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**BEHAVIOUR OF HYDROPHILIC COMPONENTS
IN PAPERMAKING SUSPENSIONS**

PART II. EXPERIMENTAL HYDRATED HYDROPHILIC MODELLING SYSTEM
- ITS PROPERTIES AND BEHAVIOUR

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The hydrated hydrophilic modelling system enables us to study the action and influence of various components in aqueous medium on behaviour and character of hydration forces operation therein.

Introduction

The hydrated hydrophilic systems are the main objects of interest in pulp and paper industry. In part¹ I a theoretical concept of behaviour of these systems was described. The essence of SCHL theory and the idea of the so-called "hydration forces" following from this theory was explained.

Hydration forces in real systems:

The idea is very simple, however, in real systems such as pulp where different

hydration forces and other colloid forces are operative, the situation is very complex. A simple idea of real hydration forces is shown in Fig. 1². Surfaces interacting occur at equilibrium at definite distance from one another. As it was shown formerly this fact plays an important role in concentrated hydrated hydrophilic systems such as pulp, gelatinated and various quasi-gelatinated systems etc.

Dividing h.h. systems with respect to optical properties:

Generally, hydrated hydrophilic systems can be divided into optically homogeneous (transparent) ones and optically nonhomogeneous (opaque) ones. This state depends on concentration of hydrophilic molecules in water system and on distribution and intensity of attractive hydration forces or attractive forces of van der Waals type.

Requirement of simple h.h. systems for modelling hydration forces:

If these hypotheses are correct and of practical importance, they must have general validity. This means there must exist some systems other than cellulosic or other polysaccharidic ones in which similar phenomena are simpler to investigate.

Evaluation of the effect of hydration forces³

Measurement of CDD value:

Hydrated hydrophilic systems presenting themselves with the so-called critical degree of dilution (CDD) make possible simple modelling of the action of hydration forces. This behaviour is typical of some hydrophilic substances of oligomer nature, such as several pre-condensates (UF) and polyesters, which in concentrated state form optically homogeneous systems with water. As you can see from Fig. 2, when gradually diluted, the oligomeric solution after having reached the CDD, gets turbid. This is caused by coacervation of the individual hydrated hydrophilic molecules.

Evaluation of CDD and relative hydration factor g^4 :

Presuming V_0 is initial volume of the hydrated hydrophilic solution and V is the dilution volume added that induced turbidity, then $CDD = V/V_0$. The CDD value characterizes indirectly the extent to which hydration forces operate. The addition of substances that interfere with attracting hydration forces increases the CDD value, and the addition of substances that interfere with repulsing hydration forces decreases the CDD value. It is preferable from

practical reasons to evaluate the relative effect of these additives in relation to distilled water by means of hydration factors f and g . If CDD_0 is the critical degree of dilution with distilled water and CDD is the critical degree of dilution with a solution of the tested substance, then the relation is:

$$f = (CDD - CDD_0) / CDD_0 = g - 1, \quad \text{where } g = CDD / CDD_0$$

A positive f -value ($g > 1$) indicates a decrease of attracting hydration forces or an increase of repulsing forces. On the other hand, a negative f value ($g < 1$) indicates a decrease of repulsing forces or an increase of attracting forces.

Explanation of behaviour of the modelling system⁴

The behaviour of such systems can be simply explained by the concept of hydration forces. Figures 3,4 represent the behaviour mechanism of these systems.

Mechanism of the rupture of space network by dilution:

For such behaviour to take place, hydrated, hydrophilic, nonisometric, oligomer molecules of relatively rigid nature have to be present in water. As shown in Fig. 4, both ends of the nonisometric hydration sphere are formed by water molecules with opposite orientation. The whole hydrated molecule thus appears to be bipolar considering it from the point of view of the effect of hydration forces. The distribution of localities with equally oriented water molecules need not have to be symmetrical.

Hydration shells around ions, etc.:

Due to the fact that hydration shells are found to be more or less extended around each molecule as well as ion, the hydration forces will also influence the motion and behaviour of single ions.

Changing distribution of hydration forces around oligomer molecules with other additives:

From Fig. 4 we can see that hydrated molecules of other additives are drawn to the appropriate localities of the hydrated oligomer molecule by attractive hydration forces that operate, changing the distribution of water molecules orientation in these localities.

Accordingly, depending on the composition of oligomer molecules, the localities with < orientation of water molecules can predominate around some molecules, and localities with > orientation predominate around others.

Detailed mechanism of the rupture of the space network of oligomeric molecules as modelling compounds at dilution:

As represented in Fig. 3, individual oligomeric molecules are evenly distributed in the whole water area at concentrated state (at room temperature, when hydration forces are functioning to a sufficient extent). Minimum internal energy can be reached if all water molecules are contained only in mutually diffusing hydration spheres around the oligomeric molecules. The whole system is isotropic with regard to the sizes of its structural units and more viscous owing to the attraction of hydration forces. (The lower CDD, the higher viscosity.) In the system, hydration forces that repulse alternate regularly with hydration forces that attract.

Stretching space network by dilution and rupture at the suitable moment:

On gradual diluting, hydrated oligomeric molecules separate from each other, becoming more free and mobile owing to the uneven effect of attractive and repulsive forces and to the heat. They are less and less limited in their motion, so that they take a more preferable orientation in their collisions. Owing to their nonisometric form, some molecules take a new, better arranged state at a suitable moment after breaking a space network, becoming oriented to each other in a certain order similar to the initial concentrated state

Coacervation takes place at the situation, in which the properties of individual coacervate particles resemble the initial highly concentrated system of the hydrated hydrophilic oligomer compound. The whole system of oligomeric molecules behaves during dilution like a stretching space network which is gradually ruptured after reaching CDD.

Experimental observations

Comparison of the behaviour of UF with PES⁴

Comparison of the behaviour during dilution of UF and PES

Figure 5 shows the relation of the relative hydration factors g determined by means of two qualitatively different hydrophilic systems

- urea formaldehyde (UF) pre-condensate,

- oligomeric polyester (PES).

Recall that rel. hydration factor changes with the amount and the type of the water soluble ionic and monoionic chemicals added. The data in Fig. 5 were obtained mainly by use of various chemicals. The relationship between the hydration factors of UF pre-condensate and PES can be described by the following equations (r_{xy} is the correlation coefficient),

$$g(UF) = 1.381 * g(PES) - 0.026 \quad \text{with } r_{xy} = 0.5383 \text{ or}$$

$$g(UF) = \exp[2.29 * g(PES) - 2.68] + 0.44 \quad \text{with } r_{xy} = 0.6078$$

Explanation of difference in behaviour of both UF and PES:

In accordance with these equations, the only mutual relationship between this rel. hydration factors is the qualitative one. The experimental data are considerably dispersed, but this variance is not caused by a poor reproducibility in the method. Instead, it is caused by qualitative differences in the behaviour of both systems with regard to the nature of hydration forces at work. These differences can be explained theoretically by the concept illustrated in Fig. 4. For instance, the < orientation of water molecules around interacting oligomer molecules prevails in the first system, whereas the > orientation prevails in the second.

Properties of the UF pre-condensate system during dilution with water

Results of surface tension measurements

Figure 6 represents the relationship between surface tension of two UF pre-condensates measured by the Wilhelmy plate method and the degree of dilution (DD).

$$DD = (V_{UF} + V_{water}) / V_{UF} = V / V_0$$

From Fig. 6 it follows that, after coacervation, sedimentation of the coacervates and separation of these two phase, the surface tensions of coacervates have distinctly greater values in comparison with the clarified supernatants or initial samples of UF. The surface tension of a UF sample with lower value of CDD_0^2 has a distinctly greater value in all cases.

These observations correspond very well with the theoretical suppositions and expectations.

Explanation of this behaviour:

Increase in surface tension signifies a relatively stronger bonding among surface molecules of liquid at the liquid-air phase interface. That is to say, the oligomeric molecules of UF pre-condensate are bonded one to the other through water by stronger forces (hydration forces) in coacervates than in the supernatants or initial samples of UF or coacervates of UF samples with a higher value of CDD_0 . This enables us to estimate the relative magnitudes of these forces. The lower the values of CDD_0 , the stronger attractive hydration forces are effective in the water system of UF. These pieces of knowledge and explanations support further densitometric and viscosimetric measurements.

Densitometric measurements

The dependence of density ρ of both liquid phases (sedimented coacervates and supernatant) upon the degree of dilution is presented in Fig. 7. As follows from Fig. 7 the density of the coacervates phase has a substantially greater density than that of the supernatant phase. The density of coacervates further increases with the gradually increasing degree of dilution while the density of the supernatant imperceptibly decreases. Surprisingly, the UF coacervates isolated by high degree of dilution, i.e. by low concentration, have a greater density than the initial concentrated UF pre-condensates. It means that with gradual dilution of UF pre-condensate, coacervates are formed having a more compact structure at the final state than in the initial UF pre-condensates. This particularly dominates in the systems with lower value of CDD_0 .

Viscosimetric measurements

These results also correspond very well to the viscosimetric measurements as it can be seen from Fig. 8. In this Figure are presented the dependences of the mean viscosity coefficient upon the degree of dilution of the coacervates isolated from UF pre-condensates of a different degree of condensation characterized by CDD_0 . Again as we expect now, the viscosity of coacervates increases with the increasing degree of dilution. The apparent viscosity coefficient increases fast with the coacervates prepared from UF pre-condensates with lower value of CDD_0 and vice versa.

Explanations:

The explanation of this behaviour is based upon the concept of a stretched space network formed by the oligomeric molecules of UF pre-condensates connected together in knots by means of attractive hydration forces (see Fig. 9). By gradual dilution this space network is stretched and at CDD_0 , due to the bonds fluctuation, the weakest bonds in some parts of this network are ruptured and the system undergoes coacervation. The released oligomeric nonisometric molecules of UF then take a new, better arranged nonstretched state. The remaining space network is connected together by more flexible and relatively stronger remaining forces. The dilution process and the coacervation connected therewith can continue further.

Gradually arising coacervates are formed by stronger and stronger bonds - the coacervates are changed into a more compact form. The scheme of this mechanism is presented in Fig. 3.

Heat effects of coacervation

As a rule, redistribution of molecules, constituting new structures by coacervation, etc., must be connected with adequate heat effects, particularly exothermic ones. As we can see from Fig. 10 the heat effect arising by dilution of UF pre-condensate fully confirms this assumption. By gradual dilution of UF pre-condensate the exothermic heat increased evenly but in the CDD area it changed by jump.

Influence of other compounds on properties of coacervates

A lot of components influence the attractive forces connecting the individual links of space network of UF pre-condensates and also the properties of these coacervates. This influence is either a positive one, i.e. an increase of the attraction, or a negative one, i.e. a decrease of the attractive hydration forces. Typical components having a positive influence on attractive forces as well as a practical importance are lignosulphonates or spent sulphite liquor. This may be seen from the following Figs 11 - 16.

Influence of CDD_0 on CDD_r of UF-lignin precipitates

Figure 11 represents the dependence of CDD of different UF pre-condensates characterized with CDD_0 upon concentration of spent sulphite liquor at 20 °C. With this concentration increasing, the value of CDD decreased and arrived at the steady state characterized by the value CDD_r . The value of this parameter characterizes the level of

bonding compactness among links of space network of the UF-lignin precipitates (coacervates). The greater the CDD_r value, the weaker are the bond strength and the compactness due to the amount of bonds present in agglomerates. As we can see from Fig. 12, with the increase of the CDD_o value of the original UF pre-condensate the steady value CDD_r of lignin coacervates must logically also increase. That means, that the initial UF-condensate is more compact, i.e. it is formed by a stronger bond system, the more compact will be the UF-lignin coacervates. The reciprocal value of CDD characterizes the level of strength of the attractive hydration forces operating in the system.

Extent of attractive forces

The extent of these forces influenced by added components is characterized by the reciprocal value of relative hydration factor g . The more this factor is near to one, the smaller amount of the attractive forces is influenced. The maximum extent of these forces influenced by spent sulphite liquor can be determined from the dependence of g upon a dosed amount of sulphite liquor - see Fig. 13.

The maximum extent of these forces is thus given by the reciprocal value of g_r . The decreasing tendency of g_r with increasing CDD_o logically follows from the dependence of g_r upon different UF pre-condensates characterized by the value of CDD_o (see Fig. 14). That means that the extent of attractive hydration forces which can at most be influenced by additives increases with CDD_o , i.e. with decreasing degree of condensation of UF pre-condensate. In other words, g_r decreases with decreasing level of strength of bond system in the original UF pre-condensate.

Characterization of coacervates with gelling temperature T_g

As it follows from schematic Fig. 9, the coacervate particles are in fact microgel particles. That also means that by heating after crossing the so-called T_g (the gelling temperature) the whole coacervated system is getting liquid. As we can expect this T_g temperature will be increased due to increasing attractive hydration forces, i.e. with increased amount of the spent sulphite liquor added. Figure 15 reveals this fact but, surprisingly, the position and shape of these curves are changed with the change of concentration of spent sulphite liquor too.

Explanation of effect of addition of the spent sulphite liquor on properties of coacervates:

The explanation of this phenomenon results from Fig. 16 which was constructed on the

basis of the results following from Fig. 15 representing the dependence of the composition of coacervates (in g of spent liquor per g of UF pre-condensate) at $T_g = 40\text{ }^\circ\text{C}$ upon concentration of water (in %) in these coacervates. The next condition varied was the addition of starch. The dependences in Fig. 15 reveal a very strong influence of water on the properties of coacervates. In order to retain equal properties of coacervates characterized by the gelling temperature T_g we must, with increasing water concentration, decrease the content of sulphite liquor (i.e. the components that strengthen the bond system of attractive hydration forces in coacervates) in coacervate very rapidly. On the other hand, the starch reveal deteriorate effect on this bonding system, i.e. getting weaker this one.

Behaviour of ionic compounds in hydrated modelling systems

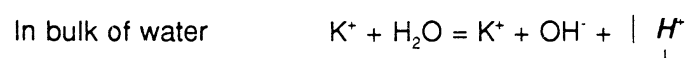
It is well known that most ions are hydrated, i.e. covered with hydration shells, which also means, in correspondence to this theory, that their interaction can be influenced not only by electrostatic forces but also by hydration forces. Of course, even if the role of electrostatic forces generally prevails in the behaviour of ions, we have to calculate with the influence of hydration forces in some similar cases. In highly hydrated hydrophilic systems of gels or semigels hydrated ions will be pulled in or pushed out due to existence of hydration forces in the hydration layers. (We suppose that most of ions are hydrated with prevailing the orientation of water molecules by H-atoms to anions (proton-acceptor groups) and by O-atoms to cations (electron-acceptor groups).) Due to this effect the concentration of these ions in bulk of water will be changed.

In order to satisfy the condition of electroneutrality chemical ionic reactions will have to take place here e.g. the acid-base ones which lead to changes in pH.

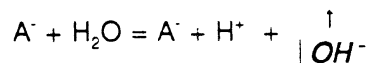
Theoretical examples

Explanation of increasing pH:

For instance, in a coacervates system pulling in of hydrated anions A^- into the water shells of microgel particles of the coacervates prevails. Due to this effect the concentration of cations K^+ and anions A^- must prevail in bulk of water and water shells, respectively. In accordance with the condition of electroneutrality, the ions will then have to react with water as follows:



In water shells



The water molecules must dissociate to produce more OH^- and H^+ ions which are repelled due to electrostatic forces and high mobility into bulk of water and water shells, respectively, i.e. the pH of supernatants increases.

Explanation of decreasing pH

In case of the systems in which the pulling in of hydrated cations K^+ into water shells of microgel particles prevails the pH will be changed with the opposite tendency, i.e. the pH of solution will be decreased.

All these effects are known⁵ as Pallman's effect of colloids and suspensions and have not been explained in satisfactory way up to this time.

Observations

Anomalous changes of pH:

As we can see from Table I this behaviour can really be observed in the cases of the hydrated systems with CDD. In all the cases the pH was measured with a combined conventional glass electrode. In comparison with distilled water the pH in hydrated systems of UF pre-condensate and polyester (PES) is different, being further changed, sometimes in an anomalous way, by dilution with distilled water.

The behaviour of PES system differs from that of UF pre-condensate system. Particularly interesting is the behaviour of sodium and ammonium acetates: both of them increase the pH of PES (originally 3.25) to the values of 4.15 and 4.75, respectively, which is surprising because the pH values of comparable aqueous solutions (concentration of the both acetates in PES and water was 5%) of the two acetates are 8.2 and 5.5, respectively.

Experiment with moving electrode:

After dilution of UF pre-condensate (e.g. 5 %), addition of 5 % NH_4NO_3 and sedimentation of coacervates, the pH was measured with combined conventional glass electrode. Moving of the electrode up and down in the system causes simultaneous moving of the pointer of pH meter from 4.2 (supernatant) to 3.6 (coacervate) and vice versa.

The explanation of this observations is based on the above-mentioned theoretical examples. A typical rule for the given phenomenon is strong relation of the pH of such systems

to the concentration of hydrated hydrophilic oligomer systems.

Conclusion

According to the experiments, water and aqueous medium play a very important role in the behaviour of all hydrated hydrophilic systems. Experiments with the model systems characterized by the so-called CDD reveal that their behaviour and phenomena connected with them can simply be explained with the help of the concept of hydration forces and SCHL theory.

It can be stated that the behaviour of modelling systems, particularly those of UF pre-condensates, is in full accordance with the theoretical assumption of SCHL theory. Owing to this information the modelling system of UF pre-condensate is shown as a useful simulating tool for measuring the properties of water medium from the viewpoint of hydration forces, i.e. from its influence on the level of hydration forces which is of use in the hydrated hydrophilic systems. This influence is given by the value of the relative hydration factor g .

If $g \geq 1$ (in comparison to distilled water), then water medium acts in a negative way on the level of hydration forces, i.e. decreases the action of attractive forces and increases the action of repulsive forces.

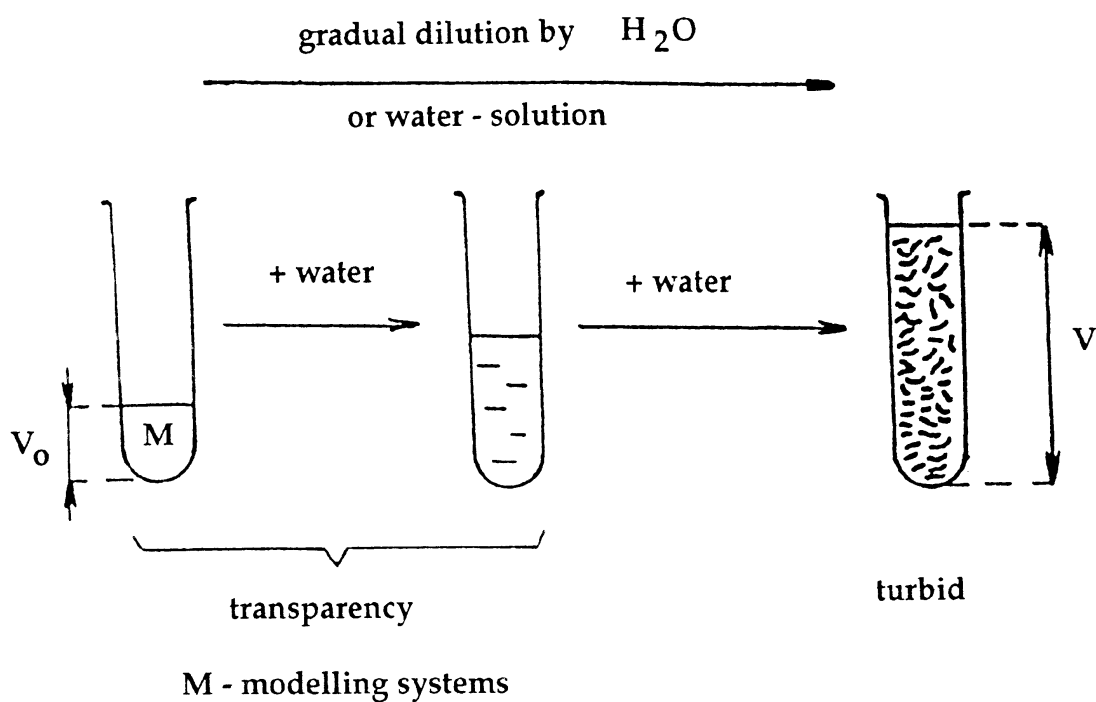
If $g \leq 1$ then water medium acts in a positive way on the level of hydration forces, i.e. increases the action of attractive forces.

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Table 1. Anomalous changes of pH in water systems created with hydrated hydrophilic oligomeric systems of the UF precondensate and PES

Concentration of added components (%)	pH in				
	Distill.H ₂ O	UF precondensat(50%)		Polyester (PES)(50%)	
				Diluting with distill.water	
-	6.6	7.3	fall	3.25	insignificant
Urea (5 %)	7.0	7.5	fall	2.85	fall
NH ₄ SCN (5 %)	5.3	3.0	go up	2.2	fall
NH ₄ NO ₃ (5 %)	5.2	3.1	go up	2.7	fall
K ₂ Cr ₂ O ₇ (5 %)	3.7	5.3	fall	-	-
NH ₄ OH (5 %)	11.3	9.5	insignificant	-	-
NH ₄ polystyrenmaleinat (5 %)					
NaSCN (5 %)	10.9	6.1	-	-	-
	5.8	-	-	2.15	fall
CH ₃ COONa (5 %)	8.2	-	-	4.15	fall to 3.7
CH ₃ COONH ₄ (5 %)	5.5	-	-	4.75	fall
Dikyandiamid (5 %)	6.6	-	-	2.85	fall



$$CDD = \frac{V}{V_0} : V = V_0 + V_k$$

CDD_0 - Critical degree of dilution in distilled water

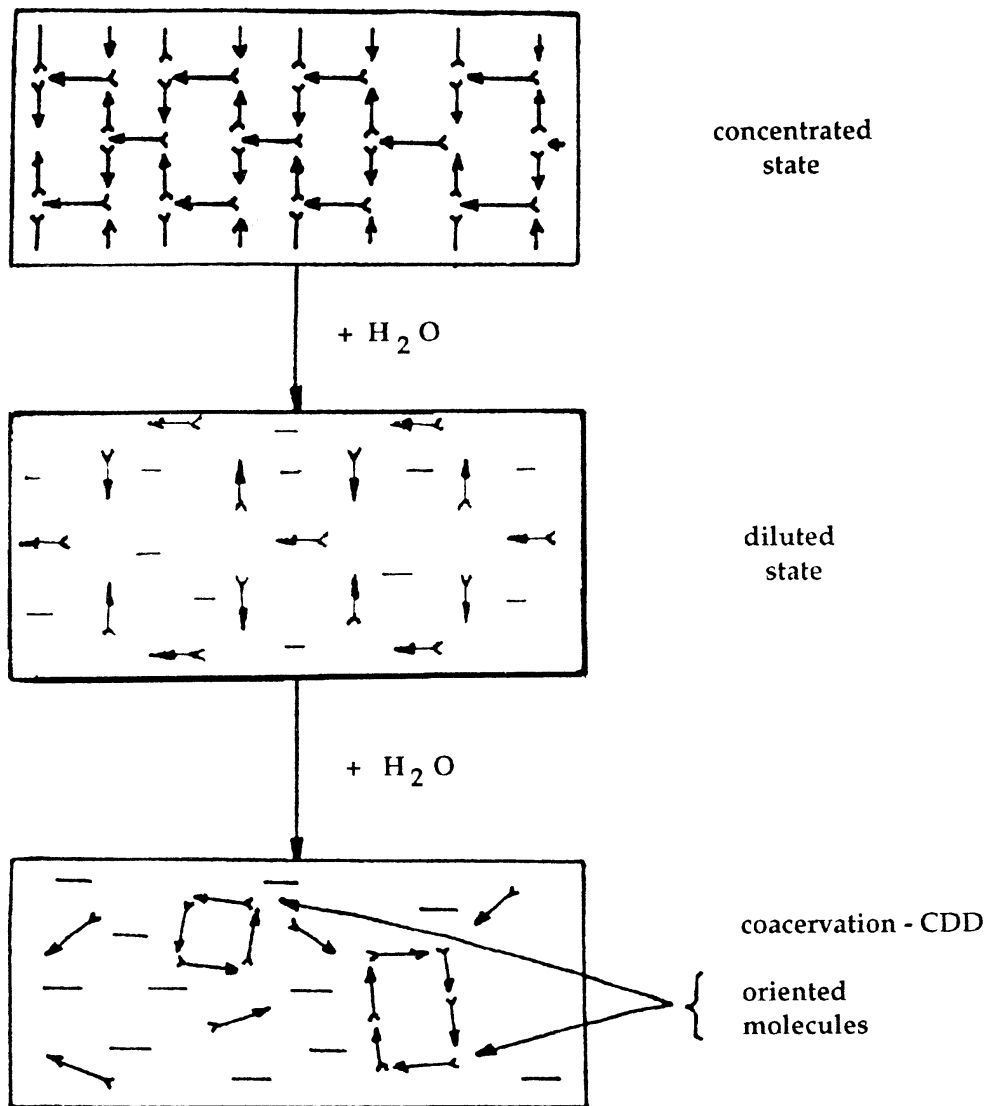
CDD - Critical degree of dilution in water - solution

$$g - I = f_H = \frac{CDD - CDD_0}{CDD_0} \quad \text{Relative hydration factor}$$

If $g < 1$ or $f_H > 0$ - Increase of influence of attractive forces in the bonding system of hydration forces

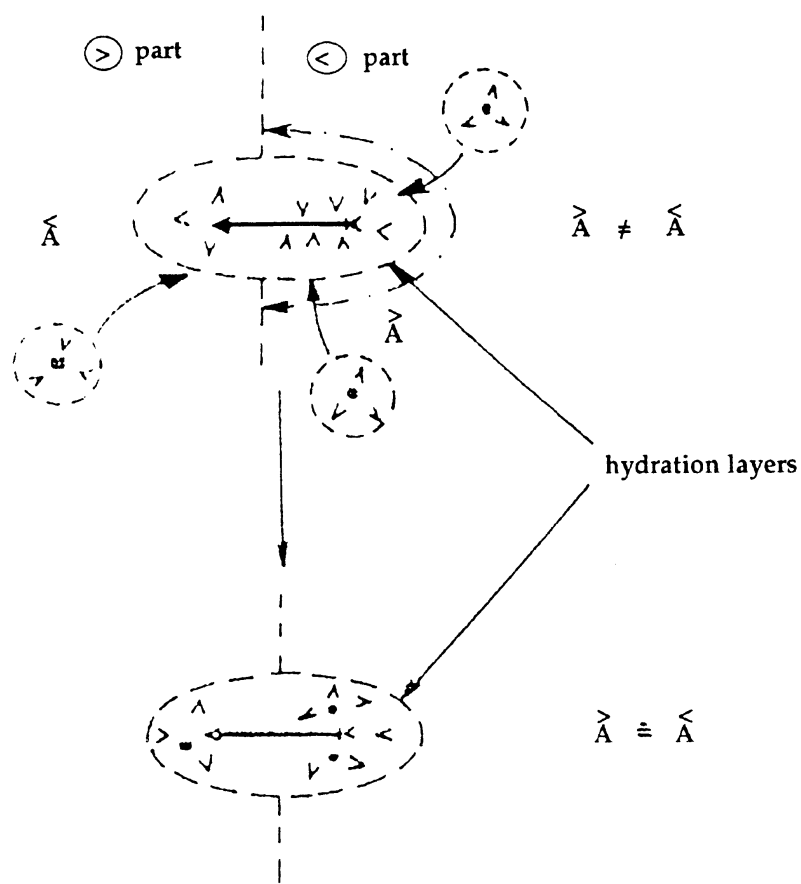
If $g > 1$ or $f_H < 0$ - Increase of influence of repulsive forces in the bonding system of hydration forces

Fig. 2 Evaluation of the effect of hydration forces by means of hydration hydrophilic modelling system



← - schematic representation of the "bipolarity" of a hydrated oligomer molecule caused by the different orientation of water molecules at both ends of the molecule
 _ - free water molecules outside hydration spheres

Fig. 3 Schematic representation of the behaviour mechanism of the bipolar, hydrated, oligomer CDD system during its dilution with water



→ - oligomer molecule of "bipolar" nature from the point of view of the orientation of water molecules in the hydration sphere

•• - hydrated molecules or ions of "monopolar" nature from the point of view of the orientation of water molecules in their hydration spheres

<,> - the orientation direction of water molecules in hydration spheres

\hat{A}, \check{A} - surfaces of the hydration apheres with the opposite orientations of the water molecules

Fig. 4 Schematic representation of the mechanism changing the orientation of water molecules in hydration spheres around oligomer hydrophilic molecules of bipolar nature during the addition of other compounds - from the point of view of the orientation of water molecules

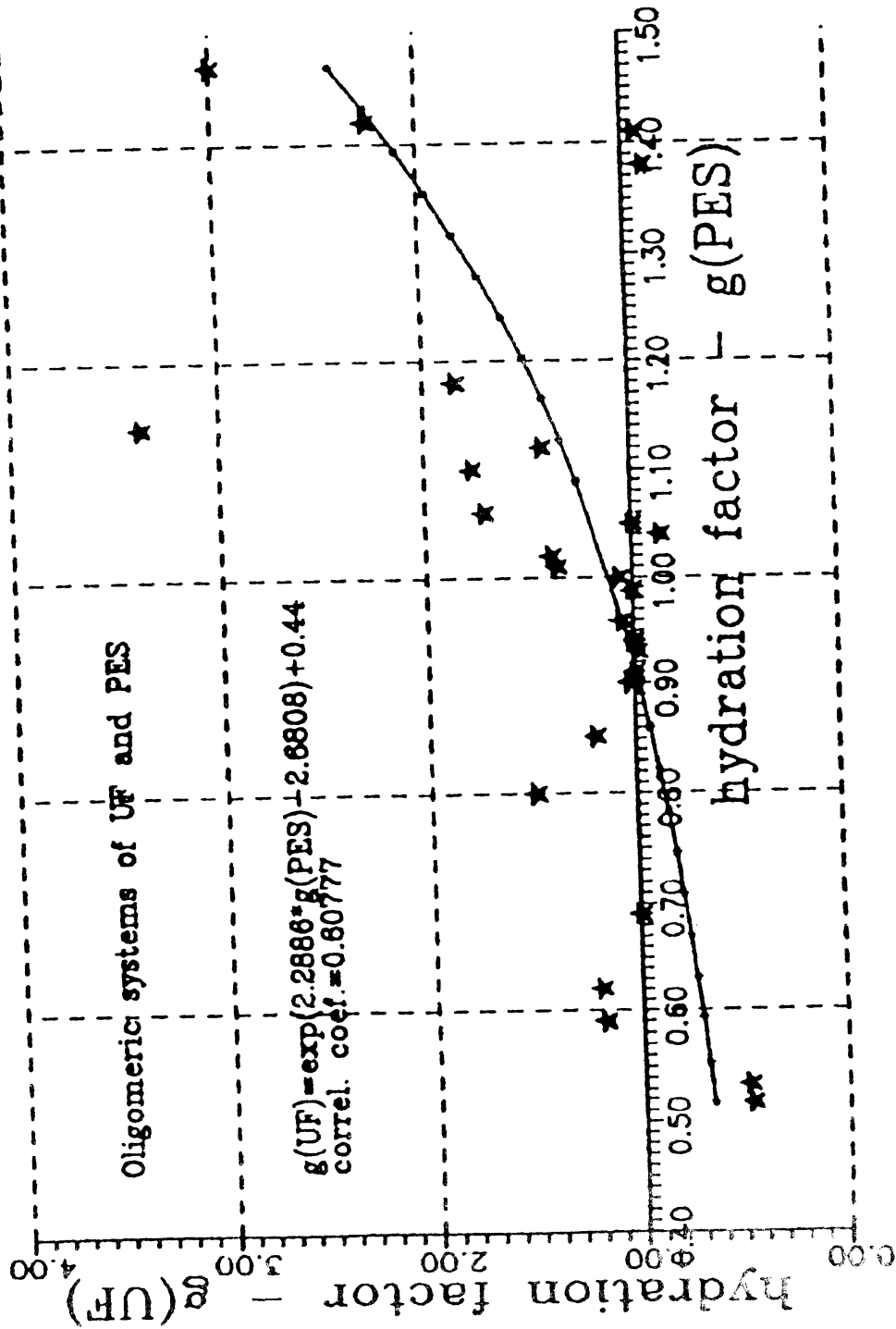


Fig. 5 Relationship between the hydration factors-g of hydrated hydrophilic systems characterized with CDD; g = CDD/CDD (in distilled water without other components)

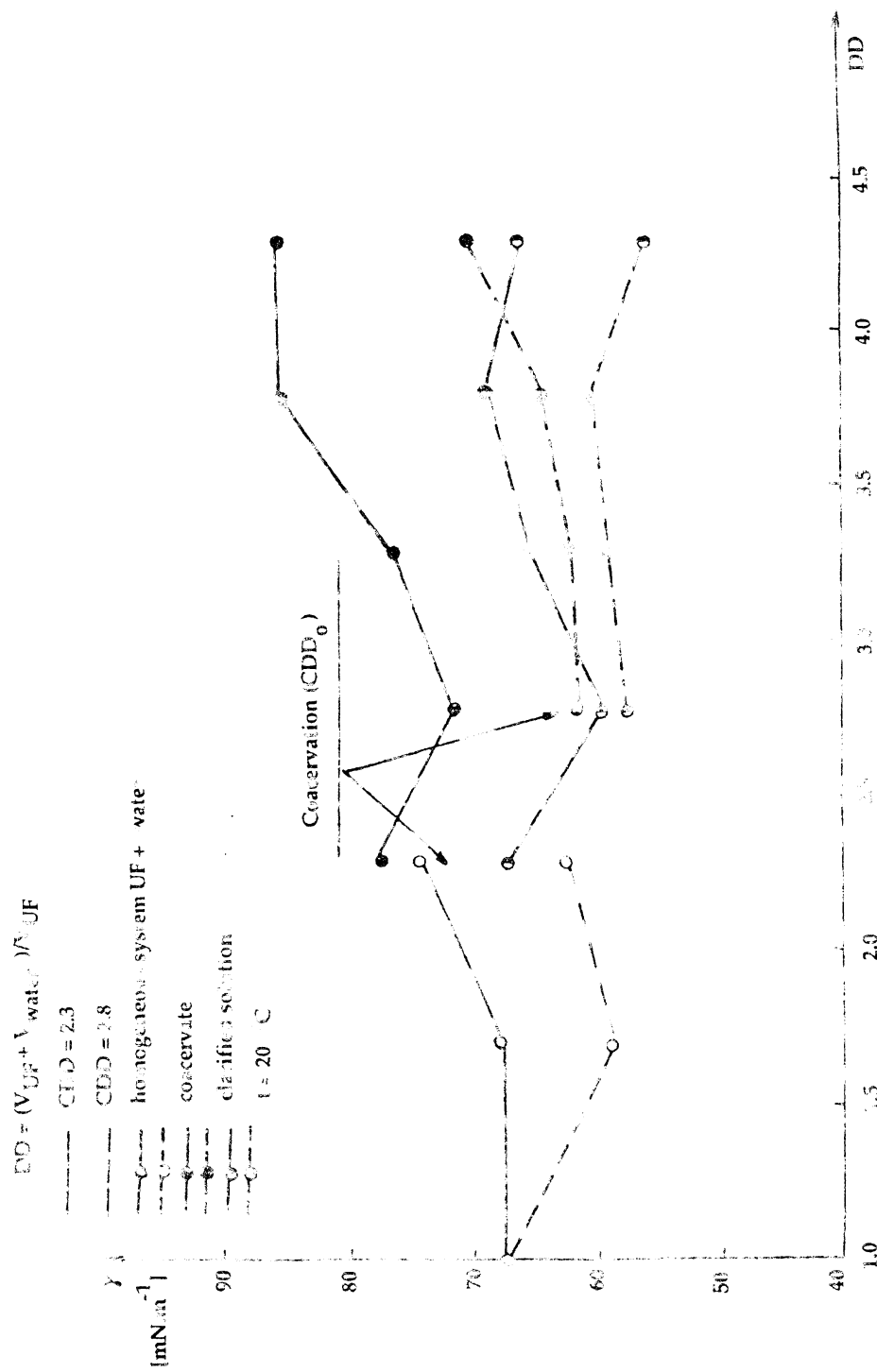


Fig. 6 Relationship between the surface tension of UF pre-condensate and the degree of dilution (DD)

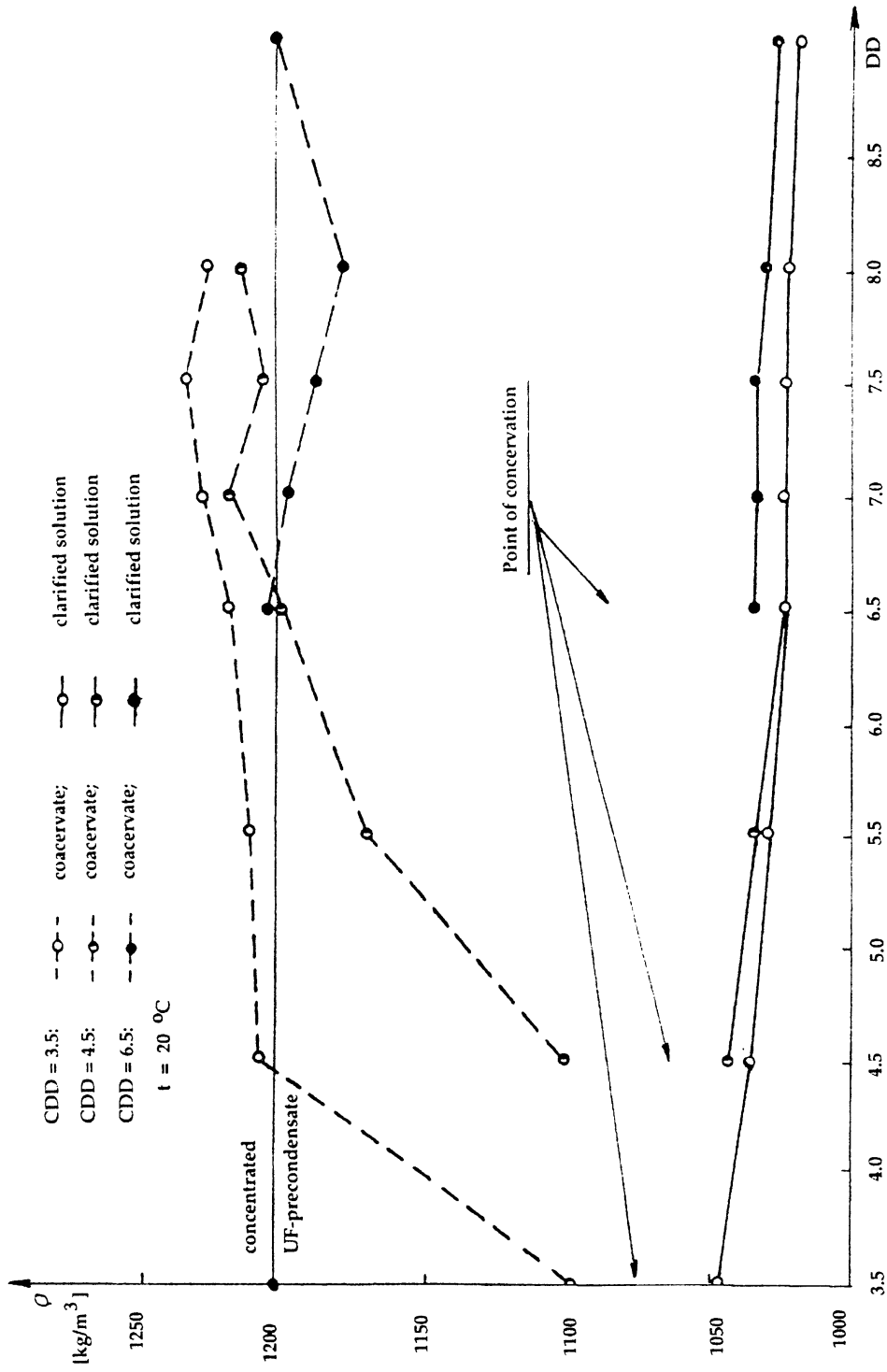


Fig. 7 Dependence of density both liquid phases upon the degree of dilution (DD)

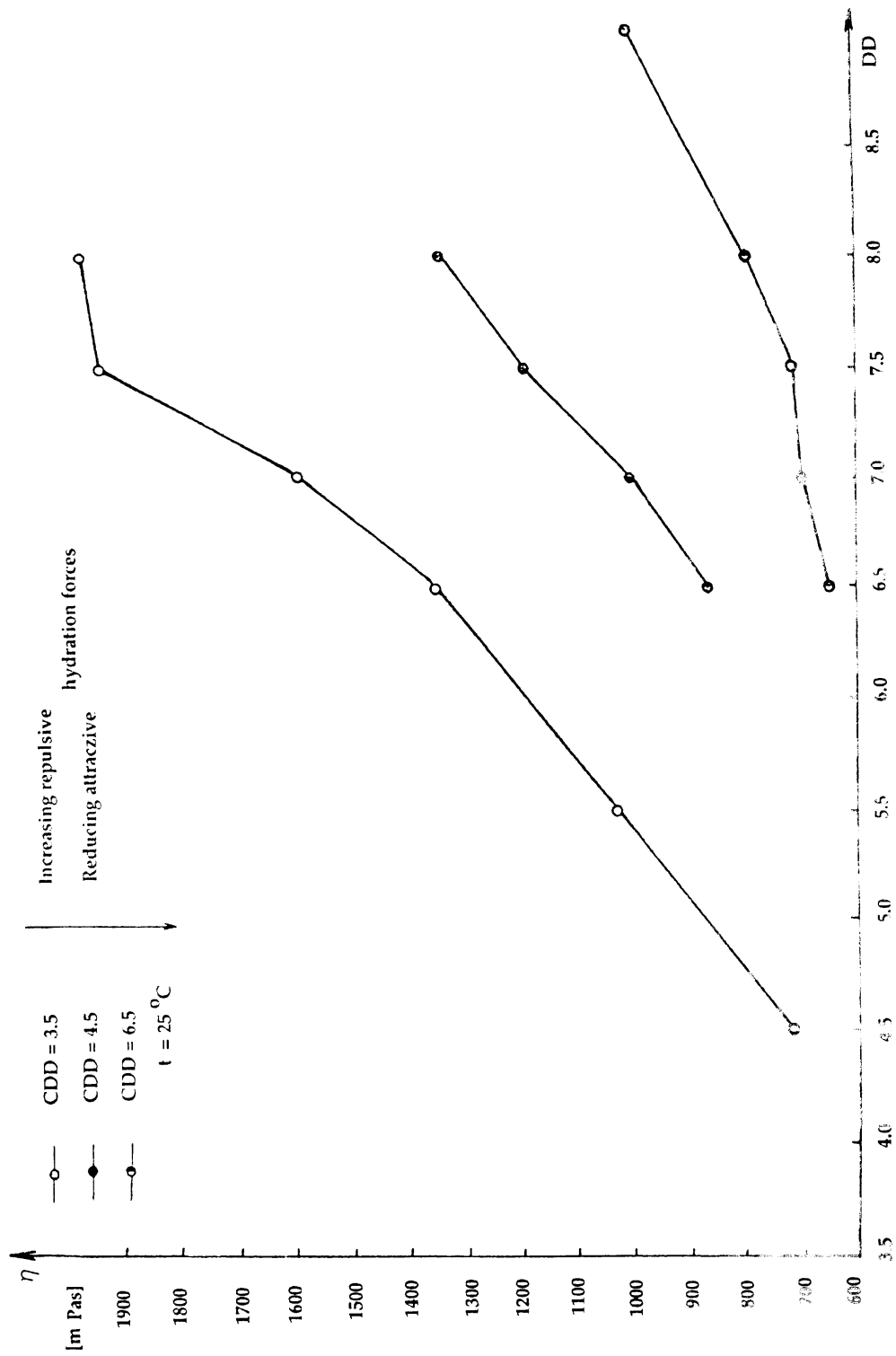


Fig. 8 Dependence of viscosity coefficients of coacervates upon the degree of dilution (DD)

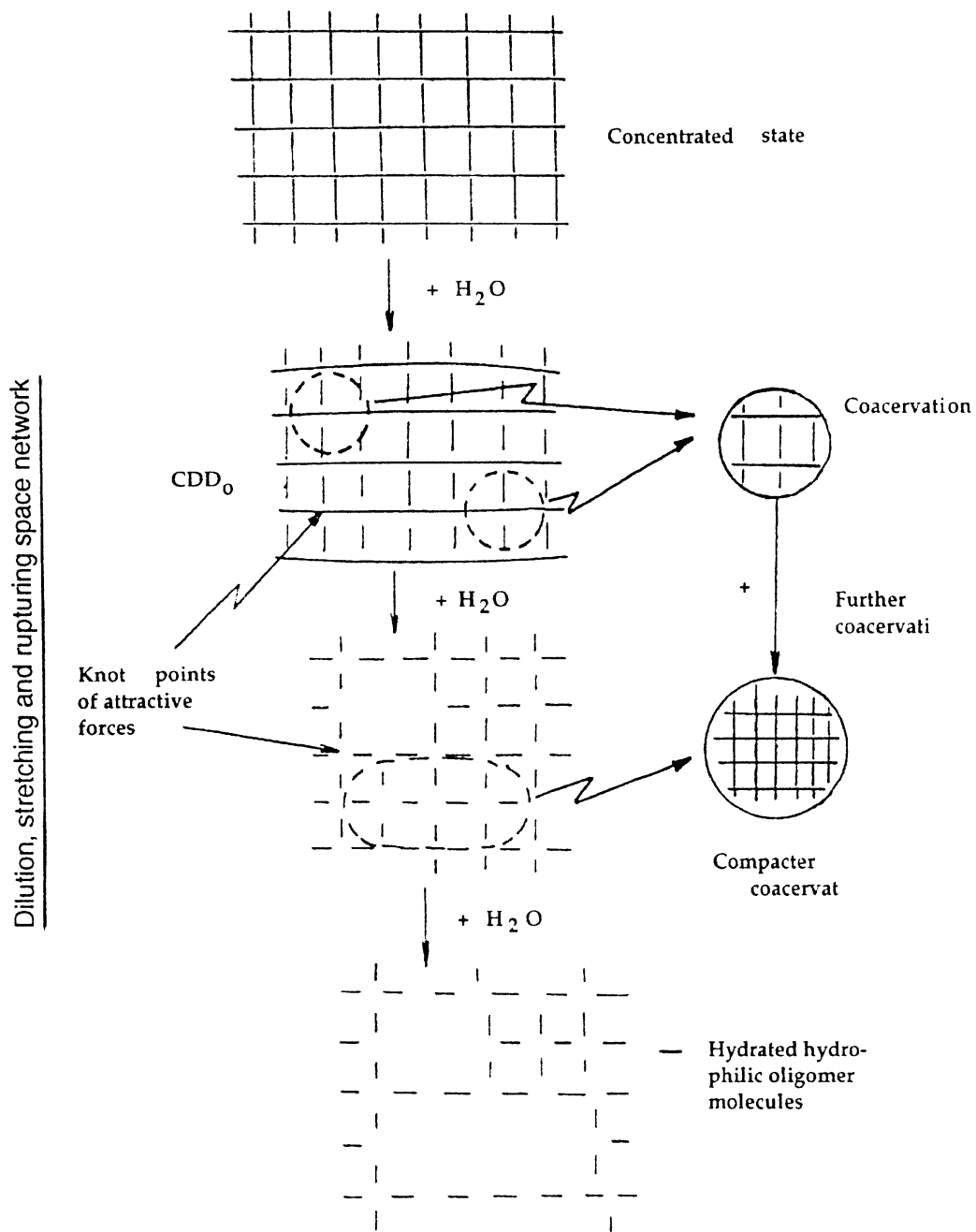


Fig. 9 Mechanism of the rupture of the stretching space network caused by gradual dilution

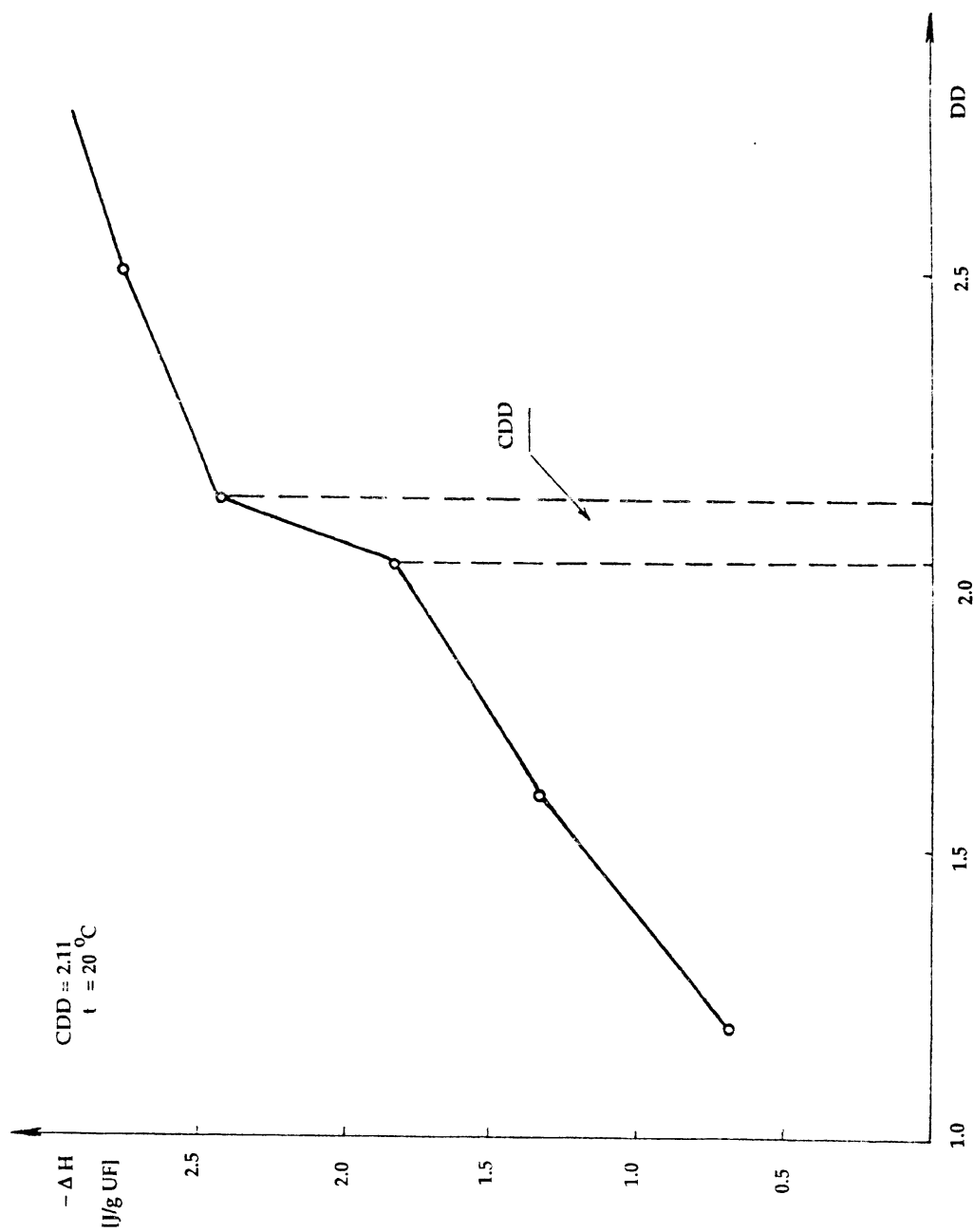


Fig. 10 Enthalpiometric measurements. Dependence of heat of interaction upon the degree of dilution (DD)

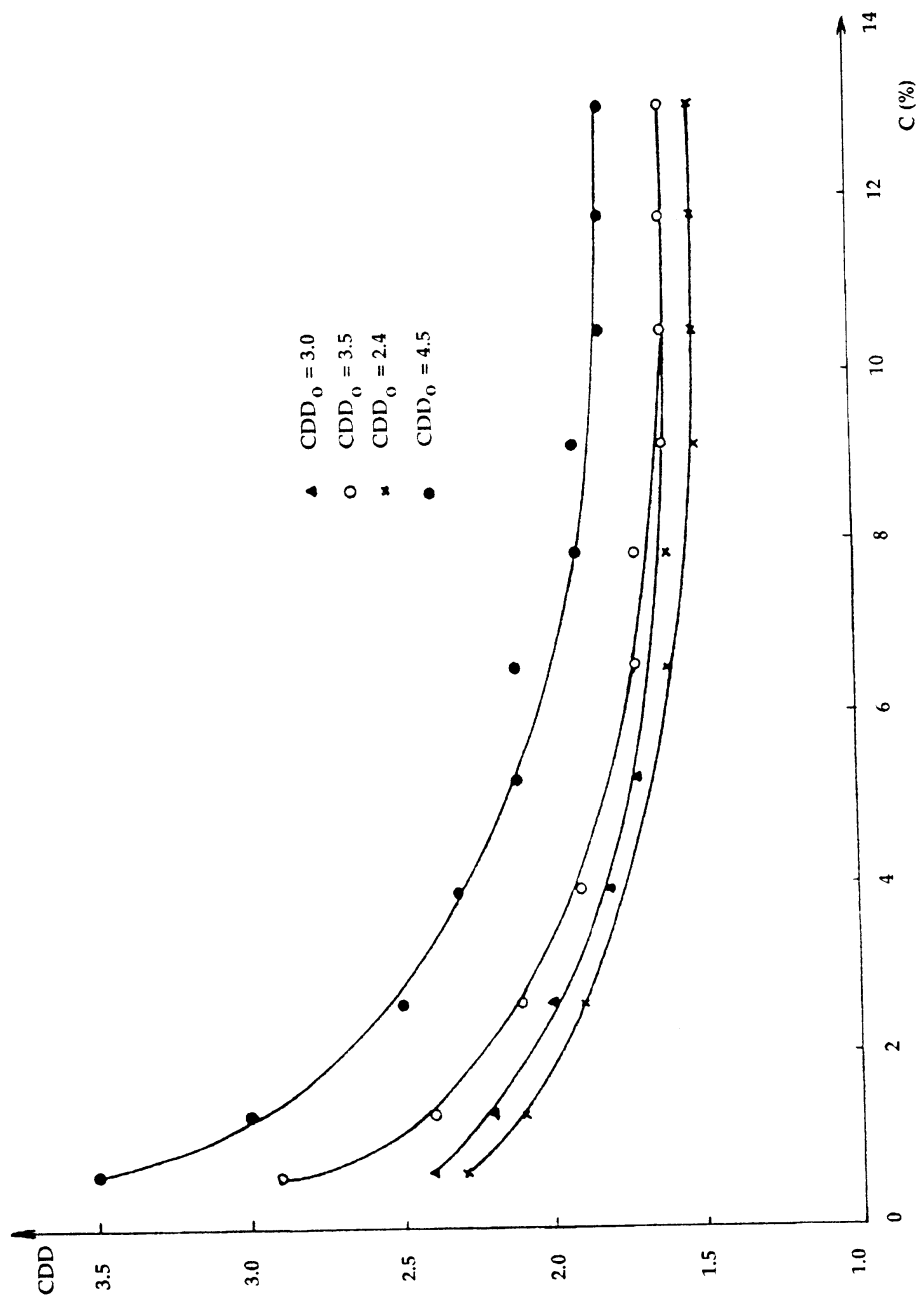


Fig. 11 Dependence of critical degree of dilution (CDD) on concentration of spent sulphite liquor

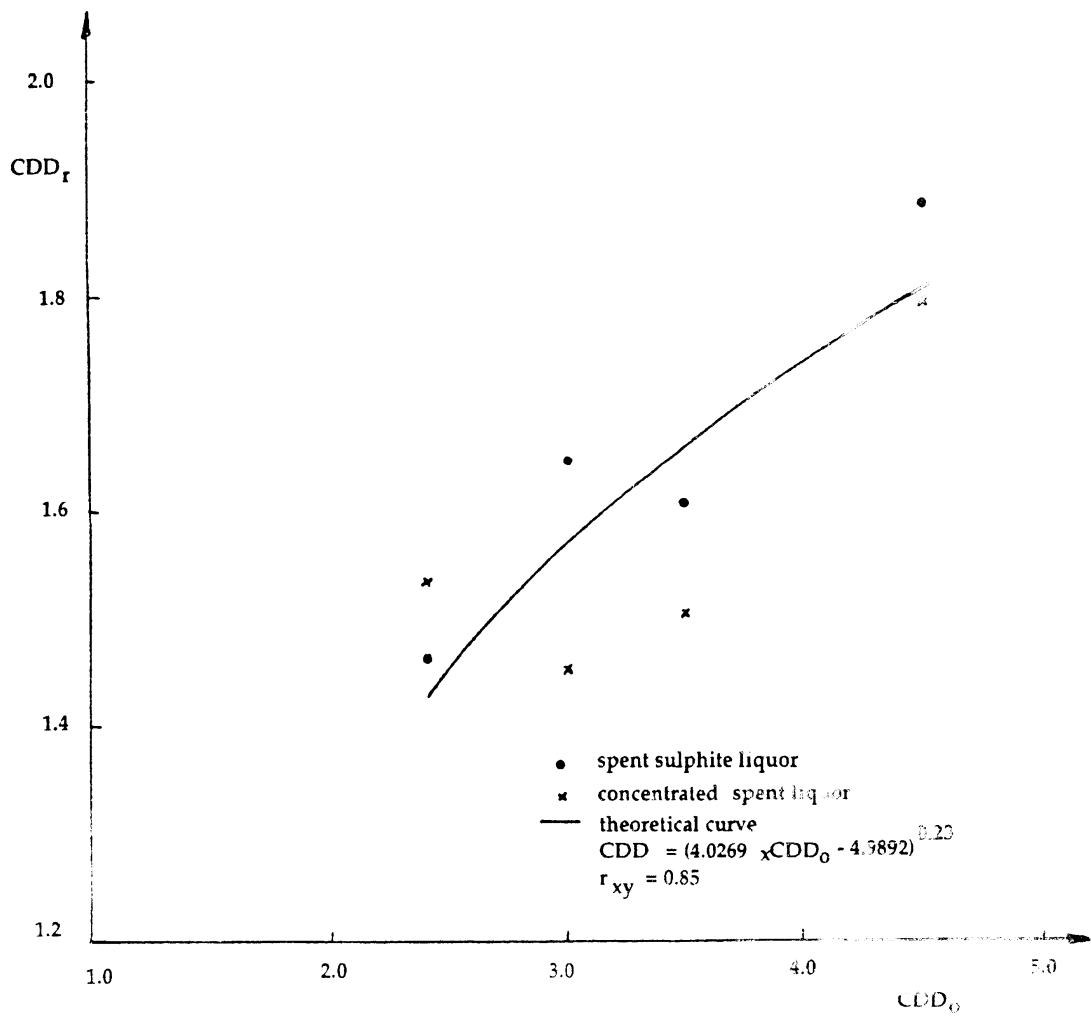


Fig. 12 Dependence of the steady value of CDD (CDD_r) upon CDD_0 , UF pre-condensate

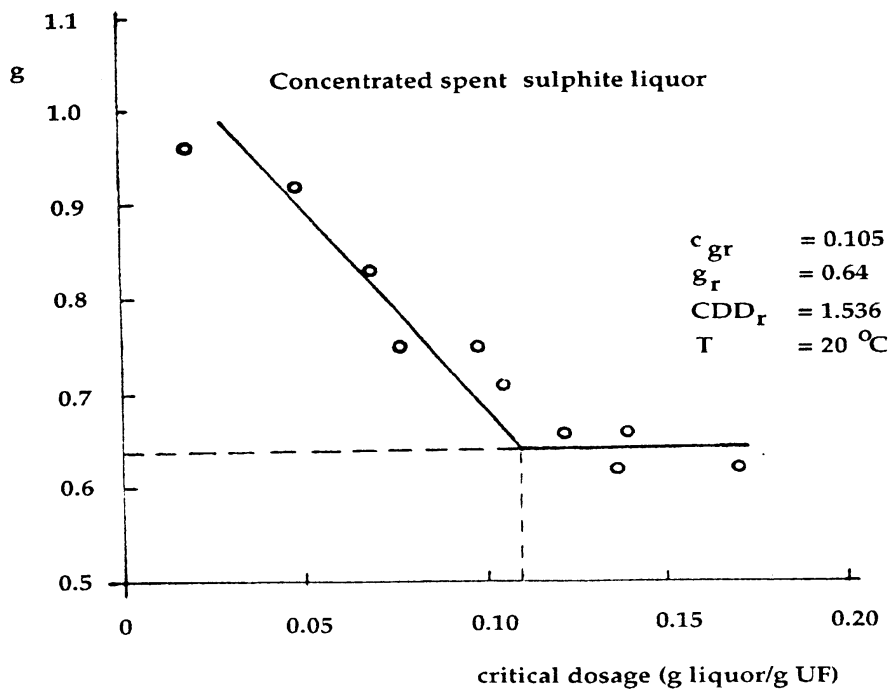
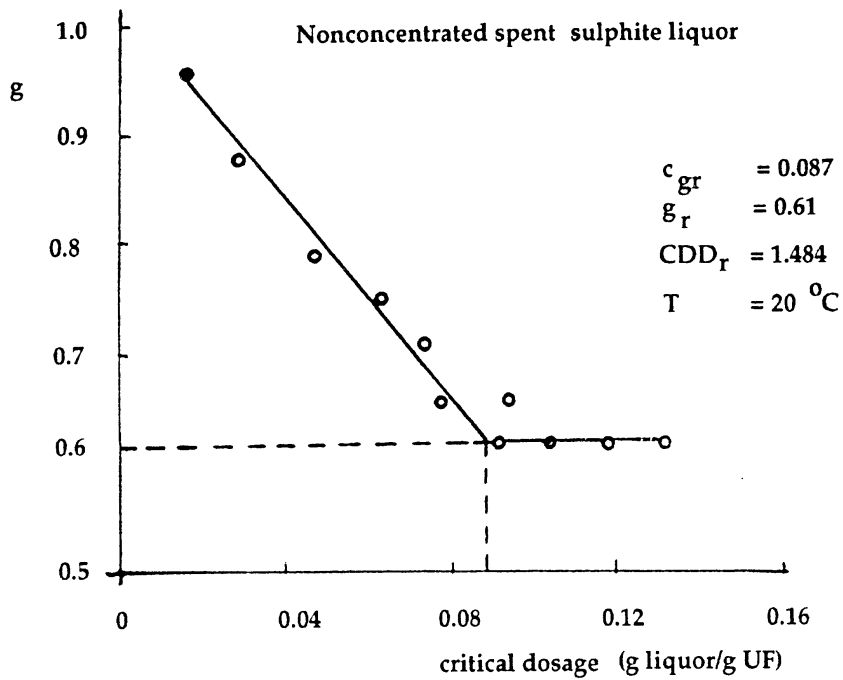


Fig. 13 Relationship between rel. hydration factor upon the critical amount of spent sulphite liquor added (UF precondensate with $CDD_0 = 2,4$)

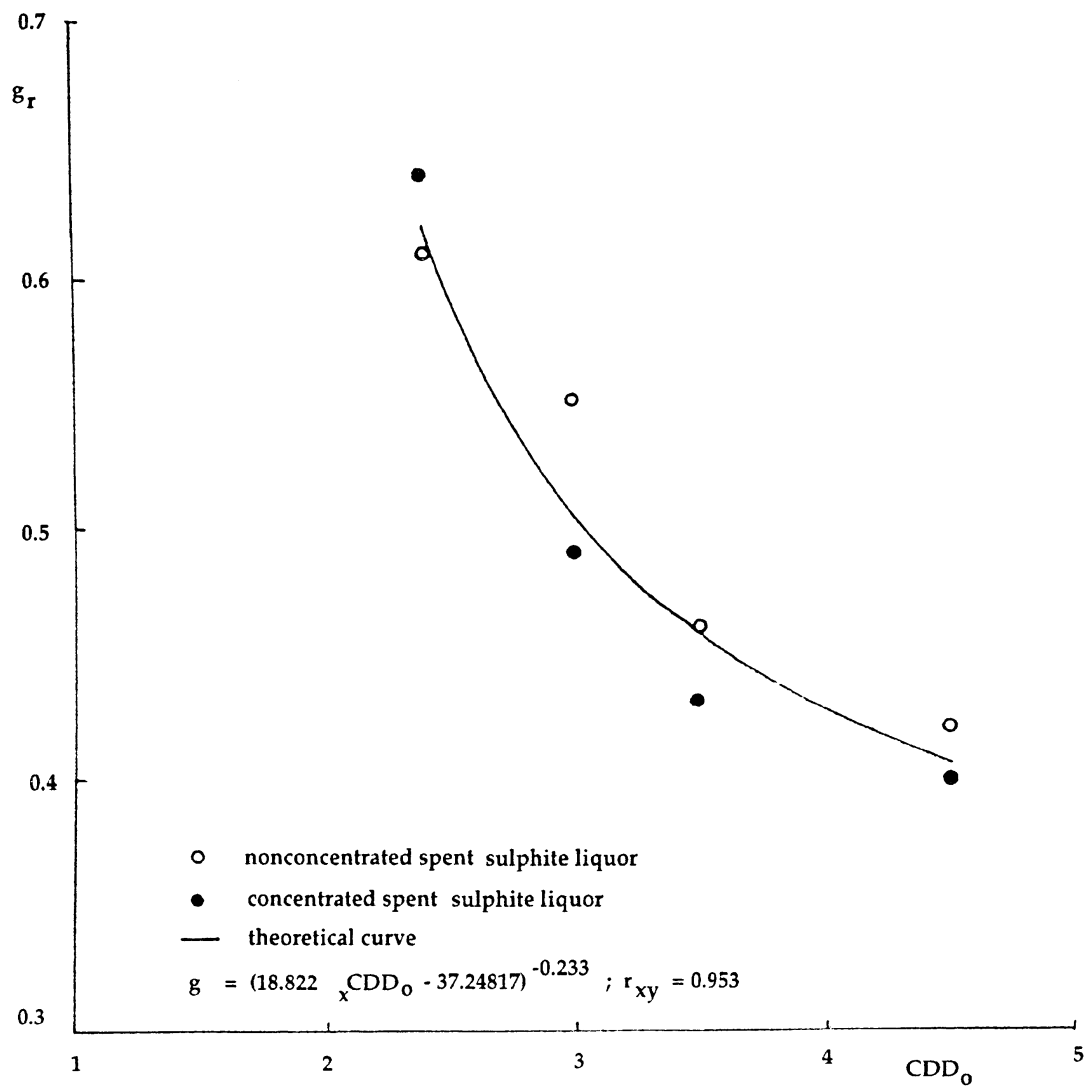


Fig. 14 Relationship between steady value of rel. hydration factor g , and CDD_0 of UF pre-condensate ($T = 20^\circ\text{C}$)

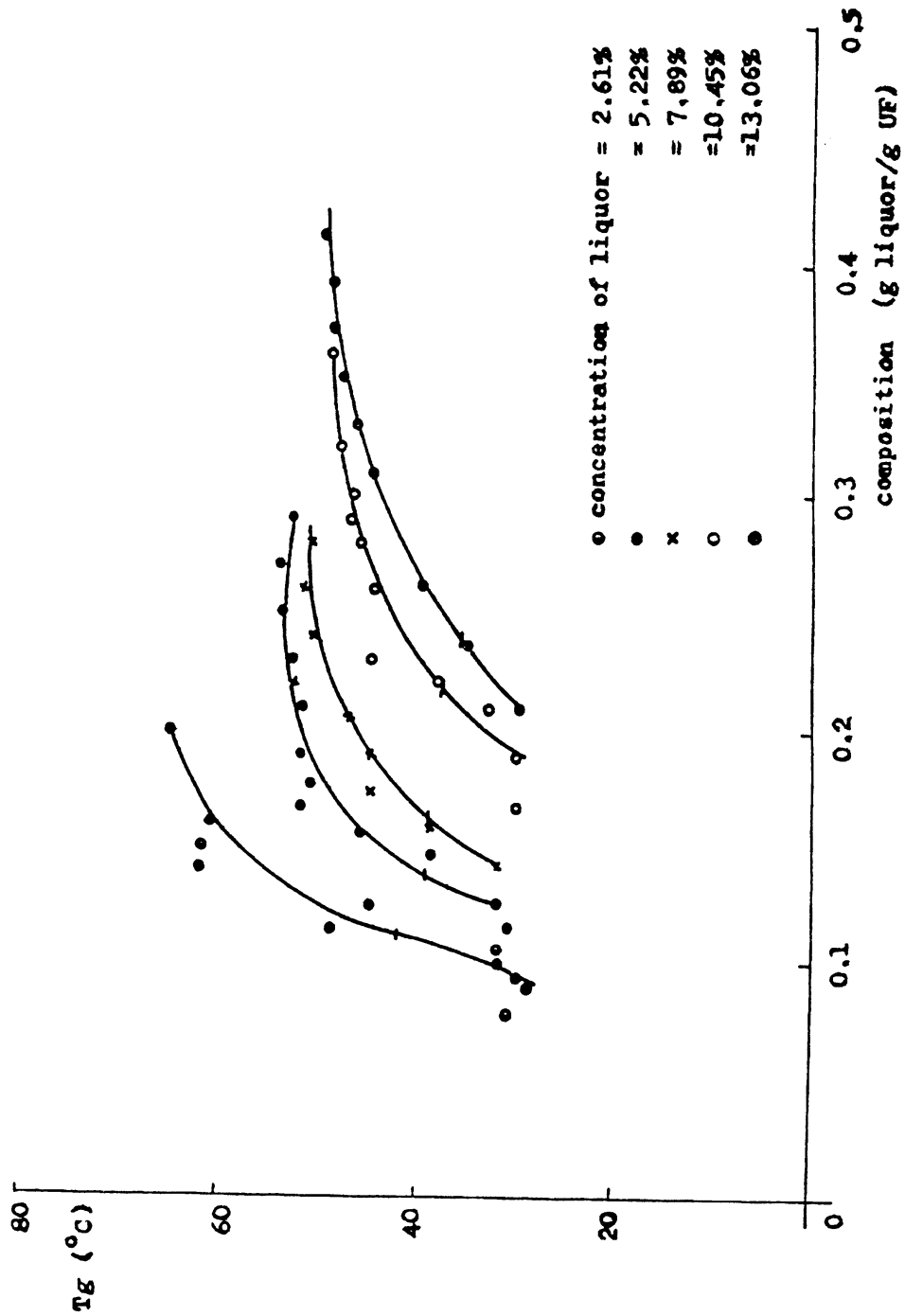


Fig. 15 Dependence of gelling temperature (T_g) upon composition of spent liquor (Nonconcentrated spent sulphite liquor, UF pre-condensate with $CDD_0 = 4.5$)

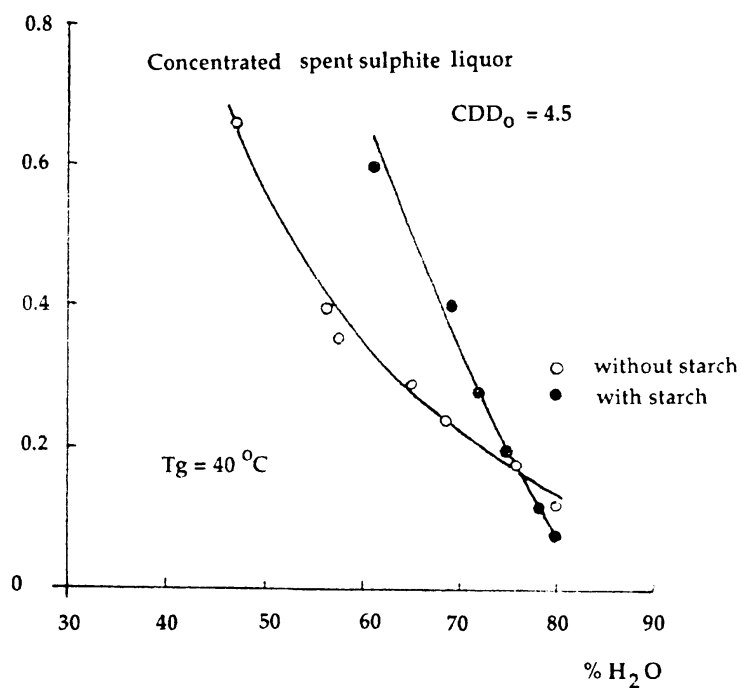
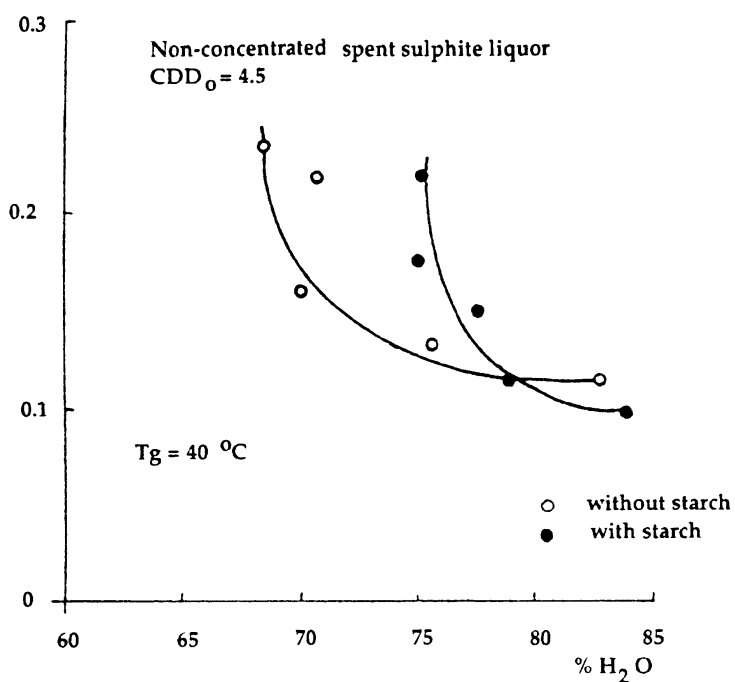


Fig. 16 Relationship between composition of coacervate in the point of equivalence and concentration of water