BEHAVIOUR OF HYDROPHILIC COMPONENTS IN PAPERMAKING SUSPENSIONS

PART I. INTERACTIONS AMONG HYDRATED PARTICLES - THEORY OF STRUCTURAL CHANGES IN HYDRATED LAYERS

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Principal description of behaviour of hydrated hydrophilic systems according to the SCHL theory (Structual Change in Hydration Layers) is presented.

Introduction

Main object of our interest:

Colloidal systems, fine and coarse fibre dispersion systems of pulp and other components in diluted and concentrated state are the main object in pulp and paper industry especially in papermaking. All of them are hydrophilic aqueous systems, i.e. hydrophilic hydrated systems.

The existing concepts of describing the interactions of particles in the dispersion system are based on mutual action of forces of electrostatic and van der Waals types or several other forces, e.g. polymer forces due to activity of adsorbed polymers. Other forces might be evoked

in the dispersion system due to the action of external fields like electric fields, magnetic fields, due to the gravity and hydrodynamic forces[1-2], etc. The theory which is well known under the name DLVO[3-4] was originally used for describing the behaviour of hydrophobic colloidal systems. That means, the behaviour of dispersion systems without the influence of the dispersing medium, its molecules, on character and order of interactions. Practical experience and experimental observations have proved the DLVO theory to be unsatisfactory for explanation of the behaviour of hydrophilic hydrated systems especially in concetrated state.

Systems with immobilized water:

Hydrophilic (in general lyophilic) systems are characterized by their hydration (solvation) layers on phase interface known in literature under various names, such as immobilized water[7-10], vicinality water[5-6], gel water, non-solute water[11-12], etc. Logically we have to deal with this phenomenon to explain the behaviour of hydrophilic systems in water, especially in concentrated state, i.e. under condition (small distances) in which layers of immobilized water penetrate into one to another. For this reason a hypothesis has been developed concerning the structure of hydration layers and their changes in interactions of hydrated surfaces.

Principles of the SCHL theory[13-15]

Orientations of water molecules on phase interface:
The principle of the theory of structual changes in hydration layers (SCHL) in the interactions of hydrated surfaces is based on the typical dipole character of water molecules and on their two extreme possible orientations in hydration layers (see Fig. 1):
- orientation of H-atoms in water molecules in the direction towards the phase interface
- orientation of the O-atoms in water molecules in the direction towards the phase interface.

These two different basic orientations of water molecules are caused by typical "amphoteric" nature of water molecules depending on available hydrogen bonds. The water molecule can be linked with other molecules, groups, etc., on the phase boundary with such a kind of hydrogen bond in which, according to their character, it may play the role of either the donor or the acceptor of the proton.
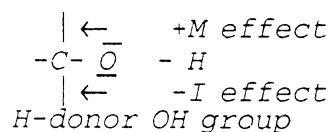
The intermolecular force field, produced by the hydrogen bonds formed will then spread by means of other water molecules throughout the hydration shell under the influence of this orientation of water molecules, becoming more and more diffused until it reaches the zero value in bulk of water.
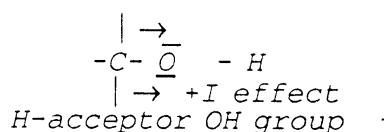
Dividing of H-bond groups:

According to this theory, the groups forming hydrogen bonds with water can be divided into three kinds of groups:

- H-donor (H-D) groups and molecules such as primary alcoholic groups, secondary amino groups in aliphatic compounds, partly also primary amino groups, NH_3 etc.,

- H-accepting (H-acceptor) groups such as hemiacetal oxygen in saccharides, carbonyl groups, tertiary amino groups, etc. (A-H groups),

- Amphoteric groups and molecules such as water, secondary alcoholic groups in polysaccharides (e.g. cellulosic materials), partly also primary amino groups, etc.

Amphoteric groups are able to perform both functions. The behaviour of these amphoteric groups will depend considerably on the structure and composition of molecules or macromolecules in which they are present. For instance the character of these groups will be changed by action of the surrounding groups having inductive or mesomeric effect. For example, surrounding groups having - I effect will intensify the H-donor nature of oxygen in these groups.

$$
\begin{array}{l}
\quad\ \mid \leftarrow \quad\ +M\ effect \\
-C-\ \underline{O} \quad -\ H \\
\quad\ \mid \leftarrow \quad\ -I\ effect \\
H\text{-}donor\ OH\ group
\end{array}
$$

The mesomeric effect has an opposite influence. The +I effect of surrounding groups will strengthen the H- acceptor nature of hydroxyl groups.

$$
\begin{array}{l}
\quad\ \mid \rightarrow \\
-C-\ \underline{O} \quad -\ H \\
\quad\ \mid \rightarrow\ +I\ effect \\
H\text{-}acceptor\ OH\ group
\end{array}
$$

Idea and definition of hydration forces:

What happens if these two hydrated surfaces interact?

In the case of interaction of two surfaces in the form of flat formations (see Fig. 4), if the orientation of water molecules is the same to each of the surfaces, both surfaces will affect each other by so called repulsive hydration forces. In the opposite case, i.e. with a different

orientation of water molecules to each of the surfaces, both surfaces will influence each other by attractive hydration forces. Although the processes mentioned above seem relatively simple at first sight, a closer look changes the matter.

Classification of main factors influencing of hydration forces:

The extent to which hydration forces are affected depends upon:

1. The heterogeneity of interacting surfaces, caused by the fact that qualitatively different types of groups are present in each surface unit, accepting water molecules of different orientations by means of H-bonds.

2. The quality or size and type of H-bonds between the individual groups and water molecules at the phase interface.

3. The quantity of qualitatively equal groups in a unit of interacting surfaces which accept water molecules by means of H-bonds.

Also, to originate hydration forces, it is necessary for water molecules to reach a suitable orientation in the hydration shells. This orientation is determined by H-donor and H-acceptor groups, by their amount and by the strength of the hydrogen bond formed with water, or in other words by the value of interface tension $\gamma_{l,s}$. All hydrated systems with high specific surface behave in this manner. These include various porous systems filled with water and aquenous solutions, gels, quasi-gelous systems, etc.

Principles of mathematic description[14]

Mathematic description of the idea of controlled orientation of water molecules around a hydrophilic phase interface (see Fig. 1) and their distribution into the bulk of water (see Fig. 2) is very complicated. A simplified description is based upon known equations fenomenologically describing the spreading of force field around the homogeneous force source. Owing to these simplifications the description is well illustrative but sometimes controversial with rigorous theoretical chemical physics.

Suppositions:

1. Homogeneous hydrophilic surfaces with regularly alternating equal sites.

2. Water molecules at the first adjacent layer are bound to the hydrophilic sites-groups by hydrogen bonds.

3. Owing to the controlled orientation of water molecules due to H-bonds in the first

adjancent layer other water molecules are oriented towards the bulk of water (see Fig. 1).

4. However, the trajectories of these orientations are not straight lines but, due to kinetic energy of water molecules (given by temperature), are with increasing distance from phase interface, more and more dispersed and this character fully disappear in the bulk of water (see Fig. 2) - outside of the hydration shell.

5. The force effect evoked by the first layer of water molecules then entails the reorganization of water molecules in other layers and transfers this force effect in the direction of potential gradient (perpendicular to the line or surface unit of phase interface) into bulk of water.

6. However, owing to more and more dispersed trajectories of water molecules orientations, this force effect towards the bulk of water is weaker and also more and more dispersed.

7. As the evoked force gradient is perpendicular to the line or a surface unit of the phase interface, any water movements around this surface are possible (e.g. see the behaviour of small iron splinters around the magnetic pole).In accordance with the above mentioned principles we can also mathematically write:

$$div\ f\ \neq\ 0 \qquad\qquad (1)$$

$$rot\ f\ =\ 0 \qquad\qquad (2)$$

f is the force influencing the water molecules perpendicular to a unit line (twodimensional space - see Fig. 3) or surface (threedimensional space) parallel to the phase interface because

$$f\ =\ -\ grad\ \varphi \qquad\qquad (3)$$

and φ is the potential of a water molecule, $\varphi = \varphi_i - \varphi_f$ where φ_i is potential energy of water molecule in bulk of water and φ_f is potential energy of water molecule in the hydration layer at a distance d from the phase interface.

If the force field is homogeneous the following equation is valid in accordance with Gauss's laws:

1. For threedimensional space
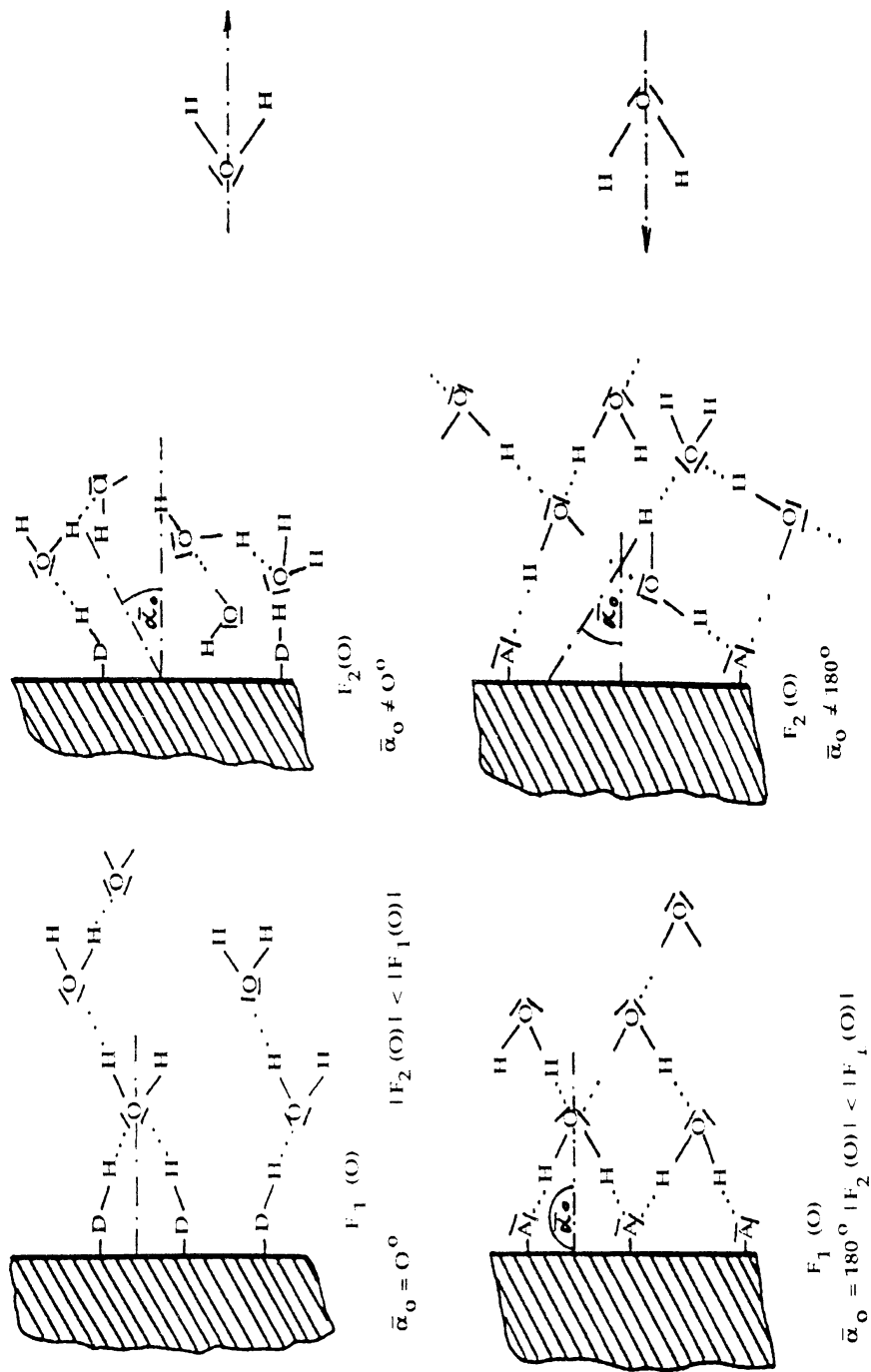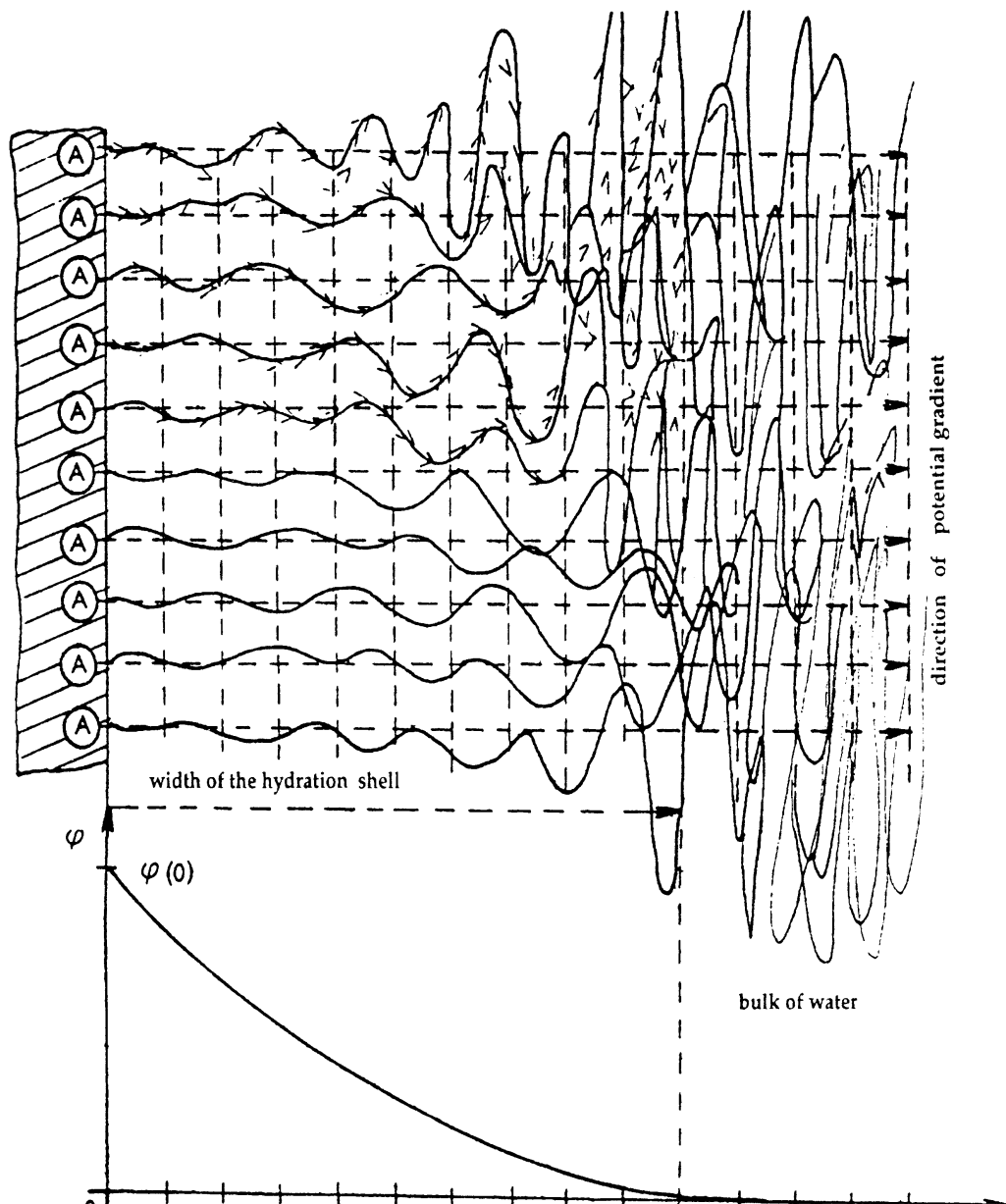
Fig. 1 Conception of the orientation of water molecules on various types of phase interfaces.

$\bar{\alpha}_o$ - averge axis angle of water molecules related to the phase interface normal at its close vicinity; F(0) - potential energy of water

molecule in d(distance) = 0

$F_2(O)$

$\bar{\alpha}_o \neq O^o$

$F_2(O)$

$\bar{\alpha}_o \neq 180^o$

$F_1(O)$

$\bar{\alpha}_o = O^o$

$|F_2(O)| < |F_1(O)|$

$F_1(O)$

$\bar{\alpha}_o = 180^o$ $|F_2(O)| < |F_1(O)|$

> - orientation of water molecules;

A - proton-acceptor group; homogeneous hydrophilic surface

Fig. 2 Schematic representation of the orientation of water molecules around hydrophilic surface and distribution of this orientation into the bulk of water. Owing to this distribution the rel. potential energy of water molecules, φ, decreases with increasing distance from phase interface.

$$\iiint div \; f \; . \; dV \;\; = \;\; \oint\oint f \; . \; n_o . \; \cos \alpha \; . \; dA \;\; = F(A) \qquad (4)$$

2. For twodimensional space (see Fig. 3)

$$\iint div \; f \; . \; dA \;\; = \;\; \oint f.n_o \; . \; \cos \alpha.dl \;\; = \;\; F(L) \qquad (5)$$

From these equations (4) and (5) it follows that div f = dF(A)/dV or analogously for twodimensional space (Fig. 3) div f = dF(L)/dA (6) The combination of Eq. (6) and Eq. (3) gives Eq. (7)

$$-\nabla.\nabla \; \varphi \;\; = \;\; -\Delta \; \varphi \;\; = \;\; \frac{dF(A)}{dV} \; or \; \frac{dF(L)}{dA} \qquad (7)$$

where are ∇ or Δ Hamilton's or Laplace's operator, respectively.

Example:

If div f = 0 then the force field is the same in every distance from the phase interface, of coarse in direction perpendicular to this phase interface. It means that all water molecules are connected with one other by the same force in the direction of potential gradient. In case of straight phase homogeneous interface (see Fig. 2) where
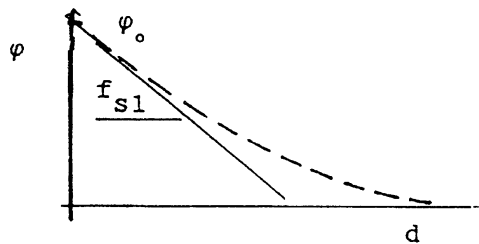
$$\frac{-d \; \varphi}{dd} \;\; = \;\; const. \;\; = \;\; f_{s1} \qquad (8)$$

we can, after integration

$$\int_{\varphi_0}^{\varphi} d\varphi = -\int_0^d f_{S1} dd \qquad , write$$

$\varphi = \varphi_0 - f_{S1} \cdot d$ or graphically draw the dependence as follows:

Note 1:

Dashed line in this Fig. represents the real case according to Eq. (1).

Composition of differential equation

However, in our real situation we must, in accordance with Figs 2,3, bear in mind a harmful effect of the temperature on this initial force f_{S1} and, due to this effect, a slower decrease of rel. potential with the distance.

In view of Eq. (6) it is logical that the change of force field with distance have to be proportional to the amount of water molecules (per volume unit at isopotential - φ) which participate in this change ($N_0 - N_\varphi$). As the force field spreads into space of the bulk of water, which is only due to the water molecule, the difference ($N_0 - N_\varphi$) characterizes how high this change will be within the space (with infinitesimal width) of the isopotential φ. If the amount of water molecules influenced by rel. potential - $\varphi(N_\varphi)$ is the same as in the bulk of water (N_0) then the force field change is zero and the potential φ linearly decreases with distance as is described above or it is zero (no change was evoked on phase interface). If N_φ = constant, the arrangement N_φ of water molecules in every isopotential φ is the same but they are connected to one another by means of different linearly decreased forces (in the direction of the potential gradient). However, the resulting φ - d dependence has a nonlinearly decreasing character. In view of this fact, from equation (7) then follows:

$$-\nabla.\nabla \varphi = -\Delta\varphi = f_{s_1} \cdot (N_o - N_\varphi) / (N_o \cdot \Delta x) , \qquad (9)$$

where f_{s_1} is the force effect on one water molecule in the phase interface in the direction of potential gradient, φ is the rel. potential of one water molecule, Δx is the length of the space perpendicular to phase interface where two water molecules interact.

Determination of N_φ:

If a nonoriented force field influencing the dipolar (or exactly quadrupolar) water molecules (their orientation) in the space is randomly distributed, than Eq. 10 must be valid:

$$N_o = \frac{1}{2} \int_{-1}^{1} N_o \cdot d\cos \alpha \qquad (10)$$

The amount of water molecules having the energy $\delta\varphi$ or greater in nonoriented force field is then given according to the Maxwell-Boltzman law by:

$$N_{\delta\varphi} = \frac{1}{2} N_o \cdot \int_{-1}^{1} e^{\frac{-\delta\varphi}{\cdots}} \cdot d\cos \alpha = N_o \cdot e^{\frac{-\delta\varphi}{\cdots}} \qquad (11)$$

It means that the orientation of water molecules is randomly distributed in all directions in the same manner. However, a different situation is encountered in the case of the action of a space oriented force field like the field evoked by hydrophilic surfaces.

Note 2:

It is possible to receive eq. (10) according to the following consideration too. Let consider φ_s to be as the lowest possible potential energy of water molecules in the bulk of water at the temperature T. Then the infinitesimal volume fraction with these water molecules has a corresponding concentration of N_s water molecules per a volume unit. However, owing to fluctuations the mean potential energy of water molecules is φ_i, and the corresponding concentration N_o, in accordance with the Maxwell-Boltzman law, is then given by equation.

$$N_o = N_s \cdot e^{\frac{-(\varphi_i - \varphi_s)}{kT}} \qquad (12)$$

(All these equations are valid for twodimensional space).

The concentration of water molecules in the individual layers of hydration shell of energy φ_t is then given analogously by equation.

$$N_\varphi = N_s \cdot e^{\frac{-(\varphi_t - \varphi_s)}{kT}} \qquad (13)$$

The combination of Eq. (12) and Eq. (13) results in Eq. (14)

$$\frac{N_\varphi}{N_o} = e^{\frac{(\varphi_i - \varphi_t)}{kT}} = e^{\varphi/kT}; \quad \varphi = \varphi_i - \varphi_t \qquad (14)$$

However, in view of the space orientation of the effective potential φ we have to take this reality into account, and eq. (11) will not be so simple. Upon full spreading of potential φ in the direction perpendicular to the phase interface, only the water molecules oriented in the direction of potential gradient take part, i.e. those the angles of which are $\alpha = 0$ (or cos $\alpha =$ = 1).

Other orientations then disperse ($\pi/2 \geq \alpha > 0$) or even disturbe ($\pi \geq \alpha > \pi/2$) the spreading of this force field. It means, the water molecules with orientations $\alpha \neq 0$ behave at the potential level φ like molecules with orientations $\alpha = 0$ at the potential level $\varphi.\cos \alpha$. Owing to this assumption, in accordance with Eq. (11), we can write:

$$N_\varphi = \frac{1}{2} N_o \int_{-1}^{1} e^{\frac{(\varphi.\cos \alpha)}{kT}} \cdot d\cos \alpha = N_o \cdot kT \cdot \frac{\sinh(\varphi/kT)}{\varphi} \qquad (15)$$

Combining of this equation (15) with Eq. (9) then results in Eq. (16)

$$-\Delta\varphi \;=\; \frac{f_{si}}{\Delta x} \cdot \left[1 \;-\; \frac{kT \cdot \sinh(\varphi/kT)}{\varphi}\right] \qquad (16)$$

Analytical solution of partial differential equation

The analytical solution of Eq. (16) is very complicated. Without complication it is possible only for some simplified cases. For instance, in the case of infinitely large, homogeneous hydrophilic plane (see Fig. 2) we can write Eq. (16) as:

$$\frac{-d^2\varphi}{dx^2} \;=\; \frac{f_{si}}{\Delta x}\,[1 \;-\; kT.U(\varphi)] \qquad (17)$$

$$\text{where} \quad U(\varphi) \;=\; \left[\frac{\sinh\,(\varphi/kT)}{\varphi}\right].$$

If we perform the substitutions Y = dφ/dx and suppose that $\varphi \ll kT$, then it is possible to replace the function U(φ) by McLaurin's series in the form

$$U(\varphi) \;=\; \frac{1}{kT} \;+\; \frac{1}{6}\cdot\left(\frac{1}{kT}\right)^{3} \cdot \varphi^{2} \;+\; \ldots \qquad (18)$$

and the Eq. (17) gets the form:

$$-Y \cdot \frac{dY}{d\varphi} \;=\; \frac{f_{si}}{6\Delta x} \cdot \left(\frac{\varphi}{kT}\right)^{2} \qquad (19)$$

After integrating Eq. (19) at boundary conditions:

$$\begin{array}{llll}
\varphi &=& 0; & d\varphi/dx \;=\; 0 \\
\varphi &=& \varphi(0); & x \;=\; 0
\end{array}$$

and as it is $f_{S1} < 0$, it results:

$$\frac{d\varphi}{dx} = \pm\, a \,.\, \varphi^{3/2},\qquad (20)$$

where $a = (-f_{S1}/\Delta x)^{0.5}/(3kT)$. At the same time, only the negative sign has a physical significance.

Other integration of Eq. (20) results in final solution represented by Eq. (21).

$$\varphi = \frac{\varphi(0)}{\left[1 + \frac{a}{2}\sqrt{\varphi(0)}\,.x\right]^2}\qquad (21)$$

For the determination of parameters a and $\varphi(0)$ see Note 3.

Mutual interactions of both surfaces with hydration shells - origin of the hydration forces. An interaction of two infinitely large, hydrated hydrophilic flat formations can be mathematically described by Eq. (16) or (17). However, this differential Eq. (17) was solved for a different boundary condition. For interactions of two qualitatively different but homogeneous surfaces we obtain:

For x = 0 is $\varphi = \varphi1\ (0)$ - 1. surface

  x = d is $\varphi = \varphi2\ (0)$ - 2. surface

1. At attraction for $\varphi = \varphi_d$ ↑ is $d\varphi/dx = 0$

2. At repulsion, for $\varphi = $ ↓ - φ_d is $d\varphi/dx = 0$

By solution of Eq. (17) within these boundaries it then results:

  1. In the case of attraction the first integration leads to Eq. (22)

$$1.\ surface\ \frac{d\varphi}{dx} = -\,a_1(\varphi^3 - \varphi_d^3)^{1/2}$$

$$2.\ surface\ \frac{d\varphi}{dx} = -\,a_2(\varphi^3 - \varphi_d^3)^{1/2}\qquad (22)$$

where

$$a_1 = (-f_{s1})^{0.5}/\ 3kT \quad and \quad a_2 = (-f_{s2})^{0.5}/3kT.$$

2. In the case of repulsion, Eq. (23) then results analogously

$$\frac{d\varphi}{dx} = -a_i(\varphi^2 + \varphi_2^2)^{1/2} \tag{23}$$

where $a_i = (-f_{si})^{0.5}/\ 3kT$ for each individual surface.

The value φ_d (in J per one surface water molecule) or φ_d . N_A (in J per mol of surface water in first adjancent layer of the interacting surfaces), where N_A is the Avogadro number, then represents the real interaction potential or characterizes the force (so called hydration force) wich attracts or repulses two interacting hydrophilic surfaces in water medium.

Better is the solution of equations (22) or (23) in the terms of relative potential, i.e. in the following form of Eq. (24):

$$\frac{d\Phi}{dx} = -b_i(\Phi^2 \pm \Phi_2^2)^{0.5} \tag{24}$$

where $b_i = a_i$. $\sqrt{\varphi_i(0)}$, $\Phi = \varphi/\varphi_i(0)$ and $\Phi_d = \varphi_d/\varphi_i(0)$ for $\varphi_1(0) \geq \varphi_2(0)$.

As $\varphi_2(0)/\varphi_1(0) = k_i \leq 1$ then for the 1. surface - $\Phi_0 = 1$, and for the 2. surface - $\Phi_0 = k_i$.

Note 3:

In the case of surface tension solid - liquid ($\gamma_{l,s}$) the relation (25) results from Eqs (3) and (20)

$$\lim_{x \to 0} \left| \frac{d\varphi}{dx} \right| \cdot \frac{1}{\Delta x} = \gamma_{l,s} \tag{25}$$

and with respect to Eq. (20) we obtain Eq. (26)

$$\gamma_{1,s} = -a' \cdot \varphi(0)^{3/2};$$ (26)

If we assume the width of hydration shell as a width of a layer where the relation $\varphi(\underline{1})$ = 0,01 . $\varphi(0)$ is valid (where $\underline{1}$ means the width of this hydration shell) then after combining with Eq. (21) we obtain Eq. (27)

$$\underline{1} = \frac{18}{a\sqrt{\varphi(0)}}$$ (27)

When combining Eqs (26) and (27) we finally obtain the following equations:

$$a = \left(\frac{18}{\underline{1}}\right)^{3/2} / \left(\Delta x . \gamma_{1,s}\right)^{1/2}, \qquad 1/(N.m^3)^{1/2} \qquad (28)$$

$$\varphi(0) = \frac{1}{18} \cdot |\gamma_{s,1}| \cdot \underline{1} \cdot \Delta x, \qquad J/water\ molecule \qquad (29)$$

from which we can calculate, at a given temperature, the unknown parameters a, $\varphi(0)$, of course if we know the surface tension $\gamma_{1,s}$ and width of hydration shell $\underline{1}$. Both of these quantities are very difficult to measure. Value of Δx is known from literature and usually it is Δx = 0.25 - 0.3 nm[14].

The simulated theoretical results were obtained by calculation with these quantities:

1. $|\gamma_{1,s}|$ = 4.0 mN/m; $\underline{1}$ = 6.0 nm;   T = 20 °C
2. $|\gamma_{1,s}|$ = 0.8 mN/m; $\underline{1}$ = 10.3 nm;   T = 20 °C

By verification of experimental results of Afshar-Rad[18] and Israelachvili at all[19] for interaction of the surfaces of mica in water solution of 1.10^{-3} M KNO_3 according to Eq. (31) we received the following results:
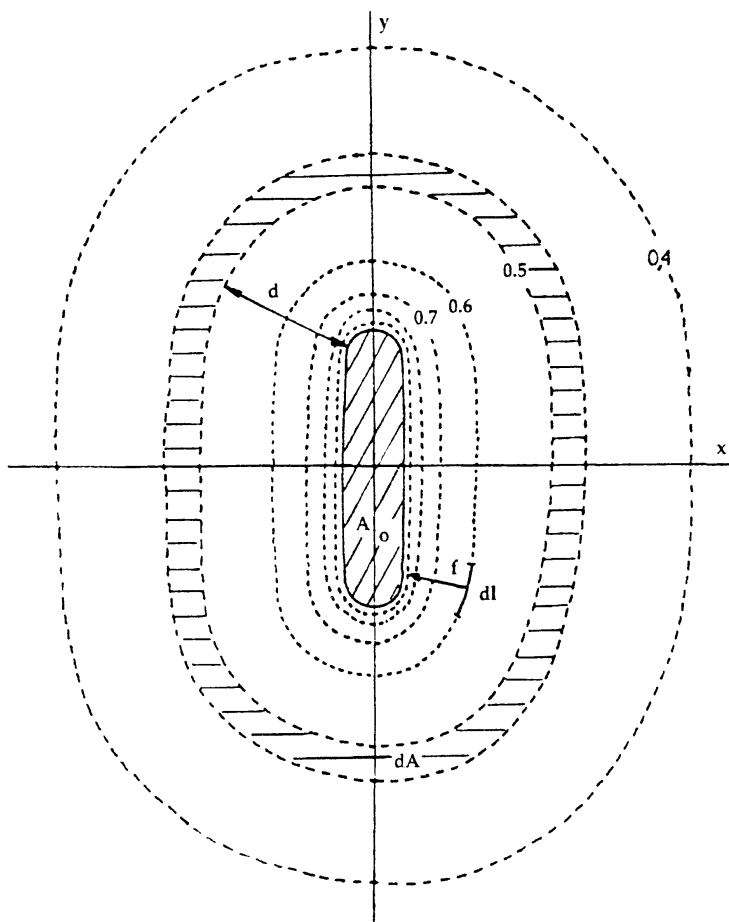
Fig. 3 Distribution of isobare (i.e.lines with equal affecting forces) around hydrophilic surface line. For circle integral every isobar results:

$$\oint_{L(A)} f.n_o.cos\alpha.dl = F(L), \text{ where}$$

α = angle between force vector f and normal vector of line dl - n_o. As f = -gradφ, then

$cos\alpha$ = 1 and F(L) = f.L, where L is the whole length of isobar, $L = \oint_{L(A)} dl.$

The whole force evoked with hydrophilic phase interface is then $F(L_o) = f_o.L_o,$ where

$$L_o = \oint_{L(A_o)} dl$$

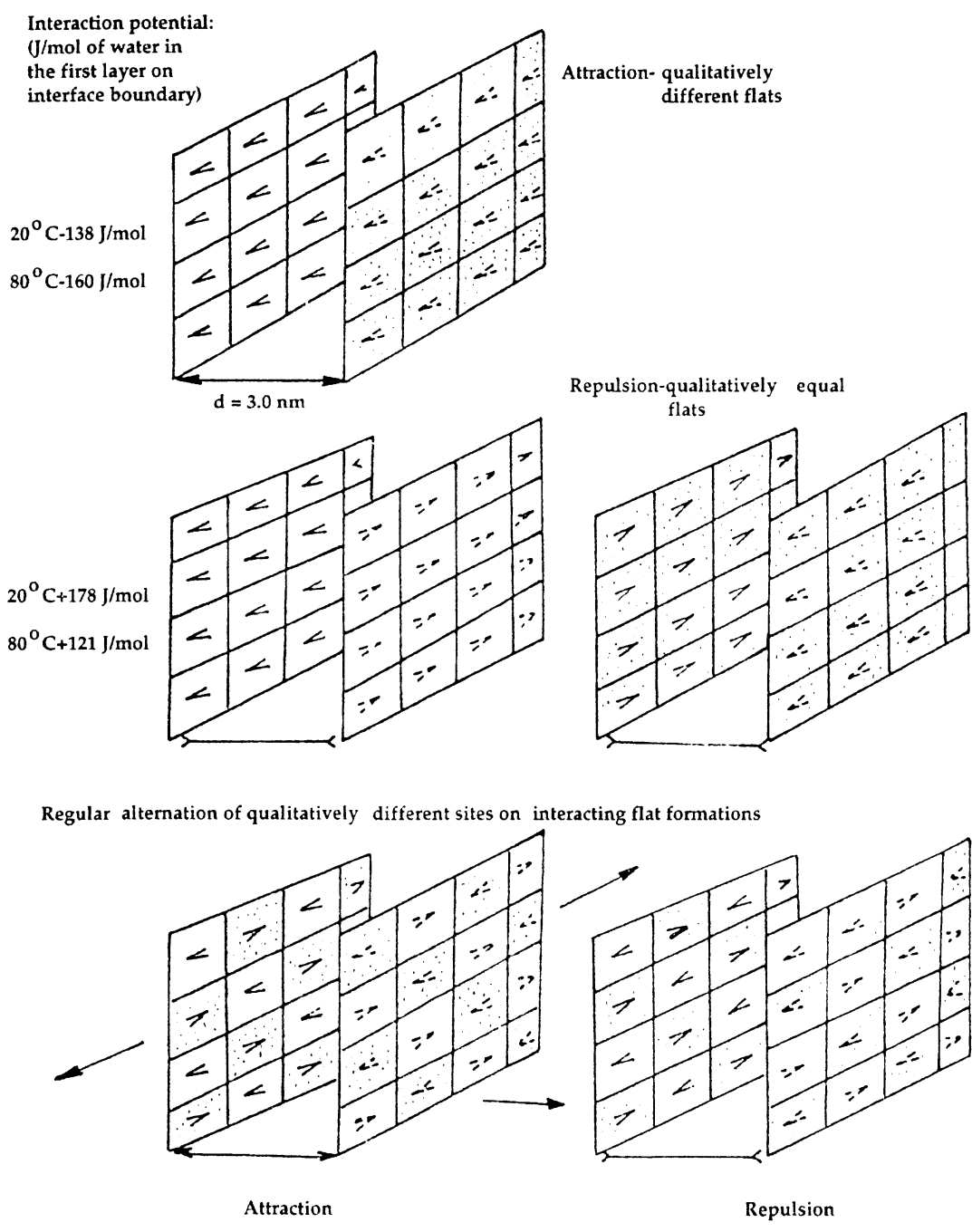Interaction potential:
(J/mol of water in
the first layer on
interface boundary)

Attraction- qualitatively
different flats

20°C-138 J/mol

80°C-160 J/mol

d = 3.0 nm

Repulsion-qualitatively equal
flats

20°C+178 J/mol

80°C+121 J/mol

Regular alternation of qualitatively different sites on interacting flat formations

Attraction

Repulsion

Fig. 4 Graphic description of interaction of two flat formations according to next Fig. 5.
Homogeneous and quantitatively equal sites

$\phi(0) = 4.06 \cdot 10^{-23}$, J/water molecule; $\underline{1} = 16.7$, nm;

$a = 1.6869931 \cdot 10^{20}$, $1/(N.m^3)^{1/2}$; $|\gamma_{s,i}| = 0.147$, mN/m; $\gamma_i = 4.2$, N/m.

The correlation coefficient of this verification was 0.9932.

Schematic presentation of the idea of hydration forces:

The relative potentials of water molecules of such a force effect between two homogeneous, quantitatively equal parallel surfaces at various distances from each other are plotted in Figs 5,6. These interacting flat formations were described graphically in Fig. 4. These interactions are practically identical with those of heterogeneous nondeformable flat surfaces with regularly alternating quantitatively equal but qualitatively different sites where the boundary effects were omitted.

Dependence of interacting potential upon the distance[14]:

Figure 5 shows the interaction of surfaces with opposite orientation of water molecules - i.e. attraction, and Fig. 6 shows the interaction of surfaces with the same orientation of water molecules (the arrows >,< denote the direction of water molecules orientations to the surface) - i.e. repulsion. The value Φ_d is the relative potential of interaction (interaction potential) of the two surfaces at a distance d from each other. The dependence of absolute values of interaction potentials (in J/mol of water in the first adjacent layer on interface boundary - is proportional to the specific surface) upon the distance is presented in Fig. 7.

The properties of the interaction potentials:

Surprisingly, under equal conditions, the repulsive forces are effective over a greater distance[14-15] (Figs 5-7). This difference appears important in the interactions of heterogeneous surfaces in which repulsive and attractive hydration forces are affecting simultaneously. Figure 8 introduces the simplest case of these heterogeneous interactions - the interaction between two nondeformable flat formations covered with regularly alternating quantitative equal sites of attractive and repulsive hydration forces of the mosaic type. The relationship between the interaction potential of these sites and the distance where the boundary effects were neglected is shown in Fig. 9. This one has been derived by adding of repulsive and attractive potential in each point of distance for two different temperature as well.
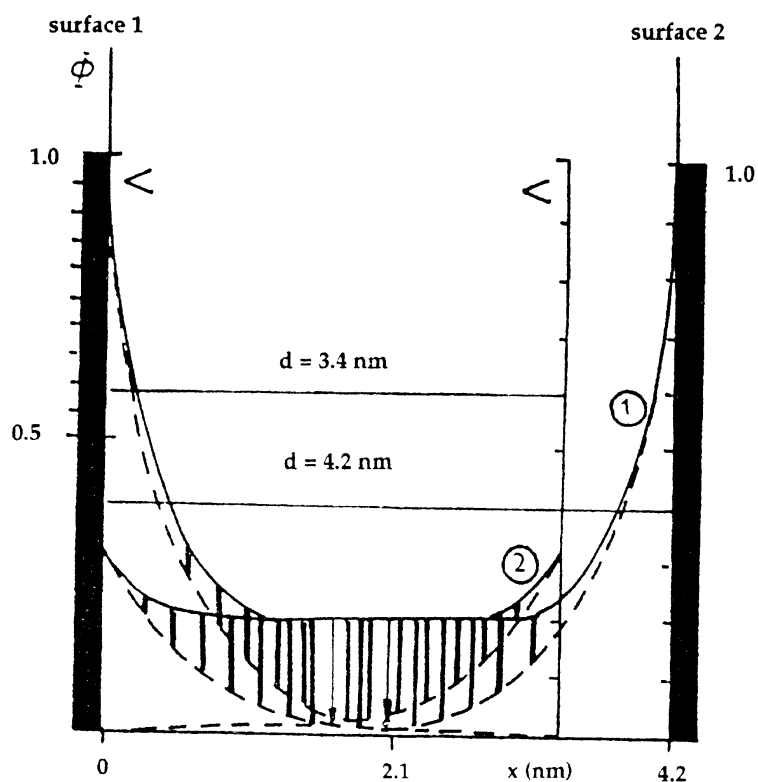
Fig. 5 The dependence of the relative potencial upon the distance in the interaction of two flat homogeneous surfaces with oppositely oriented water molecules in surface layers - attraction

_____ - after interaction; ------ before interaction

1 The 1. surface: $\gamma_{1,s}$ = 4.1 mN/m; $\varphi_1(0)$ = 4.054 . 10^{-22}J;
$\underset{1=6,0nm}{}$

The 2. surface: dtto with oppositely oriented water molecules

2 The 1. surface: $\gamma_{1,s}$ = 0.8 mN/m; $\varphi_2(0)$ = 1.35 . 10^{-22}J;
$\underset{1=10,3nm}{}$

The 2. surface: dtto with oppositely oriented water molecules
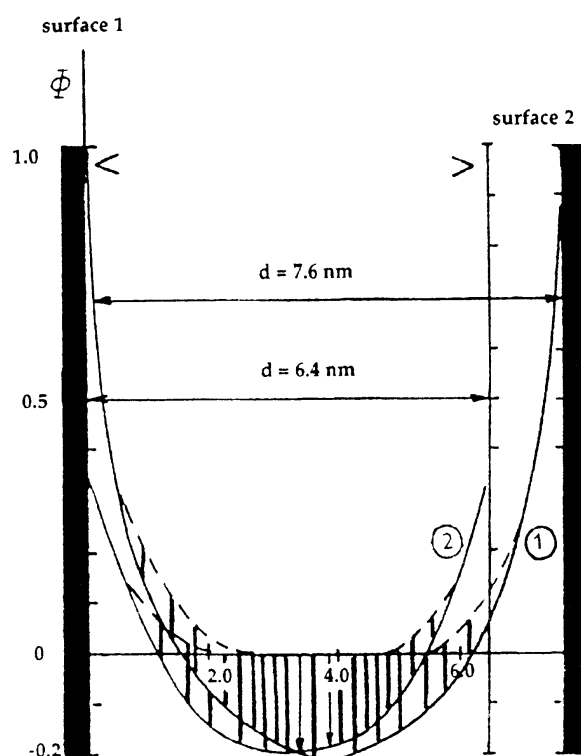Y_d = 0.2; ΔG = - 21.88 J/mol H_2O

Fig. 6 The dependence of the relative potencial upon the distance in the interaction of two flat

homogeneous surfaces with same oriented water molecules in surface layers - repulsion.

_____ - after interaction; ------ before interaction

1 The 1. surface: $Y_{1,s}\atop{l=6,0nm}$ = 4.1 mN/m; $\phi_l(0)$ = 4.054 . 10^{-22}J:

The 2. surface: dtto with equally oriented water molecules

2 The 1. surface: $Y_{1,s}\atop{l=10,3nm}$ = 0.8 mN/m; $\phi_2(0)$ = 1.35 . 10^{-22}J:

The 2. surface: dtto with equally oriented water molecules
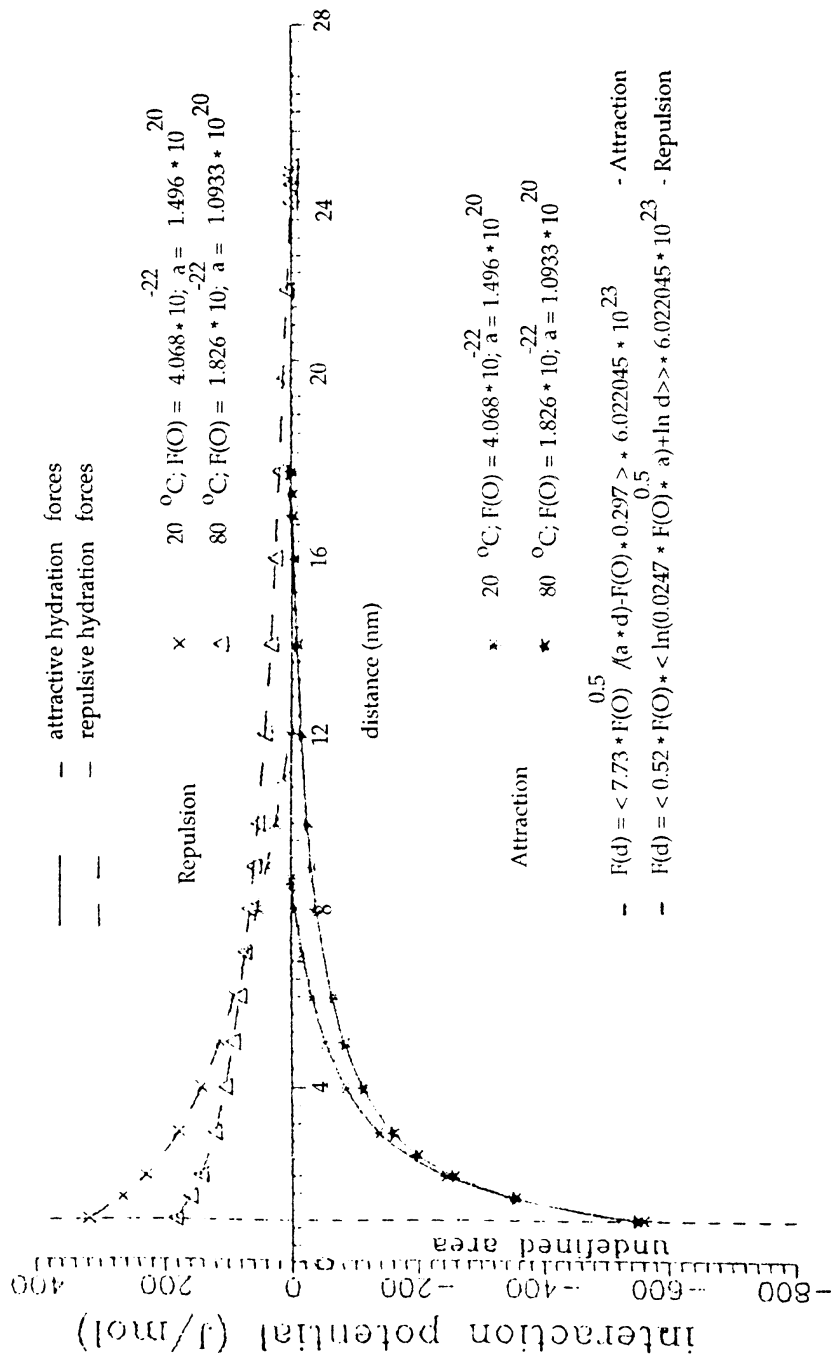
Y_d = - 0.2; ΔG = 23.52 J/mol H_2O

Fig. 7 Dependence of interaction potentials (absolute values) upon the distance of interacting homogeneous and quantitative equally flat formations
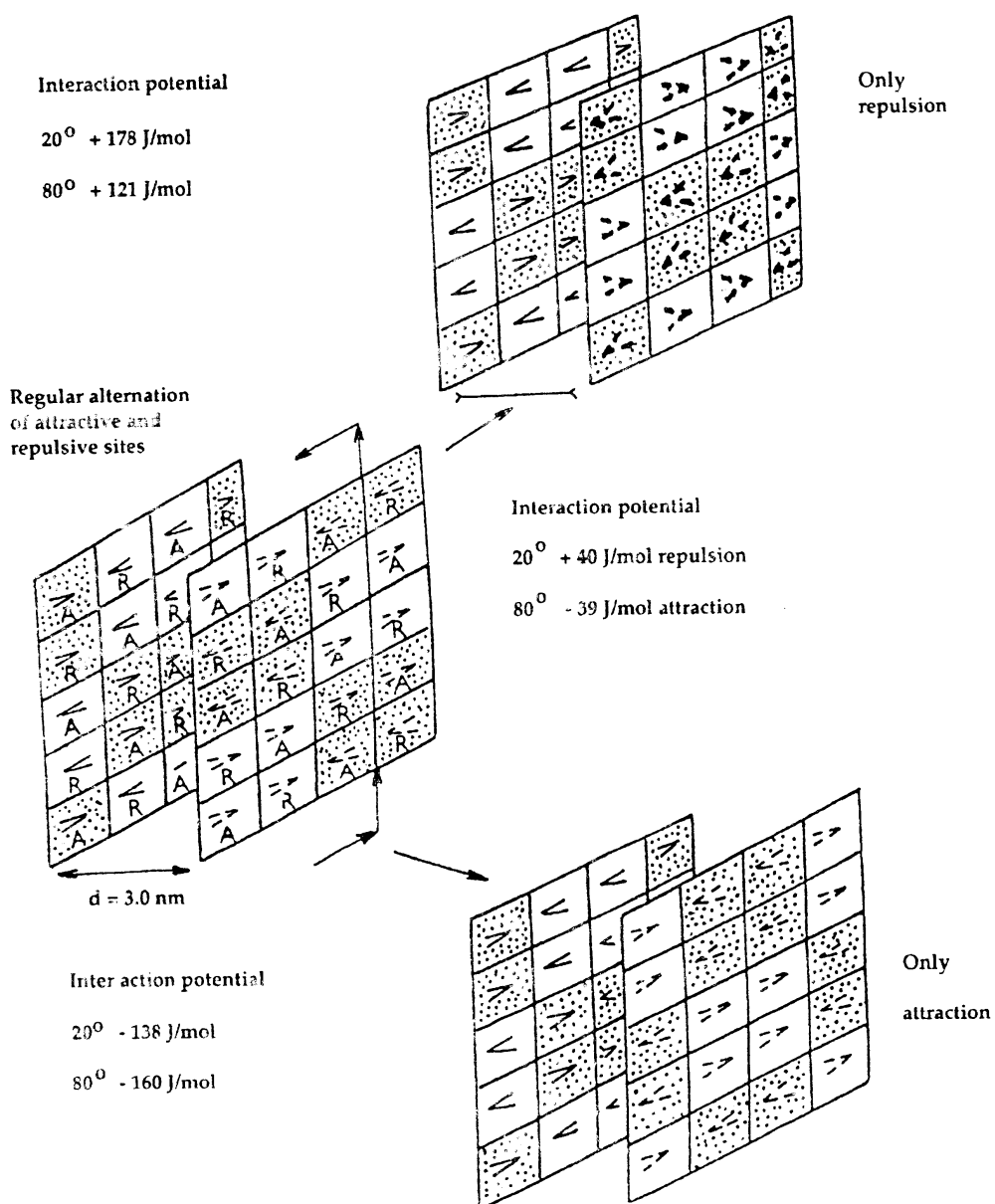
Interaction potential

20° + 178 J/mol

80° + 121 J/mol

Only
repulsion

Regular alternation
of attractive and
repulsive sites

Interaction potential

20° + 40 J/mol repulsion

80° - 39 J/mol attraction

d = 3.0 nm

Inter action potential

20° - 138 J/mol

80° - 160 J/mol

Only
attraction

Fig. 8 Graphic description of interaction of two flat formations with regular alternation of interacting
s ites. These are qualitatively different and quantitatively equal

Properties of hydration forces[11,13]

It is logical that the effect of different forces depends not only on the distance but also on mutual acceptability. For example, London's dispersion forces can accept only nonpolar hydrophobic molecules or groups, while hydrogen bonds can merely be formed by molecules having corresponding polar hydrophilic groups.

Temperature influence[12]

As we can see from Fig. 9, the effect of hydration forces depends strongly upon temperature. The effects of hydration forces quickly disappear with rising temperature. Particularly interesting is the influence of temperature on the character of interacting systems of heterogeneous hydrated hydrophilic surfaces as shown in Fig. 8. For instance, in concentrated state, when the interacting surfaces are at small distances from each other, i.e. d = 3 nm at $20°$ C, the repulsion hydration forces dominate (practical system has a small ciscosity) but at $80°$ C the attractive hydration forces dominate (practical dispersion system has a high viscosity). This phenomenon is better schematically presented in Fig. 10 for the case of dispersion of spherical particles with heterogeneous hydrated hydrophilic surfaces of the mosaic type.

Heat effects[12,16]

In the interactions due to hydration forces, mutual diffusion of hydration layers results in the change of their structure. These structural changes are on the molecular level and should be accompanied by proper heat effects. Theoretically it has been shown that[14]:

1. The action of attractive forces is an exothermic process ($\Delta H < 0$) connected with decreasing of entropy i.e. $\Delta S < 0$ (or in other words with increasing degree of system order), while

2. The action of repulsive hydration forces (i.e. under influence of external forces) has an endothermic character ($\Delta H > 0$) connected with increasing of entropy i.e. $\Delta S > 0$. At the same time, the entropic changes are essentially smaller in comparison with enthalpic changes.

Relationship to the electrical double layer[11]

The relationship of this theory to that of the electrical double layer theory can be obseved in Fig. 11. It shows that, according to the SCHL theory, the adjacent part of the electric double layer around hydrated hydrophilic phase interfaces (sometimes called Stern's layer) is formed by hydration layers. The other molecules of ionic and nonionic character are
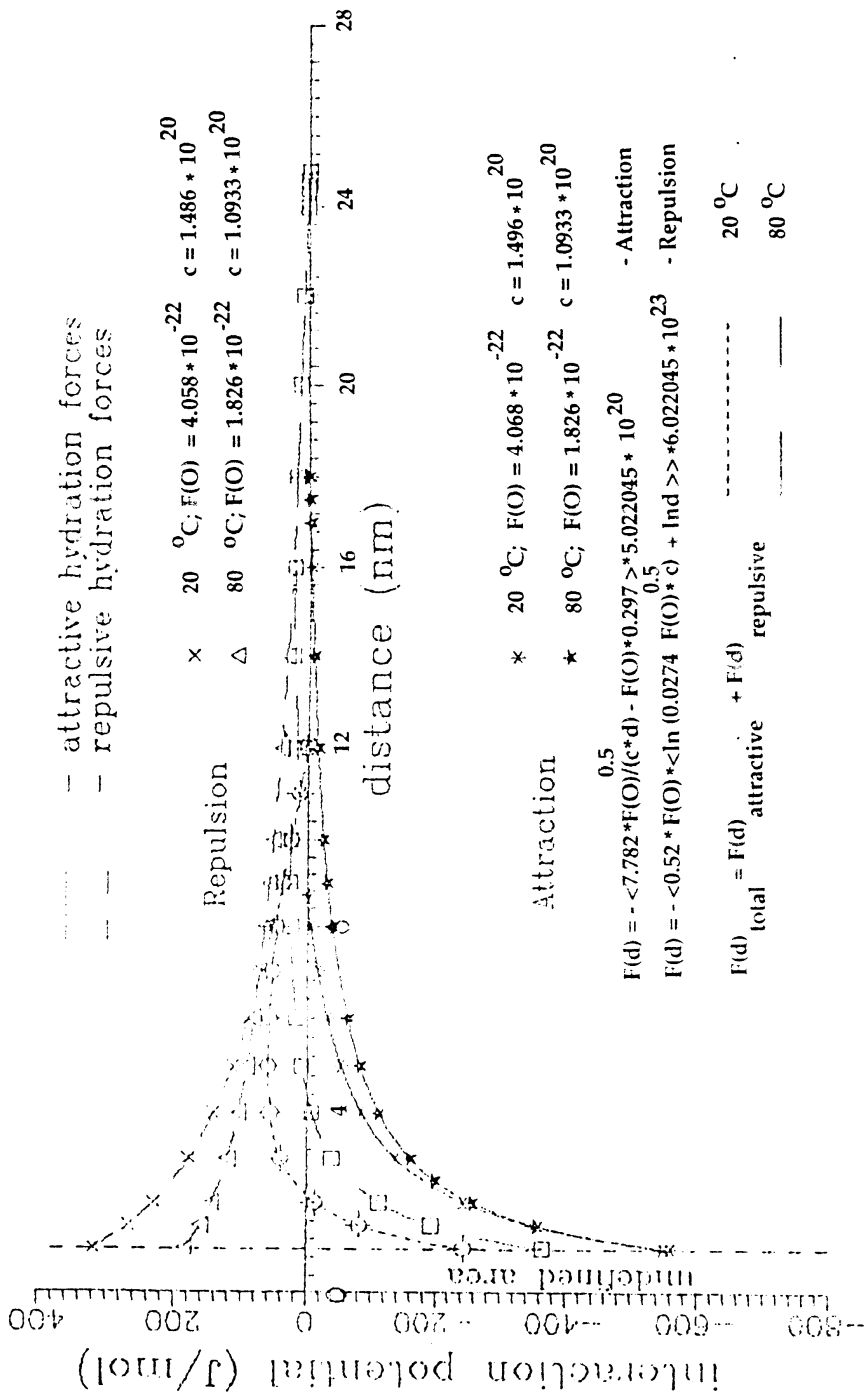
Fig. 9 Dependence of interaction potentials (absolute values) upon the distance of interacting homogeneous and quantitatively equal flat formations
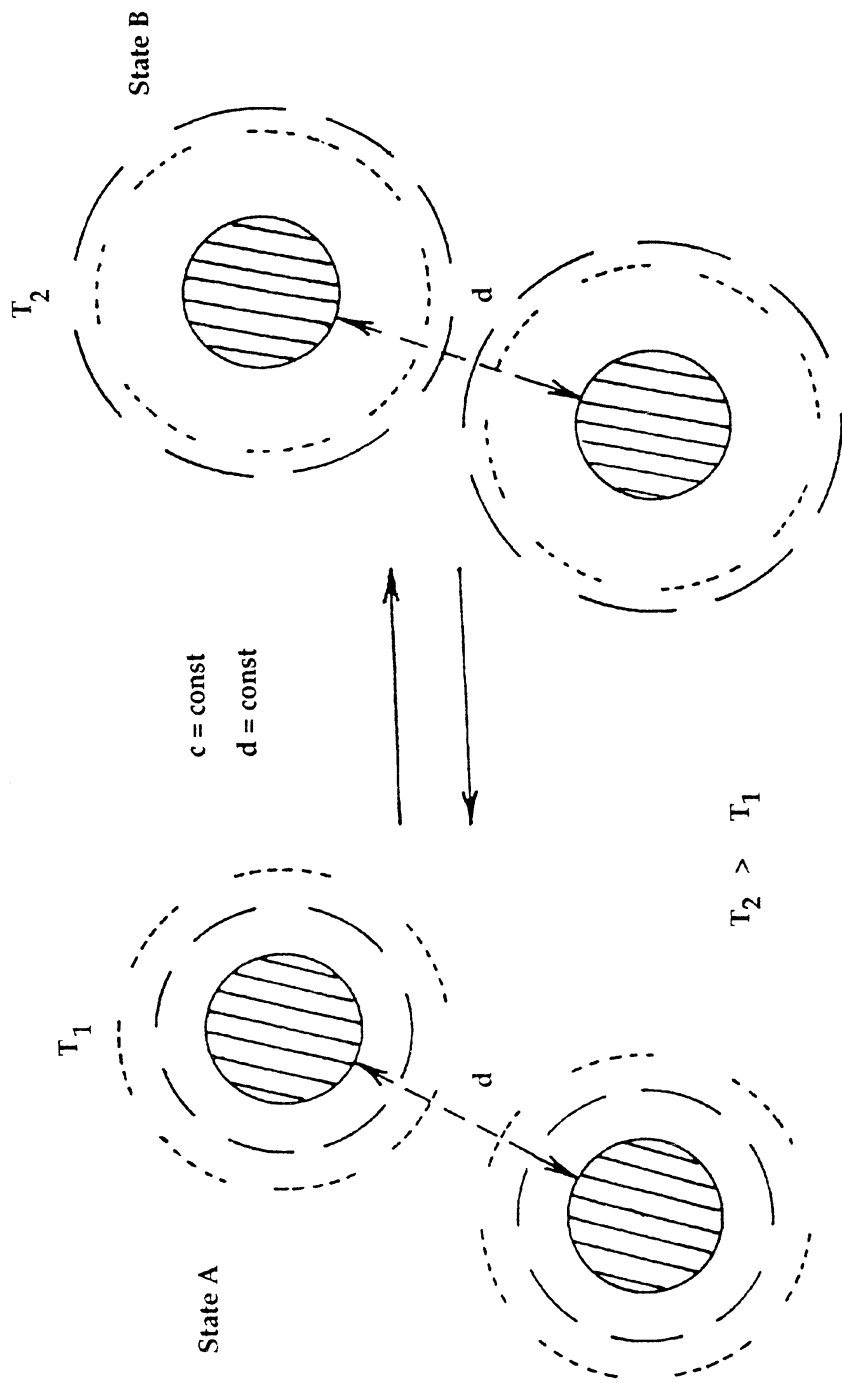
Fig. 10 Schematic representation of isopotentials around the molecules of heterogeneous character (mosaic type)

————— - area of the attractive interaction

------ - area of the repulsive interaction

then drawn in or expelled by electrostatic, hydration, van der Waals or other forces into these layers. However, the thickness of the hydration layers is considerably greater than that of the inner layer resulting from the previous electrical double layer theory, and due to its diffuse character it is not exactly limited. Its thickness depends highly on the effect of shear forces or on the velocity gradient. For this reason the value of Zeta-potential will be highly influenced by these factors. As it follows from Fig. 11, at proper conditions different results of Zeta-potentials can be found differing both in absolute values and in sign.

Clasification of the hydrophilic groups according to their abilities to form hydration forces[11,13]

As we have seen the ability of hydrophilic groups to form hydration forces depends upon the interaction of H-bonds with water. These H-bonds replace original H-bonds of dry hydrophilic material.

Destruction of the original H-bonds by water and aqueous solutions will depend not only on their strength, but also on the nature of the H-bonds. The destruction can be reversible or irreversible. The H-bonds produced from H-amphoteric groups are usually reversible H-bonds, while the groups of donor or acceptor nature usually form the irreversible H-bonds. (This is governed by thermodynamic laws because all systems tend to increase their entropy, i.e. in this case to increase repulsive hydration forces and only H-amphoteric groups have this ability). As example see cellulosic materials in p. III. and Fig. 5[17].

Role of hydration forces among others[13]

In this context, these forces do not cause chemical changes of interacting molecules, but only changes in their arrangement and their orientation in the system. We are discussing them as interactions that occur above the level of basic molecular structure and that do not alter the basic molecule.

The action of different forces depends on their distance. As shown in Fig. 12, the shortest distances are found in forces connected with chemical bonds, H-bonds follow. Finally, the colloidal (physical) forces occur in interactions above the molecular structure such as in interactions characterized by the van der Waals, hydration and electrostatic forces defined with Zeta-potential of interacting surfaces.

Conclusion

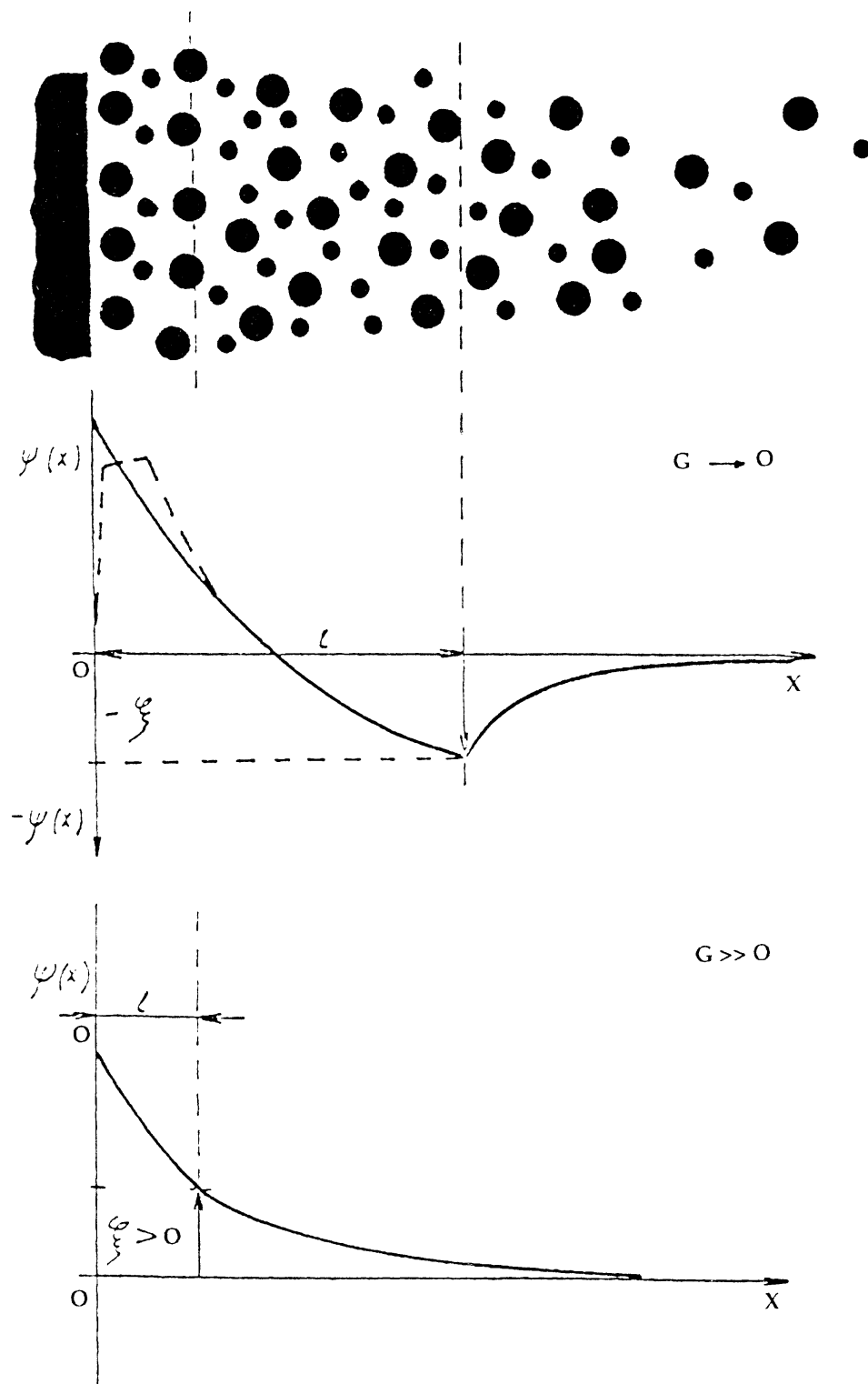Hydration forces creating a hydration bonding system between hydrated hydrophilic

Fig. 11 Schematic representation of the distribution of electric potentials in hydration layer and of the diffusion part of electric double layer according to the SCHL theory. G - shear rate (s⁻¹); 1 - thickness of hydration layers
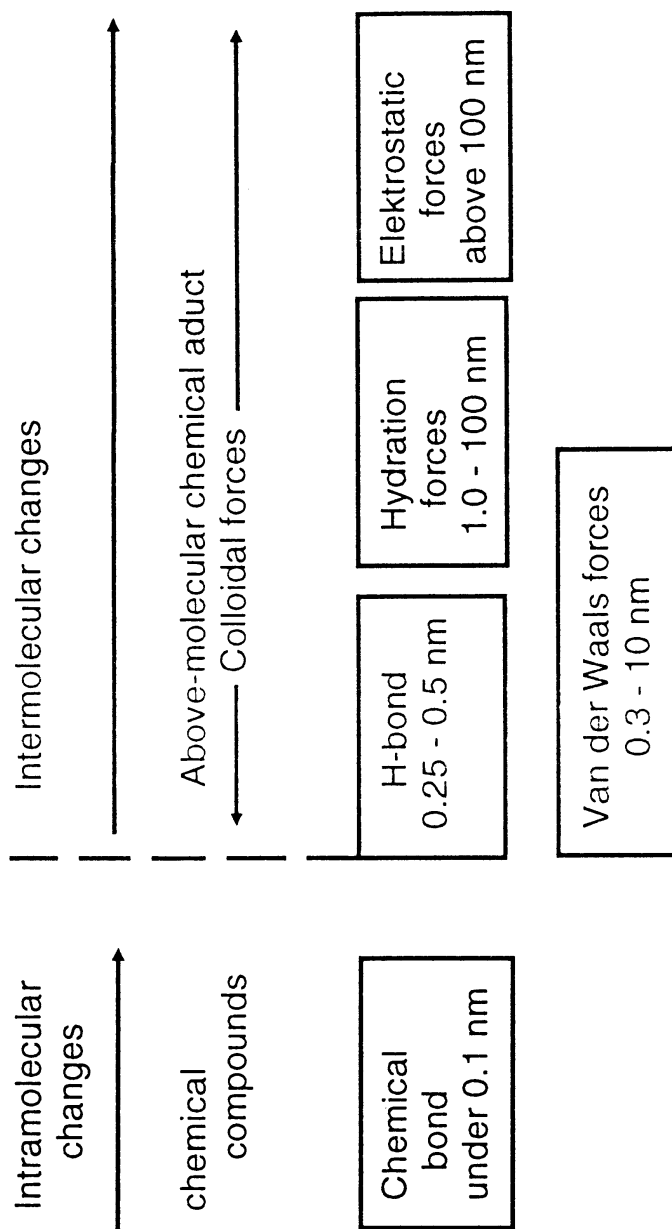
Fig. 12 Distances of the action of particular forces. Defining chemical and above - molecular chemical zone.

phase interfaces play a very important role in the behaviour of all living organisms. For example, by switching off the function of the amphoretic groups in the phase interface, we can achieve either attraction or repulsion of these interacting surfaces, i.e. their mechanic motion. This is a simple explanation of the motion in the living organism.

This phenomenon is important everywhere in pulp and paper industry particularly in the case of highly concentrated pulp and paper suspensions, which is the case for example, in the pulp beating, initial wet strength of paper web, adsorption of hydrophilic polymer sand hydrophilic particles on pulp fibers, permeability properties of wet paper web, final paper properties like the strength of wet paper web, rheological properies of high concentrated hydrated hydrophilic dispersion systems like are PVAc, PVA and starch glues, coating mixtures, etc.

What is important:

1. The hydrogen forces are formed due to the same basic orientation of water molecules in the first adjacent layers at the phase interface (repulsive forces) or due to the different basic orientation of water molecules in the first adjacent layers at the phase interface of interacting surfaces (attractive forces).

2. The action and influence of hydration forces depend very strongly on temperature, i.e. with increasing temperature their influence decreases and practically disappears at the boiling point of water.

3. At equal conditions, i.e. at interaction of quantitatively equal but qualitatively different centres or surfaces with equal potencial energy or surface tension, the attractive hydration forces will act at shorter distances than "the same" repulsive hydration forces but at the shortest distances the attractive forces are stronger than the repulsive hydration forces.

4. Hydration forces are created by mutual contact of the interacting hydration shells around the interacting phase interfaces. At distances (d) larger than the width of these shells dynamic forces, such as the hydrodynamic ones, and electrokinetic forces (characterized by potentials $\varphi_{Hd}(d)$ and $\varphi_{Ek}(d)$, respectively) are operating. At distances shorter than the width of these hydration shells (due to their mutual permeation) the effective static hydration and electrostatic forces (given by excess of adsorbed cations or anions in the first so-called Stern's layer of the electric double layer) are characterized by potentials $\varphi_{H}(d)$ and $\varphi_{Es}(d)$, respectively. The van der Waals attractive forces $\varphi_{vw}(d)$ take part in those cases at shorter distances. At distances shorter than the size of one water molecule, the H-bond characterized by potential $\varphi_{HB}(d)$ and/or van der Waals forces, such a London-van der Waals forces $\varphi_{L-vw}(d)$, are arising

among the interacting hydrophilic places.

We can generalize this idea for interaction potential $\varphi(d)$ as follows:

$\varphi(d) = \varphi_{Hd}(d) + \varphi_{Ek}(d) +$ ⠀⠀⠀⠀(Outer hydration shell)

⠀⠀$+ \varphi_H(d) + \varphi_{Es}(d) + \varphi_{vw}(d) +$ ⠀(Inner hydration shell)

⠀⠀$+ \varphi_{L-vw}(d) + \varphi_{HB}(d)$ ⠀⠀⠀⠀(Mutual phase to phase contact)

We can also divide these forces into:

⠀⠀1. Adhesion forces (van der Waals forces, H-bond) - interaction of qualitatively different surfaces.

⠀⠀2. Cohesion forces (electrokinetic and electrostatic forces, hydration forces) - interaction of qualitatively equal surfaces.

⠀⠀3. Other, e.g. dynamic forces.

The theoretical absolute values of interaction potentials for hydration forces based on the numerical solution of Eq. (24)[14] and represented in Figs 7 and 9 for homogeneous quantitatively equal surfaces can be calculated from the following equations:

Attraction (in J/water molecule):

$$\varphi_{Hd}^A(d) = 0.297 \cdot \varphi(0) \cdot \{1 - \frac{26.202}{a \cdot \sqrt{\varphi(0)} \cdot d}\}, \qquad (30)$$

Repulsion (in J/water molecule):

$$\varphi_{Hd}^R(d) = -0.52 \cdot \varphi(0) \cdot \{\ln(2.74 \cdot 10^{-2} \cdot a \cdot \sqrt{\varphi(0)}) + \ln d\}, \qquad (31)$$

For simultaneous interaction of these surfaces with the mosaic type of arrangement it then follows:

$$\varphi_{Hd}(d) = A_A \cdot \varphi_{Hd}^A(d) + A_R \cdot \varphi_{Hd}^R(d), \qquad (32)$$

where both A_A, A_R are a surface fraction of an attractive and a repulsive part of interacting surfaces, respectively, because

$$A_A + A_R = 1$$

Both the parameters $\varphi(0)$ and a were calculated according to Eq.[14]:

$$a = (\gamma_l - \gamma_{s,l})^{0.5}/(3kT), \qquad 1/(N.m^3)^{0.5}$$

$$\varphi(0) = (3kT.\Delta x.\gamma_{s,l})^{2/3}/(\gamma_l - \gamma_{s,l})^{1/3} \text{ or } (\gamma_{s,l}.\Delta x/a)^{2/3}$$

in J/water molecule, where $\gamma_l = 3.3$, N/m (see[14]) or $\gamma_l = 4.2$, N/m (was received by verification of experimental results on mica surfaces[18-19] according to Eq. 31) and k - Boltzman's constant. The temperature dependence of $\gamma_{s,l}$ for bleached pulp was calculated from following eq.:

$$|\gamma_{s,l}(T)| = 1.91 \cdot 10^{-2} - 5.12 \cdot 10^{-5}.T, \ N/m$$

where T - temperature in K. In fact the parameter a is a constant at isothermal conditions because

$$\gamma_l \gg |\gamma_{s,l}|$$

Both the equations 30 and 31 are physically restricted by the following conditions:

$$d \geq 0.3 \cdot 10^{-9}m; \ \varphi_{Hd}^A(d) \leq 0; \ \varphi_{Hd}^R(d) \geq 0 \text{ and } |\varphi_{Hd}(d)|/\varphi(0) \geq 0.01.$$

For both Eqs 30 and 31 results that at certain distances of the interacting surfaces of phase interfaces (d = d_o) it is φ_{Hd}^R (d_o), φ_{Hd}^A (d_o) = $\varphi(0)$ and d_o = 5.33 up 6.0 / (a. $\sqrt{\varphi(0)}$) nm.

We could call the hydration forces likewise intermediary forces because they arise and spread through space around interacting surfaces in consequence of the water molecule orientations.

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