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ORIGINAL CONTRIBUTION

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Colloid stability of electrostatically stabilized sols

Part III: The role of pH in hydration coagulation and peptization of SiO_2- and Al_2O_3-sols

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Abstract The dependence of the stability of SiO_2 and Al_2O_3 sols on the pH of their medium has been studied. Vapor adsorption isotherms on powders were prepared from acidic and basic sols, the immersion enthalpy (heat) of samples containing preadsorbed water have been determined and, also, the reversibility of the sol$\rightleftharpoons$xerogel transformation, i.e. the peptizability of the powders, has been investigated.

Based on the flocculation values determined with KCl, the sols have been classified into three groups. The stability of highly hydrophilic sols (acidic SiO_2- and Al_2O_3-sols) is ensured by a thick continuous diffuse lyosphere formed around the particles, as the continuity principle by Ostwald–Buzágh suggests. In this case, no electric charge is needed for ensuring stability. These sols are thermodynamically stable (group 1). Sols with medium stability are stabilized by the electrical double layer around the particles and by 1–2 layers of adsorbed water. The flocculation value of these sols is determined by the electrostatic interaction, whereas the peptizability of the flocs is related to formation of water layers. Such sols are the basic SiO_2- and Al_2O_3-sols (group 2). Sols of low stability are of hydrophobic nature. Their flocculation value with 1:1 electrolytes is smaller than $0.1\ \mathrm{mol\,kg^{-1}}$. The transformation process sol ⇒ floccule ⇒ xerogel is mostly irreversible. There are a lot of such sols (group 3). The existence of a hydrosphere is proved by the almost identical value of the hydration energy for both the acidic and the basic SiO_2 sols, in spite of an order of magnitude difference in the flocculation value. The remnants of adsorbed water after drying hinders sintering of the particles and ensures the peptizability of powders.

The highly hydrophilic sols (sequence of hydrophilicity: $SiO_2 > Al_2O_3 > \mathrm{FeO\,OH} \cdot 0.5\,H_2O$) are all oxides which are formed in acidic media.

Key words Colloid stability – sols – hydrogels – xerogels – peptizability

Introduction

In our earlier papers [1, 2] we studied the colloid stability of ferric-hydroxide sols. Colloid stability is the resistance of the system against processes causing the elimination of the colloid state. In our studies, we dealt mainly with the possible transformations from sol to heterogeneous system and the reversibility of these processes. These transformations can take place as a result of adding electrolyte to the sol (flocculation, gel formation) by increasing the concentration of the solid (ultrafiltration, ultracentrifugation, freezing [3]), or by drying the sol (close contact between surfaces). Due to these effects the sol particles come closer to each other. There are several parameters that determine whether physical forces act between the particles, or chemical forces play a role. Depending on the chemical nature of the particle, rearrangement of surface molecules takes place which promotes sintering [4, 5]. A further, important factor is the electrostatic repulsion operating between particles and the repulsive effect of water molecules adsorbed on the particle surfaces. According to Derjaguin and Churaev [6–8], these effects can be quantitatively discussed on the basis of the disjoining pressure. The electrostatic and hydration potential barriers can prevent a direct connection of surfaces. Thus the effects [3] which decrease the stability of sol produce reversible changes.

Considerable results, on how the forces between two macroscopic surfaces depend on the distance of the separation and on some other factors have been obtained [9–14]. However, there are only few results concerning forces acting between colloidal particles. In fact, there are only theoretical considerations on these forces (see references in [1, 2]). According to Derjaguin and Churaev [6]: "The molecular dynamics and Monte Carlo simulation give different structures of water layers close to hydrophilic and hydrophobic surfaces. In the first case, the dipoles of water molecules are oriented predominantly normally to the surface. This causes the appearance of a dipole potential and reduces the tangential mobility of water molecules". In accordance with the above theory, Zerrouk et al. [15] established that the SiO_2 sol is very stable in an acidic medium, due to the structural forces and the entropic repulsion between particles. An extremely high stability can originate also from the hydration energy of an adsorbed cation. Yotsumoto and Yoon [16] showed that due to this phenomenon in NaCl solutions with concentrations higher than 1 $mol\,dm^{-3}$ rutil is very stable. Thus, the generalized DLVO theory is only applicable for very hydrophilic and very hydrophobic sols [17]. Yingnian Xu et al. [18] studied commercial SiO_2 sol and gel by small angle X-ray scattering, NAM Besseling [19] presented a statistical thermodynamic theory for the surface forces arising from the interference of hydration layers at planar surfaces.

The aim of these investigations is twofold. On the one hand, we wanted to establish the hydration and stability properties of SiO_2 and Al_2O_3 sols at various pH values and to compare these sols with the $FeO\,OH \cdot 0.5H_2O$ sol [1, 2] in order to find common properties. On the other hand, we intended to establish a correlation between hydration and stability, to approach the hydration theory of sol stability.

Experimental

SiO_2 sol

6.00 g of SiO_2 powder (fumed silica, particle size: 7 nm, Aldrich), was added to 106 cm^3 water to disintegrate possible aggregates, 14 cm^3 NaOH solution of 2 M was added. After allowing the mixture to stand for 2 h with occasional stirring, 11 cm^3 of 2 M HCl was added and the dispersion was dialyzed against an 0.01 M NaOH solution. By lifting out the dialysis tube gradually from the solution, the sol was simultaneously concentrated. At the end of dialysis, the volume of the sol was 50–60 cm^3, the total concentration of SiO_2 was 75–85 $g\,dm^{-3}$. The total concentration of NaCl and Na_2CO_3 was 0.2–0.3 $g\,dm^{-3}$, whereas the pH of the sol was 9.3–9.7. This basic "stock sol" was made slightly acidic with HCl, and then dialyzed against 0.01 M HCl for 1 week. The pH was then 3.0–3.5. The electron micrograph of sol particles is seen in Fig. 1. The specific surface area (a_s) of particles dried at room temperature was 170–180 $m^2\,g^{-1}$. a_s was calculated from the vapor adsorption.

Al_2O_3 sol

30 g Al_2O_3 powder was suspended in 254 cm^3 distilled water. The pH of the suspension was 5.4. 6 cm^3 of 0.02 M HCl was added, and after letting it stand overnight, the particles were disaggregated by an Ultra-Turrax apparatus (Janke-Kunkel KG) for 4 min with a revolution of 3500 rpm. No dialysis was needed in this case. The pH of the sol was 4.5, the electron micrograph of this sol is shown in Fig. 2. The sol was used as an acidic "stock sol". The specific surface area determined in the same way as described above was 53–54 $m^2\,g^{-1}$.

Powders made of sols

For adsorption, immersion and peptization studies, the "stock sols" were dried at 22–24 °C, at a relative water vapour pressure (pr) of 0.5–0.6. At the beginning of drying, 1.0 cm^3 of 2 M HCl or NaOH solution was added to 180 cm^3 portions of the acidic and basic stock sol, respectively. pr values indicate that the sol was dried over a H_2O–H_2SO_4 mixture of known water tension.

The experimental methods are described in detail in our earlier publications [1, 2]. They are only outlined in this paper. In the water-vapor adsorption experiments, the required vapor pressures at $25 \pm 0.5\,°C$ were adjusted by using sulfuric acid–water mixtures. Adsorbed amounts were determined by weighing. For measuring the

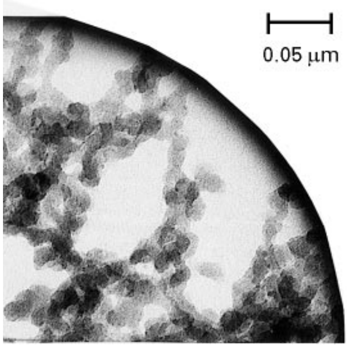

Fig. 1 Electron micrograph of SiO_2 particles of acidic stock sol

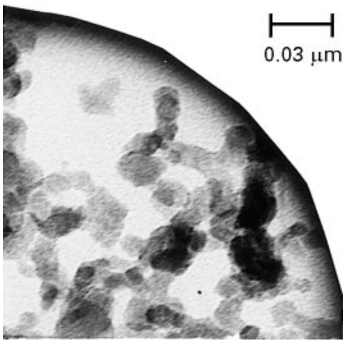

Fig. 2 Electron micrograph of Al_2O_3 particles of acidic stock sol

immersion heat (enthalpy), the samples containing preadsorbed water were prepared in the same way as described above. To measure the peptizability of these samples about 0.05 g of the powders were dispersed in a 500-times volume of diluted acid or base solution. The suspension was stirred 3 times a day for one week. After peptization, the suspension was let to sediment for a time in which the particles greater than 1 μm completely settled down. Knowing the mass of the dried sediment, the amount peptized (particles < 1 μm) could be calculated. The yield value of hydrogels formed from concentrated sols was measured by determining the force needed for drawing out a standard cylinder immersed into the sol.

Table 1a Properties of SiO_2 sols

pH	Adsorption of		Surface charge density (μC m^{-2})	Flocculation value of KCl (mol kg^{-1})
	HCl (μmol m^{-2})	NaOH		
3.0	<0.10	—	$<+0.01$	>3.1
3.5	<0.10	—	$<+0.01$	>3.1
5.4	—	0.49	-0.05	~3.1
6.5	—	1.10	-0.11	~0.54
7.2	—	—	—	0.10
7.8	—	1.33	-0.13	0.34
9.6	—	1.81	-0.18	0.34

Concentration of SiO_2: 20.7 g dm^{-3}.

Table 1b Gelation time of SiO_2 sols

pH	Electrokinetic potenial (mV)	Gelation time in 0.22 M KCl (min)
3.0	-1.7 ± 0.73	>1200
3.5	-2.0 ± 0.76	>1200
5.4	-26.4 ± 0.75	100
6.5	—	15
7.2	—	5
7.8	-35.1 ± 2.1	10
9.6	-35.7 ± 1.9	15

Concentration of SiO_2: 45 g dm^{-3}.

Table 2 Properties of Al_2O_3 sols

pH	Adsorption of		Surface charge density (μC m^{-2})	Flocculation value of KCl (mol kg^{-1})
	HCl (μmol m^{-2})	NaOH		
3.0	2.6	—	0.25	2.2
4.0	1.6	—	0.15	2.2
4.5	1.1	—	0.10	1.2
4.9	0.96	—	0.092	0.13
5.5	0.16	—	0.015	0.06
7.5	—	0.20	—	0.00
8.1	—	0.72	-0.069	0.00
9.9	—	1.6	-0.15	0.07
11.0	—	2.2	-0.21	0.10

Concentration of Al_2O_3: 100 g dm^{-3}.

Results

The stability of SiO_2 and Al_2O_3 sols was studied at several pH values. The flocculation value and the gelling time for the SiO_2 sol change in the same way (Tables 1 and 2). Both values are closely related to stability. At pH values smaller than 5.4, the sol cannot be flocculated even by very concentrated KCl and does not form a gel even in a whole day. However, it can also be established from the data (in Tables 1 and 2) that there is no correlation between the electrical properties and the stability of the sol. The surface charge density of sols with high flocculation value is nearly zero, and their electrokinetic potential is also very low. On the contrary, the basic sols have a high surface charge density and low flocculation value. In more concentrated SiO_2 sols, in addition to the pH, the electric charge of the particles has also an influence on stability. Formation of a gel requires the smallest concentration of SiO_2 at medium pH values (Fig. 3), where both the H^+ concentration

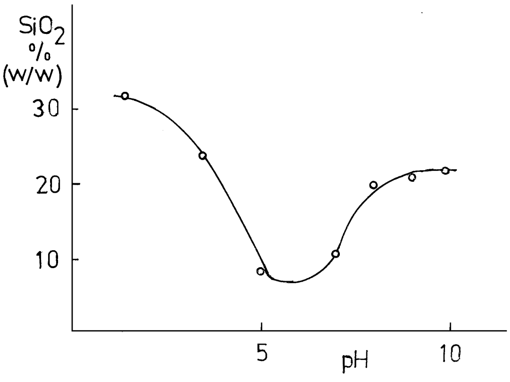

Fig. 3 Dependence of the gel formation concentration of SiO_2 on the pH, at yield values of 5–15 kPa

and the surface charge density of the negative ions at the surface are small, i.e. strong adhesion forces act between the particles.

Similar results were obtained for the Al_2O_3 sol (Table 2). At low pH values both the surface charge density of particles and the flocculation value are high. In the basic region, the flocculation value is one order of magnitude smaller in spite of the high surface charge density.

Thus the question which surface property correlates with the gelling time and the flocculation value arises. Is the hydration energy the relevant parameter, or the thickness of the hydrospheres? Surface properties were studied on powders prepared from the sols. According to preliminary investigations, a significant decrease in the specific surface area on drying occurs only in the case of SiO_2 sols. Therefore, the sols were dried at various relative water vapor pressures in order to control the effect of adsorbed water. Adsorption isotherms were determined on grinded and sieved ($d < 50\ \mu$m) powders. Because of the similar character of these isotherms, only those obtained for powders dried at $p/p_0 = 0.6$ are shown (Figs. 4 and 5). The specific surface area, and the adsorption heat for the first and second adsorption layers were calculated from the isotherms by using the BET equation modified by Tóth [20] (Table 3). The specific surface area of the basic SiO_2 significantly decreased by drying. This decrease may result from the chemical reaction induced by CO_2:

$$\equiv\text{SiO–Na} + CO_2 + \equiv\text{SiO–Na} \rightarrow \equiv\text{Si–O–Si}\equiv + Na_2CO_3\ . \quad (1)$$

Sintering decreases with the increase of vapor tension as more water remains adsorbed on the particles. The chemical reaction of the $\equiv$SiO–Na surface groups with the adsorbed water and with CO_2 may be the cause of the high adsorption heat measured on the basic SiO_2 powders, as well (Table 3). The adsorption heat of the second water layer lies in the range 2–7 mJ m^{-2}.

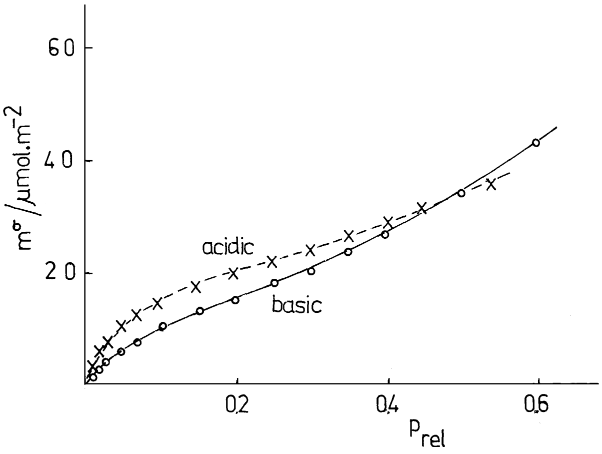

Fig. 4 Water-vapor adsorption isotherms on powders prepared from acidic and basic SiO_2 sols

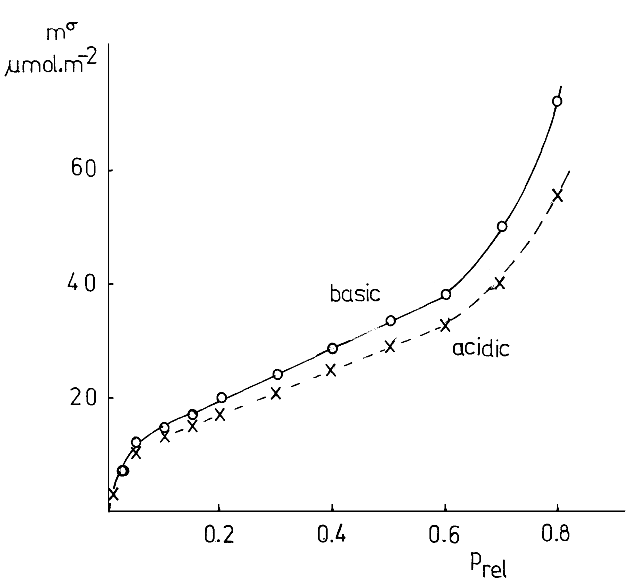

Fig. 5 Water-vapor adsorption isotherms on powders prepared from acidic and basic Al_2O_3 sols

In order to study the correlation between sol stability and the adsorption energy of water molecules, we measured the heat of immersion of powders with preadsorbed water (Figs. 6 and 7). The horizontal section of the curves is proportional to the dissolution heat of the salts present in the powders (q_s^x). The amount of water is considered as adsorbed water, when the heat of immersion is at least by $1/2kT$ larger than q_s^x. If the immersional heat of a dry powder is q_s^0, and that of a sample containing **n** preadsorbed water layers is q_s^n, then for second molecular layer (q_s^{II})

Table 3 Specific surface area, a_s, of powders prepared from SiO_2 and Al_2O_3 sols and adsorption heat of the first adsorbed water layer, λ_1^a, the water vapor pressure, pr, during drying

pr	a_s ($m^2 g^{-1}$)	λ_1^a	
		($J mol^{-1}$)	($mJ m^{-2}$)
Acidic SiO_2			
0.0	161	5450	88.9
0.6	177	5490	88.0
0.9	179	5400	87.1
Basic SiO_2			
0.0	75.2	8880	145
0.6	98.1	7690	125
0.9	115	6940	113
Acidic Al_2O_3			
0.6	54.0	8000	130
Basic Al_2O_3			
0.6	53.5	7500	122

Values calculated from the data in Figs. 4 and 5.

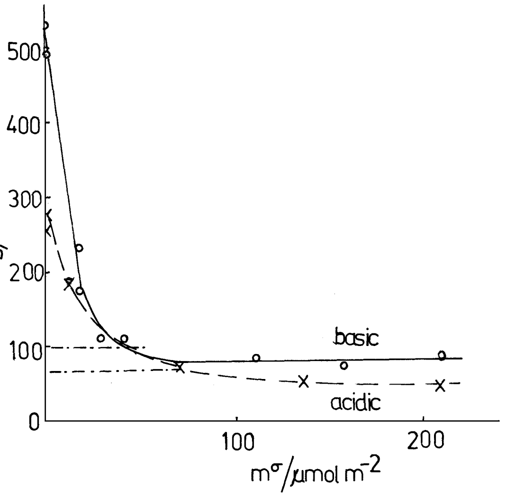

Fig. 6 Immersion enthalpies, q_s, of SiO_2 as a function of the amount of preadsorbed water, m^σ

and for all layers (q_s^T):

$$q_s^{II} = q_s^1 - q_s^2 , \quad (2)$$

$$q_s^T = q_s^0 - (q_s^x + 1/2\,kT) . \quad (3)$$

The total number of adsorbed layers is determined from m^σ at $q_s = q_s^* + 1/2\,kT$ (Fig. 6). The immersion heats are calculated by Eqs. (2) and (3) (Table 4). Again the high stability of acidic sols against electrolytes is not accompanied by high immersion heats. On the other hand the immersion heat of the basic SiO_2 powders is very high.

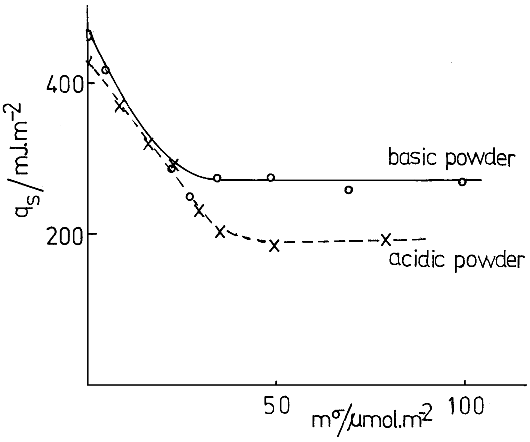

Fig. 7 Immersion enthalpies, q_s, of Al_2O_3 as a function of the amount of preadsorbed water, m^σ

Table 4 Differences in immersion enthalpy of SiO_2 and Al_2O_3 leaded with different numbers of water layers

Layer thickness (nm)	Immersion enthalpy ($mJ m^{-2}$)			
	Al_2O_3		SiO_2	
	Acidic	Basic	Acidic	Basic
0.00–0.16	55	75	48	130
0.16–0.32	45	55	46	130
0.32–0.48	45	45	36	115
0.48–0.64	45	0	22	35
0.64–0.96	0	0	20	0
0.96–1.28	0	0	10	0
0.00–1.28	190	175	174	410

Calcuated from the date in Figs. 6 and 7. The thickness of a monomolecular water layer is taken as 0.32 nm.

Table 5 Peptizability (in mass%) of powders prepared from acidic and basic stock sols in relation to the water vapor pressure, pr, during drying

p_r	Concentration of peptizing agent						
	NaOH ($mol dm^{-3}$)				HCl ($mol dm^{-3}$)		
	0.05	0.02	0.01	0.005	0.005	0.02	0.03
Acidic SiO_2							
0.0	34	22	11	6.5	1.5	5.5	4.0
0.6	43	34	21	18	11	14	13
0.9	64	63	38	33	27	30	29
Basic SiO_2							
0.0	34	—	13	7	1.5	—	0.5
0.6	43	—	21	15	8.0	—	9.0
0.9	56	—	32	27	18	—	12

The amounts of peptized SiO_2 powder are shown in Table 5. With decreasing vapor tension (p_r) used during drying, the peptizability of powders decreases, since the amount of water remaining adsorbed and which hinders sintering decreases. The effect of the nature of peptizing agent is surprising: the peptization of powders is in acidic

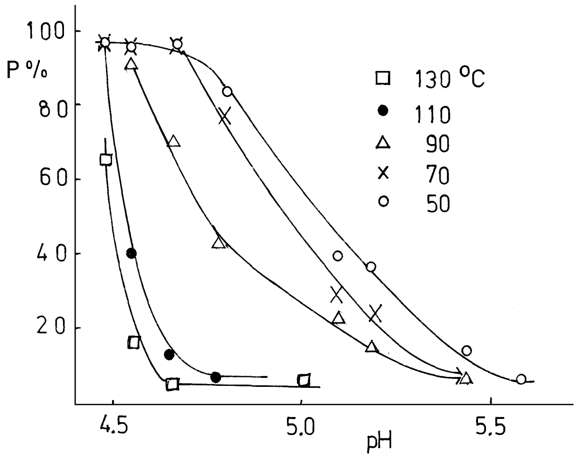

Fig. 8 Dependence of the peptizability of powders prepared from basic Al_2O_3 sols on the pH after a heat treatment for 1.5 h. P%, peptized amount expressed in mass%

medium smaller than in a basic medium. The sequence is opposite to sol stability.

Before peptization of Al_2O_3 powders, the amount of water adsorbed on the sample at pr = 0.6 was decreased by raising the temperature (Fig. 8). Peptization of Al_2O_3 powders – in accordance with the stability of the sol – is higher in the acidic region, probably because the sol particles in acidic medium acquire electric charges, as in the basic region. The SiO_2 powder is less peptizable in acidic medium since the particles only have considerable electrical charges in basic medium.

Discussion

Sols can be transformed into heterogeneous system through different states (Fig. 9). During the transformation the water content is reduced. The occurrence of the individual processes of coagulation and the rate of transformation depend on the surface properties of the particles. For a sol with suitable surface properties, a thick diffuse hydrosphere can be formed around the particles when the water content is sufficiently high and formation of the hydrate layer is not hindered by sterical reasons. These sols are called hydrophilic sols, as the electric charge of the surface is not a precondition of their stability. Such a system is the SiO_2 sol in acidic medium (Table 1). For maintaining stability, it is probably necessary that 1–2 layers of water molecules are strongly bound to the surface. This is not enough, however, for extremely high stability, since this condition is also ensured in basic sols (Tables 3 and 4), the flocculation value of which is small. The flocculation value for acidic sols of highly hydrophilic nature with 1:1 electrolytes is higher than 1 mol kg^{-1}, and this value is of the same order of magnitude as the electrolyte concentration necessary to precipitate neutral hydrophilic polymers. Thus, in order to flocculate acidic sols of highly hydrophilic character, the water structure must be destroyed by a high salt concentration.

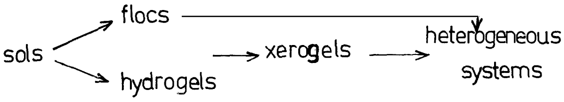

Fig. 9 Transformation of sols into heterogeneous systems

There is no significant difference in the heats of hydration (adsorption and immersion heats) between the acidic and the basic SiO_2 and Al_2O_3 sols, thus the extremely high stability of the acidic sols should be attributed to the entropy barrier. According to the continuity principle by Ostwald and Buzágh [21], such sols are thermodynamically stable, as a continuous adsorption layer between the particles and the medium can be formed, resulting in zero interfacial tension.

If there is no entropy barrier between the sol particles, stability is ensured by the electrical double layer. If the particle surface is less hydrophilic, i.e. the flocculation value of the sol with a 1:1 electrolyte is smaller than 0.1 mol kg^{-1}, the flocculation is quickly followed by an irreversible sintering of the surfaces. In this state, the flocks cannot be peptized, and the original particle size cannot be restored. A great number of such sols is known (AgI, As_2S_3, metal sols).

For sols of medium stability, 1–2 layers of adsorbed water belong to the electrical double layer formed around the particles. The flocculation value of these sols is in the order of magnitude of 0.1 mol kg^{-1}. Stability against flocculation is ensured by the electrical double layer, whereas sintering is prevented by the adsorbed water molecules. Such sols are the basic SiO_2 and Al_2O_3 sols (Tables 1 and 2), and the acidic $FeOOH \cdot 0.5\ H_2O$ sol (Tables 3 and 4 in [2]). The flocs of these sols can be very easily peptized even after a longer aging time. Their peptizability is preserved in the powder, except for the case, when the adsorbed water is removed by drying (Table 2 in [1]).

For formation of sols with extremely high stability, the development of an adsorption layer with continuous diffuse structure is necessary. This idea is supported by the data shown in Table 5 and Fig. 8. The SiO_2 sol is extremely stable in acidic medium, but the powder prepared from this sol can be hardly peptized in acidic medium. In our opinion, this is the reason why strong hydration is not a satisfactory condition for the separation of sintered edges and vertices. On contrary, the charge density of the Al_2O_3 even in acid medium is high and the peptizability is even better in acidic, than in basic medium (Fig. 8). The chemical nature of particles plays also an important role in coagulation processes and in their reversibility. Differences in the chemical properties are the biggest obstacle to elaborate a stability theory of general validity.

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