of principal data

| Points | SOLS A | B | C |
|---|---|---|---|
| 1 Total amount of HCl (mmol $dm^{-3}$) in original sols | 229 | 175 | 115 |
| 2 Amounts of adsorbed HCl (mmol $g^{-1}$) | 1.64 | 1.63 | 1.13 |
| 3 Maximum value of the potential barrier (mJ $m^{-2}$) | 8.0 | 10.5 | 12.6 |
| 4 Flocculation value (mmol $dm^{-3}$, $KNO_3$) | 320 | 320 | 120 |
| 5 Sol concentration (w/w) required to get a yield value of 5 kPa | 48 | 47 | 24.5 |
| 6 Absorbance after flocculation (20 mmol $dm^{-3}$ $MgCl_2$) and repeptization | 0.37 | 0.30 | 1.02 |
| 7 Peptized amounts (percent w/w of sols) peptizer: 2 mmol $dm^{-3}$ HCl | | | |
| 0.0 | 90 | 0 | 0 |
| $p/p_0 = 0.3$ | 100 | 0 | 0 |
| 0.5 | 100 | 100 | 0 |
| 8 The necessary peptizer concentration (HCl in mmol $dm^{-3}$) required to get an adsorbance of 0.4 of the powders dried at $p/p_0 = 0.3$ | 4 | 15 | 25 |

with high water content (points 4–6) change proportionally (directly or inversely) with the amount of HCl adsorbed. Sol C has the smallest stability. For sols A and B the amounts of adsorbed HCl are almost equal and the data of points 4–6 are close to each other. On the other hand, points 4–6 and the values of potential barrier (point 3) are contradictory. According to point 3, the stability of sol C should be largest. The contradiction is not surprising because of the well known fact that the DLVO theory is valid only for hydrophobic sols, while the $FeO(OH) \cdot 0.25\ H_2O$ sols are considered hydrophilic. Hydrophilic properties are proved by the values of the adsorption and immersion enthalpy and a bimolecular water adsorption at $p/p_0 = 0.38$. However, sol C has the lowest hydrophilicity among the three sols. It is assumed that its hydrophilicity increases in concentrated $MgCl_2$ solutions (Table 4).

The other important conclusion is that peptizability of samples with small water contents (points 7–8) increases with the total HCl concentration of the sols (point 1). In this case sols A and B have different peptizabilities. This is related neither to the surface nor electrokinetic potential. The values of the electrokinetic potential are sol A: 31.8 ± 7.7 mV; sol B: 45.2 ± 3.5 mV; sol C; 36.8 ± 2.5 mV.

To evaluate the role of water layers on the particle surface, the total potential energy of interaction $V_T$, and the free energy by water vapor adsorption $\Delta\gamma$, were plotted against the separation (see calculation in [1]). The separation between the particles is an average distance because of the surface roughness. The average distance was assumed to be proportional to the amount of adsorbed water [1]. If the adsorption of water increases from 4 to 5 mmol $g^{-1}$, the differential heat of adsorption is $\approx 1$ kJ $mol^{-1}$ (Fig. 2). Thus the amount of water bound (binding strength $\geq 1$ kJ $mol^{-1}$) is 5 mmol $g^{-1}$ = $32 \cdot 10^{-6}$ mol $m^{-2}$. This value indicates a bimolecular adsorption layer. As one water molecule occupies 0.104 $nm^2$, four water layers are between the particles (calculated from the molar volume of water). The distance between the surfaces is then 1.24 nm.

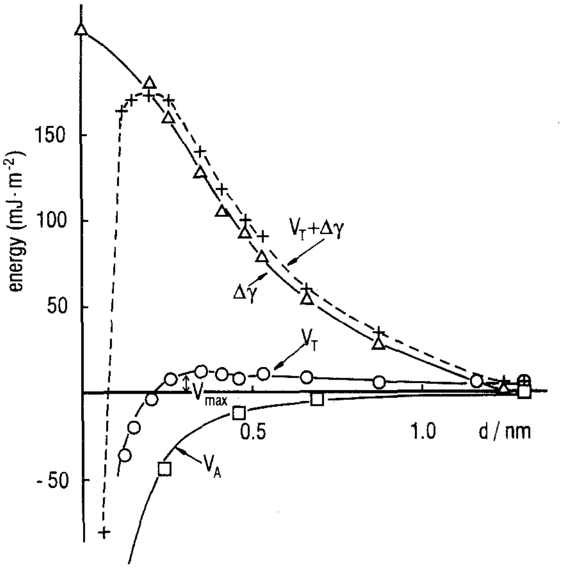


**Fig. 5** Potential curves. $V_T$: total interaction energy calculated by DLVO theory, $V_A$: van der Waals attraction energy; $\Delta\gamma$: free energy of desorption of water

The calculated values of $V_T$ and $\Delta\gamma$ as a function of separation are plotted for sol B (Fig. 5). The increase of the free energy $\Delta\gamma$ required to desorb the water molecules is substantially larger than the potential barrier $V_{max}$ calculated by the DLVO theory. The adsorption layer of the water molecules holds the particles in a larger distance ( = 1.24 nm) than the barrier $V_{max}$( $\approx 0.3$ nm) and this determines the hydrophilic character of the sol.

The difference in hydrophilicity of sols A, B and C cannot be obtained in the described way because the measurements of the heats of immersion and adsorption above $p/p_0 = 0.35$ were disturbed by capillary condensation and are related to different amounts of HCl adsorbed. The different hydrophilicity of the sols may be derived from points 4–6 in Table 5.

The position of the barrier $V_{max}$ is not necessarily inside the adsorbed water layer. Taking into account the possible situations three most important cases are imaginable

**Table 6** Influence of the relative thickness of adsorbed water layers ($d_q$) and the distance of potential barrier from surface ($d_{V\max}$) on the colloid stability. ($V_{\max}$ being the same for all sols)

| | $d_q$ | $d_{V\max}$ | Flocculation value | Sintering of flocs |
|---|---|---|---|---|
| 1 | thin | $d_q < d_{V\max}$ | small | strong |
| 2 | thick | $d_q < d_{V\max}$ | small | weak |
| 3 | thick | $d_q > d_{V\max}$ | large | weak |

(Table 6). If the DLVO potential barrier is eliminated by addition of salts flocculation does not occur in case 3 because of the pronounced structure of the adsorbed water layer. To flocculate the sol, a larger electrolyte concentration is needed to disrupt the water structure. After flocculation, the sintering begins, with highest rate in case 1 because the adsorbed water layer is thin.

Chemical reactions play a role during sintering. When the sols are dried, chemical bonds are formed at contact points. At the i.e.p. (pH = 8–9) the numbers of dissociated positive and negative surface groups are equal ($\rangle \mathrm{Fe}^+$, $\rangle \mathrm{FeO}^-$). Beside these groups, there are undissociated ⟩FeOH groups. At the contact points, oppositely charged groups attract each other and promote development of ⟩Fe–O–Fe⟨ bonds (local sintering). The ⟩Fe–O–Fe⟨ bonds can also be formed by condensation of undissociated ⟩FeOH groups. If HCl is added to the sol, the number of groups $\rangle \mathrm{Fe}^+\mathrm{Cl}^-$ and ⟩FeCl predominates and impedes formation of ⟩Fe–O–Fe⟨ bonds. For this reason, peptizability increases with increasing HCl content. The sintering could be initiated not only during drying of the sol, but also in flocs in spite of high water contents. The size of the prismatic particles is about 2.5 × 25 nm and the particles are randomly oriented with an average distance of 1.24 nm. In spite of the hydration potential barrier, direct contact points may exist where the mentioned chemical reactions could occur. The change of the free energy of the chemical reaction may be higher than the change of the free energy for water desorption. These two energies are counteracting.

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## References

1. Rohrsetzer S, Pászli I, Csempesz F, Bán S (1992) Colloid Polym Sci 270:1243–1251
2. Schukin ED, Amelina EA (1979) Adv Coll Int Sci 11:235–287
3. Derjaguin BV (1934) Koll Z 69:155–164
4. Derjaguin BV, Muller VM, Toporov YUP (1975) J Coll Int Sci 53:314–326
5. Derjaguin BV, Churaev NV (1989) Colloids Surfaces 41:223–237
6. Churaev NV, Derjaguin BV (1985) J Coll Interface Sci 103:542–553
7. Derjaguin BV, Churaev NV (1974) J Coll Interface Sci 49:249–255
8. Tóth J (1966) Acta Chim Hung 48:27–56
9. Overbeek JThG (1982) Adv Coll Interface Sci 16:17–30
10. Pashley RM (1981) J Coll Interface Sci 83:531–546
11. Bobürenko JUJA, Paskova VI (1963) Kolloidnüj Zsurnal 35:655–659
12. Yotsumoto H, Yoon RH (1993) J Coll Interface Sci 157:426–433; 434–441
13. Pashley RM (1982) Adv Coll Interface Sci 16:57–62
14. Israelachvili JN (1982) Adv Coll Interface Sci 16:31–47
15. Skvarla J (1993) J Coll Interface Sci 155:506–508