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BEHAVIOUR OF HYDROPHILIC COMPONENTS IN PAPER
MAKING SUSPENSIONS - PART IV.
TEMPERATURE AND COMPOSITION INFLUENCE UPON
RHEOLOGY OF AQUEOUS GLUES AND COATING COLOURS

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The viscosity-temperature curves of some aqueous glues and coating colours have a more complicated shape with one or more peaks, i.e. with one or more maximums and minimums. The viscosity-temperature behaviour of these mixtures changes significantly with any change in their composition and depends on shear rate as well. The authors have attempted to explain this behaviour by means of the concept of the hydration bonding system among interacting particles of dispersion. This concept is based on effective action of the so-called hydration forces.

Introduction

The rheological properties of aqueous glue mixtures and coating colour systems play important role in technology of glueing and coating, respectively. Attention is dedicated to the flow behaviour of glues and coating systems which depends on pigment and binder concentrations, additives, shear rate, and electrolyte content of the ambient fluid. The rheological properties of these systems are of such quality that a number of important experimental corrections are needed to obtain flow behaviour characteristics. For example, a flow through a given capillary is corrected for entrance pressure losses followed by a correction for slip effects¹. A typical property of coating colours is the shear thinning or shear thickening flow behaviour. The concentration dependence of viscosity of several coating colour systems has been reviewed by Metzner². Metzner's review² includes equations of Mooney, Thomas, Maron and Pierce, and Frankel and Acrivos. In recent years, several viscoelasticity measurements have been used as a tool to study the aggregation that occurs within a coating³⁻⁵. These studies provide a broad basis for further investigations of interactions - controlled rheological properties.

A lesser attention is dedicated to temperature influence upon flow behaviour of these concentrated hydrated hydrophilic dispersion systems. As usual, the temperature dependence of viscosity has been found to obey the Andrade equation^{6,7}:

$$\eta = A \exp(E/RT) , \quad (1)$$

i.e. the viscosity vs. temperature dependence has a monotonous decreasing character. Equation (1) is used obviously to calculate the activation energy, E , for viscous flow. But, as we can see from the next figures, there exist some cases with opposite and complicated character in this behaviour.

Attempts to describe the flow behaviour involving structural change have involved a variety of theoretical approaches. Among these are the combined applications of rate processes and hydrodynamic theories. Rate processes are used to describe the formation and destruction of bonds between particles or groups

of particles, and hydrodynamic theories which are applied to the structures formed¹. Bonds are formed by aggregation of particles due to the Brownian motion and shear-induced rupture.

The theoretical background of description of this bond formation is based upon the activity of colloidal forces like electrostatic and van der Waals forces in accordance to DLVO theory⁸, and hydrodynamic forces⁹. A quantitative description of shear thinning systems is possible for instance according to the theory of Cross¹⁰. A theory of shear thickening systems has also been developed by Gillespie¹¹ for systems that can be characterized by a simple relaxation time.

Experimental

Materials

All the glues used were mixtures of poly(vinyl acetate) (PVAC) water dispersions and wheat starch solution. The PVAC dispersions were designed as follows:

- Duvilax^R BD-20, homopolymeric PVAC dispersion of 55 % dry matter substance, nonionic with 20 % dibutylphthalate and pH 5.0,
- Duvilax^R K-18, copolymeric PVAC with butylacrylate dispersion of 53 % dry matter substance, nonionic and pH 5.0, both with particle diameter 1.0 μm . The wheat starch (WS) solutions were prepared in various concentrations (1-7 %) in distilled water.

All coating colours were suspensions of kaolin clay of different concentrations, polyacrylate latex and starch as co-binder, tetrasodium pyrophosphate as dispersant and additives as defoamer, calcium stearate, sodium hydroxide and optical brightener. The dosed amounts of binders and additives were held constant. The basic concentration of kaolin clay suspensions were changed only in the range of 50 - 75 % dry matter, the dosed amount of dispersant in the range of 0.15 - 0.5 %, and the polyacrylate binder in the range of 9 - 14%, both calculated on dry matter of kaolin clay. The kaolin clay was a coating clay having an equivalent spherical diameter of 2.18 μm . The distri-

bution widths are based on the 15.9 and 84.1 percentile. The particle size analyses were performed in SediGraph 5100 - micro-sedimentation analysis system containing an internal fixed - position X-ray source/detector system and vertical all movement assembly produced by Micromeritics^R Co. As binder and cobinder were used:

- Sokrat^R 1018, poly(ethyl acrylate) latex of 40 % dry matter substance, pH=4.5, with particle diameter 0.14 μm ,
- Oxamyl^R 3009, oxidized starch from wheat corn. For mixing and preparing the coating colours the 2.2 % solutions was prepared. The screening and procedures for determining the colour density were performed as usually.

All components of glues and coating colours in the present study were commercial papermaking grades used as received.

Rheological Measurements

The viscosity measurements were carried out in a rotation viscosimeter of Searle type¹² designed as RHEOTEST II, by MLV Sitz Freital (BRD). The viscosimeter assembly have featured with the inner rotated cylinder under different revolutions. The working under shear rate in the range $D = 24.3 - 1\ 312\ \text{s}^{-1}$. The outer non-rotated cylinder was immersed in a water bath connected to the thermostat controlling unit which held the temperature of measuring cell with the accuracy of 0.5 °C. The shear stress evoked in measuring cell was detected by an inner rotating cylinder due to the force moment acting upon its surface. The rising force moment was measured electrically and this enabled us to measure (after calibration) the resulting shear stress τ directly.

We have received curves of flow behaviour characterized by curves of shear stress vs. shear rate. These curves were converted into apparent viscosity coefficient by using the relation

$$\eta = \tau/D \quad , \quad (2)$$

All the measurements were repeated at least four times. After

reaching the maximum temperature (usually 95 °C) the system was cooled down and the whole experiment was repeated again. The apparent viscosity - temperature curves in the following figures are represented by the mean values obtained after statistical treatment of the experimental results. The maximum error in apparent viscosities range was 10.5 % for 95 % confidence interval. Practically no changes of peaks location on the temperature axis were observed when repeating the experiments.

Results

Glues

Some typical results of viscosimetric observations with the above-mentioned systems of glues are shown in Figs 1 - 7. As we can see from the figures the represented dependences of apparent viscosity coefficient upon the temperature measured at various shear rates, the rheological behaviour of these mixtures are changed significantly with any changes in their composition, temperature and depend on the shear rate as well.

A typical simple shape of viscosity vs temperature curves according to eq. (1) is represented in Fig. 1. However, the viscosity - temperature curves in Fig. 2 have a more complicated shape. Some of these curves have a maximum near 70 °C and a minimum at 80 °C which disappear with increasing shear rate. It means that the bonds in the structure of interacted particles are relatively weak and destroyable with mechanical action of relatively low shear rates.

The viscosity - temperature curves in Figs. 3 and 4 have even more complicated character but, again, the two maximums disappear with increasing shear rate. At high shear rates the viscosity is independent of temperature. Remarkably these facts are evoked due to changes in concentrations (7 % and 1 %) and dosed amounts of the starch. The influence of concentration upon the shape of viscosity - temperature curves only may be seen from Figs 5 - 7 in the case of wheat starch. The starch system at concentrations of 5 % (three maximums at 40 °C, 60 °C and 80 °C) has the most complicated shape of these curves (see Fig. 5). With increasing starch concentration the maximums gradually dis-

appear - at 6 % starch concentration their number can be seen in Fig. 6 - and finally there exists only one maximum at 60 °C. For the 7 % starch concentration (see Fig. 7) the maximums practically disappear in full extent.

Coating Colours

Viscosity vs. temperature curves of coating colours with similar shape as glues are shown in Figs 8 - 12. At different concentrations of clay suspensions (62 - 70 %), and for dosed amount of dispersant (0.15 - 0.5 %), the clay concentration was held constant at 62 %. However, as usual the majority of viscosity curves shear stress vs. shear rate reveal shear thinning character with high viscosity at low shear rates and constant viscosity at higher shear rates. The flow behaviour looks like that of a Bingham and a pseudoplastic liquids.

The number, location and extent of peaks on viscosity vs. temperature curves are influenced by both the clay concentration and amount of dispersant. The curves in Fig. 8 for 62 % clay concentration and 0.15 % dispersant show three peaks (maximums) at 40 °C, 60 °C and 80 °C with decreasing character at higher shear rates. The increased concentration of clay suspension evokes a shift of peaks. Figure 9 shows that colour containing 65 % clay suspension had only two peaks at 50 °C and 70 °C and the colour containing 70 % clay suspension (Fig. 10) resulted with one but extensive peak only.

Similar behaviour can be observed in the case of dispersant. Increasing amount of dispersant evokes a shift of peaks one in respect to other (compare Figs 8 and 11). In the case of 0.5 % dispersant (Fig. 12) it seems that these peaks disappear or appear in a small extent. The viscosity is more dependent on shear rate in full range of measured temperatures.

The clay suspension by alone shows similar but a more simple character of the viscosity vs. temperature curves as compared with the corresponding coating colours (see Fig. 13). At relatively small concentrations (50 - 55 %) these curves suggest typical but inverse behaviour, i.e. the viscosity increases continuously with temperature. At a medium concentration (60 - 55 %)

this behaviour is somewhat complicated. The viscosity vs. temperature curves appear at a given temperature range the extremes or peaks. At higher concentrations (see Fig. 13) these curves show a relatively simple character again.

The viscosity vs. shear rate curves in the case of clay suspension have also shown a less complicated character than the coating colours, especially at higher concentrations of clay suspensions. The shear thinning flow behaviour at lower relative clay concentrations (50 - 60 %) is changed at higher concentrations (62 - 70 %) and at lower temperatures (in the range of 20 - 70 °C) it is shifted towards shear thickening flow behaviour.

The concentration and composition of coating colours and glues appears to be the major cause of the complicated temperature - flow behaviour. This is a result of composition influence upon phase interface of interacting components (distances among them) caused by the concentration of suspended particles which are brought into close contact with one another. It seems that both the concentration and the composition play important role in temperature - flow behaviour of these concentrated hydrated hydrophilic systems.

Theoretical Explanation

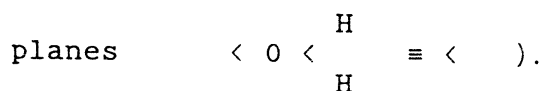
The above-mentioned complicated temperature flow behaviour can be interpreted as behaviour of a strong three-dimensional structure at very low shear rates, which breaks down into flocculi in a complicated dependence upon temperature as the shear rate increases. The complicated temperature dependences are determined by amount, character and strength of bonds in this three-dimensional structure among sites at interacting hydrated hydrophilic phase interfaces of components thus forming coating colours and glues.

At first look, a complicated temperature influence (upon bond system among components of these investigated systems) can be explained by means of the following relatively simple idea. Let us assume that two infinitely large planes are oriented parallel to each other and have the possibility of mutual movement

at a distance "d" (see Fig. 14). For example, this scheme can be interpreted as a mutual movement of two liquid layers within a real liquid system. Both of them mutually interact due to regularly alternating sites of different properties, which evoke an origin of the attractive or repulsive forces or both in dependence upon the mutual position of interacting sites. These positions can be changed by a parallel movement of the planes and will determine which force action will prevail between the interacting planes - whether only the attractive or only repulsive forces or both.

The mosaic type of sites distribution on interacting planes represented in Fig. 14 consist of two types of qualitatively different sites only, i.e. of their surface composition. One sort of surfaces is black and denoted by arrows aimed at open parts to these surfaces and the second sort is represented by white fields denoted by arrows of opposite orientation. Both surfaces have a common property - their behaviour strongly depends upon temperature. The system only achieves a minimum potential energy if attractive forces prevail between interacting planes and a maximum potential energy if only repulsive forces exist. The minimum potential energy of the system discussed is achieved at the steady state. At dynamic conditions, when the mutual movement of interacting planes is controlled, the resulting potential energy of steady state is defined by the prevailing force actions. At a constant composition of surfaces they are given by temperature and distance between the interacting planes, i.e. by the concentration of interacting sites

We can ask what kind of forces have to be used in these interactions, i.e. the interactions of hydrated hydrophilic concentrated systems? We suppose that the most suitable explanation of this phenomenon will be the so-called hydration forces. The concept of hydration forces¹³⁻¹⁶ is based upon the typical dipole character of water molecules and on their two extreme possible orientations in hydration layers (arrows in Fig. 14 denote the basic direction of water molecules orientation in the first hydration layer around interacting



The repulsive hydration forces with the same orientations of water molecules or the attractive hydration forces with the opposite orientations of water molecules are arising due to these orientations of water molecules within interacting the hydrated hydrophilic phase interfaces.

Also, for the hydration forces to originate, it is necessary for water molecules to reach a suitable orientation in hydration shells. The extent to which hydration forces are affected depends upon¹⁶:

1. How the heterogeneity of interacting surfaces, defined by the fact that qualitatively different types of groups are contained in each surface unit, accept the water molecules of different orientations by means of H-bonds.

2. The quality of water molecule orientations at the phase interface.

3. The size of H-bonds between individual groups and water molecules at the phase interface.

4. The amount of qualitatively equal groups with the same or different abilities to form H-bonds (H-bond energy), however, with the same water orientation in a surface unit of actually interacting surfaces.

Figure 14 introduces the simplest case of these heterogeneous interactions between planes covered with regularly alternating quantitatively equal but qualitatively different hydrated sites. By mutually parallel shifting of these planes we can obtain them:

- either the attraction due to hydration forces,
- or the action of repulsive hydration forces,
- or the parallel action of the repulsive and attractive hydration forces.

The relationship between the interaction potential (in J mol^{-1} of water in the first adjacent layer at interface boundary - it is proportional to the specific surface) and the distance is presented in another Fig. 15 for all three cases. The boundary effect of these interacting sites were omitted. The third case of these interactions has been originated by adding^{15,16} of the repulsive and attractive potentials at each point of distances for two different temperatures (20 °C, 80°C).

As we can see from Fig. 15, the effect of hydration forces

belongs among the physical or colloidal intermolecular forces¹⁴ and depends strongly upon temperature. They quickly disappear with rising temperature. Surprisingly, at equal conditions, the repulsive forces are effective over a greater distance. These differences appear important in the interactions of heterogeneous surfaces in which repulsive and attractive hydration forces are affected simultaneously. Particularly interesting is the influence of temperature upon the character of these interacting heterogeneous systems. For instance, in concentrated state if interacting surfaces are at relatively small distances from each other, e.g. $d = 3 \text{ nm}$, at $20 \text{ }^\circ\text{C}$ repulsive hydration forces dominate in the system (the actual system has relatively small viscosity) but at $80 \text{ }^\circ\text{C}$, on the other hand, the attractive hydration forces dominate (the system has a relatively high viscosity - see Fig. 14). In the case of spherical particles with heterogeneous hydrated hydrophilic surfaces of mosaic type this phenomenon is schematically presented in Fig. 16 (the case of constant concentration) and in Fig. 17 (the case of constant temperature). The dashed lines around interacting particles represent the isopotentials where the repulsive hydration forces are operating and full lines represent the isopotentials where the attractive hydration forces are effective. As usual, the qualitatively equal repulsive hydration forces are effective at a longer distance than the attractive forces.

Explanation of the Influence of Concentration on Viscosity

As we can see from Fig. 17 with the increasing concentration of particles the influence of attractive hydration forces will be increased due to decreasing particle distance, i.e. with increasing concentration of particles. At a certain concentration c_3 , providing that in the hydration bonding systems attractive forces prevail (compare with Fig. 15), the viscosity will be changed rapidly. Certainly, as a rule, with a temperature increase the hydration bonding system will be weakened and the viscosity will decrease again.

Explanation of the Influence of Temperature on Viscosity

As it can be seen from Figs 14 and Fig. 15, there exist a range of distances and concentrations at which, with increasing temperature the attractive hydration forces prevail in the hydration bonding system. The result of the temperature rise can be seen in Fig. 16. Owing to the increased effect of attractive forces between interacting surfaces or particles, the viscosity will increase too. Certainly, on further increasing the temperature, the viscosity will be decreased again due to increased kinetic energy of interacting components.

The existence of more than one maximum in the behaviour of these systems suggests that, in accordance with presented theoretical model, the really heterogeneous hydrated hydrophilic surfaces of mosaic type are a little more complicated. However, it is obvious that the mosaic surfaces of interacting components are not formed only with two kinds of qualitatively different surfaces as it is supposed to be the case in the theoretical model.

Maybe at least four of these partial surfaces exist in the cases with three peaks on viscosity vs. temperature curves.

Conclusion

The complicated temperature influence upon flow behaviour of some glues or coating colours can be explained by a relatively simple theoretical model. However, the description of this behaviour has an only qualitative but more illustrative character.

All the above mentioned types of flow behaviour are important particularly from technological point of view in those practical operations which are performed at low-to-medium shear rates. Important are the operations such as pumping, screening, dosing and metering of glues and coating colours. It is possible to utilize these temperature effects as well by special impregnation processes with relative high concentrated water impregnants.

As it has been introduced recently by Sandas and Salminen¹⁷

a high coating porosity (caused by high amount of evaporated water in drying process) leading to the improved rotogravure printability (heliotest) is probably a result of the high degree of interaction in the coating-colour system at the low deformation rates after the blade. The high degree of interactions in hydrated hydrophilic systems indicates a low degree of the so-called immobilization-solids due to high amount of immobilized water around molecules and particles of binders and pigments, respectively. Also the ability of the interaction-induced structure by high shear rate in a coating colour to withstand the shear has a significant influence on the practical coating process.

The viscosity-temperature curves seem to be important characteristics of complicated viscous liquid systems reflecting their hypermolecular structures in analogy to light absorption spectra of chemical compounds reflecting their molecular structures.

The special viscosity-temperature behaviour of coating colours offers new possibilities in technology of the coating especially in the so-called "hold up coating".

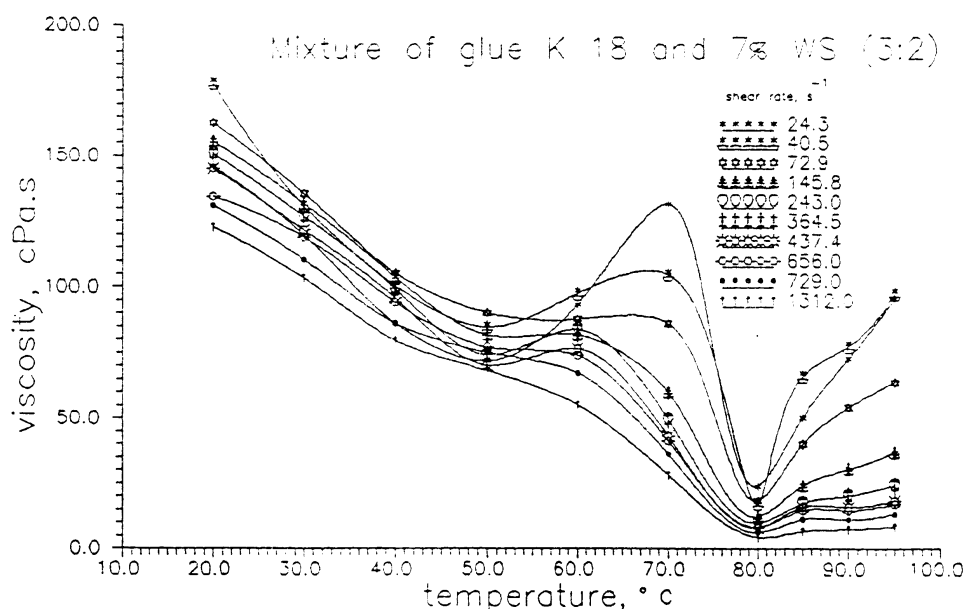


Fig. 1 Dependence of viscosity coefficients upon temperature at different shear rates for glue K18 with 7 % solution of wheat starch (4:1)

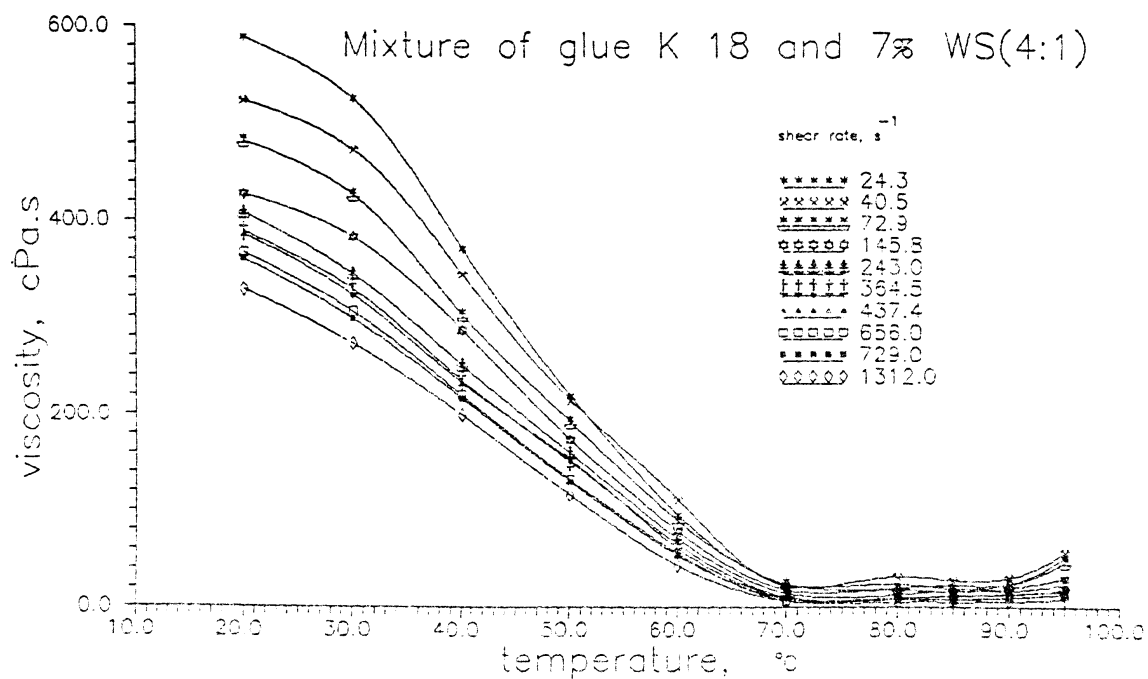


Fig. 2 Dependence of viscosity coefficients upon temperature at different shear rates for glue K18 with 7 % solution of wheat starch (3:2)

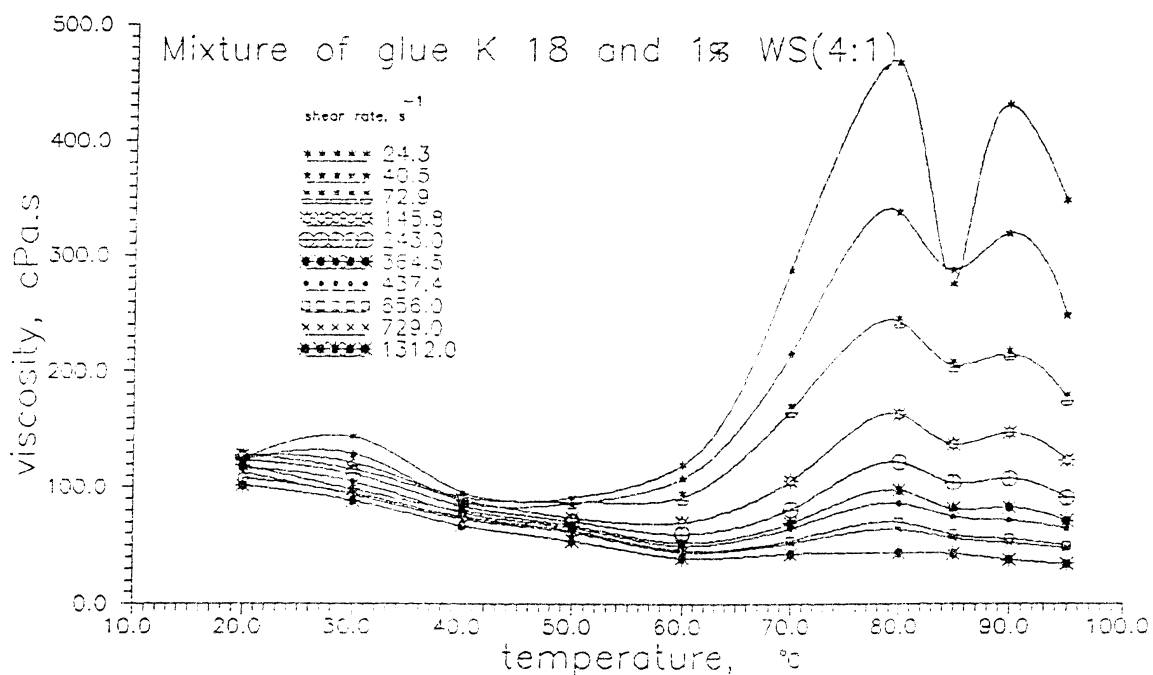


Fig. 3 Dependence of viscosity coefficients upon temperature at different shear rates for glue K18 with 1 % solution of wheat starch (4:1)

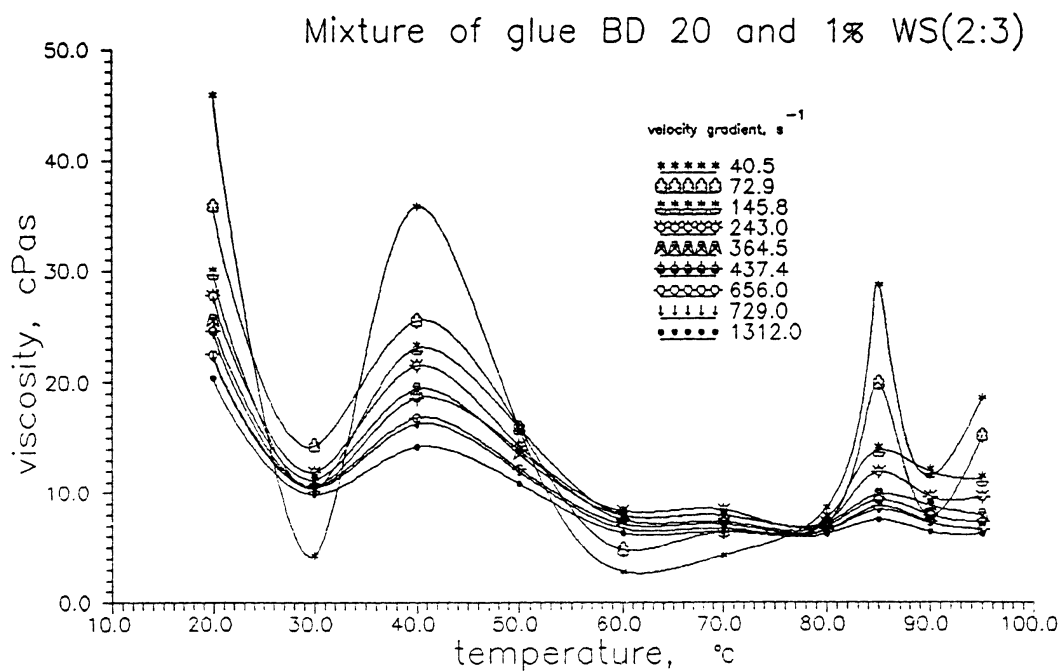


Fig. 4 Dependence of viscosity coefficients upon temperature at different shear rates for glue BD 20 with 1 % solution of wheat starch (2:3)

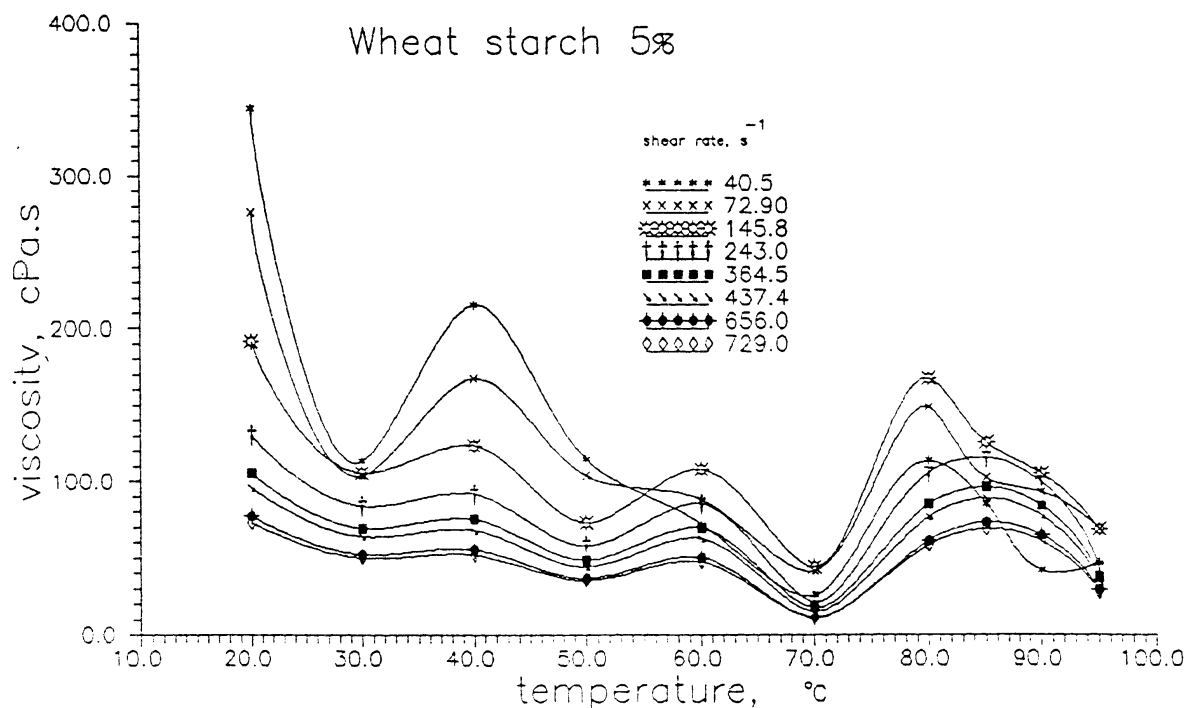


Fig. 5 Dependence of viscosity coefficients upon temperature at different shear rates for 5 % solution of wheat starch

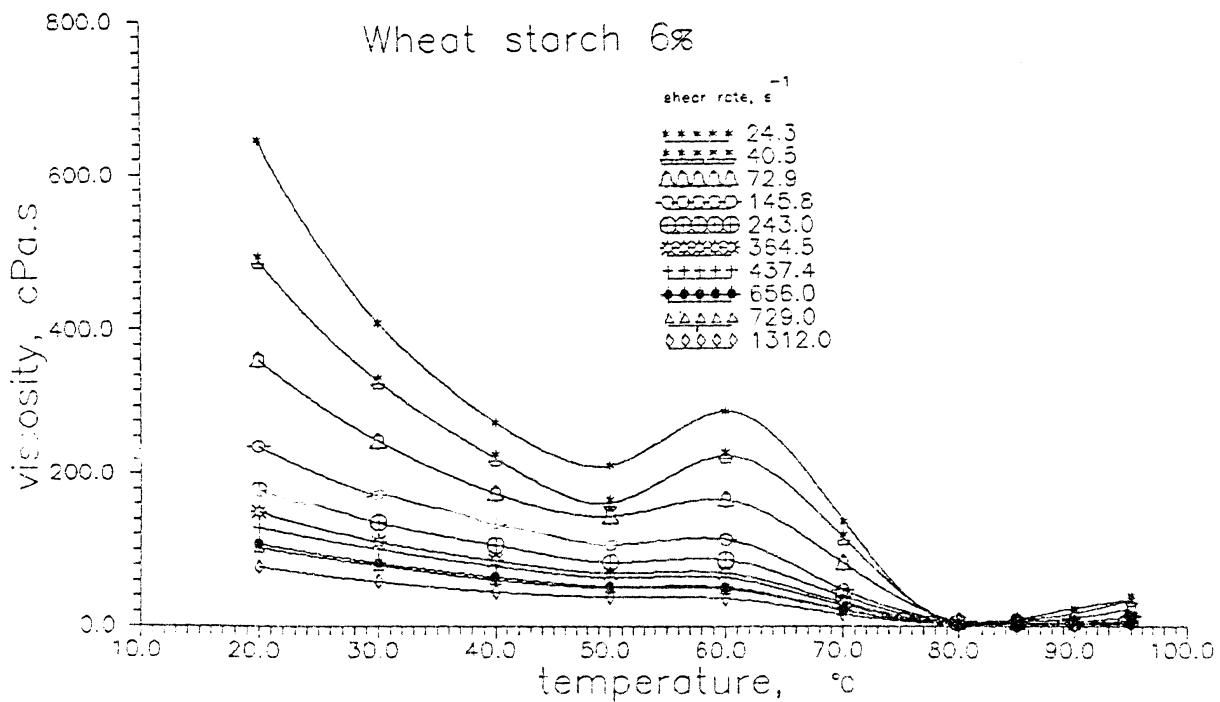


Fig. 6 Dependence of viscosity coefficients upon temperature at different shear rates for 6 % solution of wheat starch

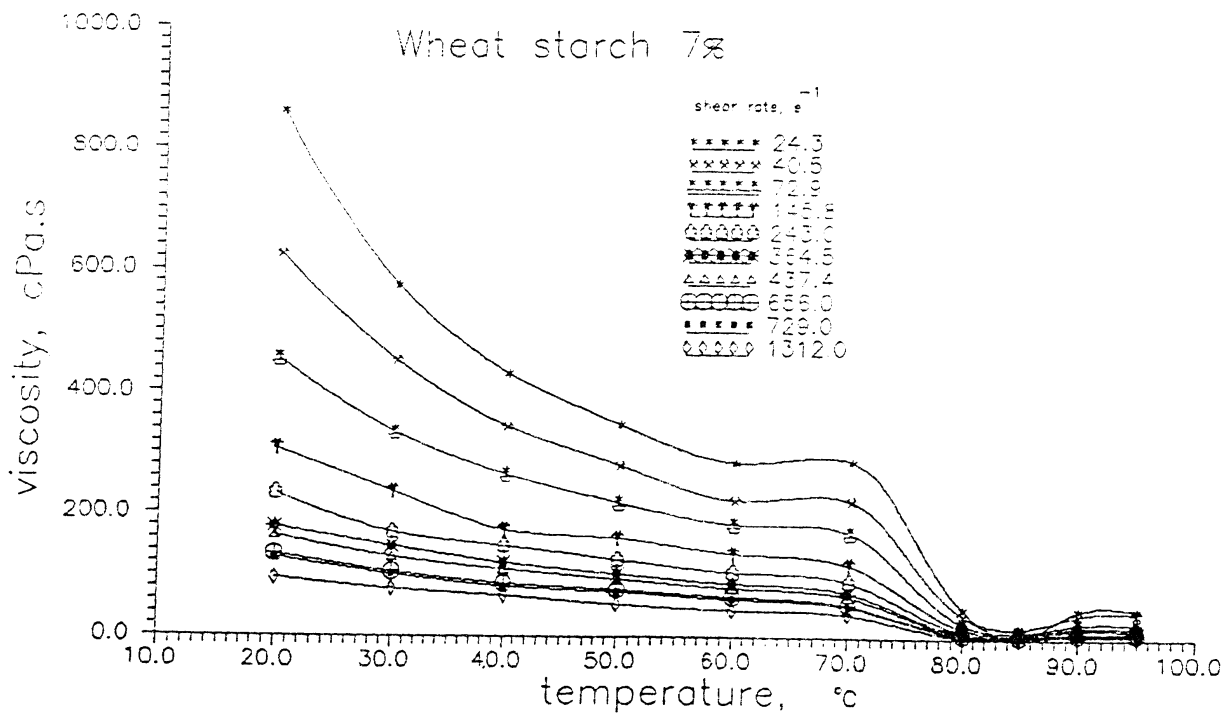


Fig. 7 Dependence of viscosity coefficients upon temperature at different shear rates for 7 % solution of wheat starch

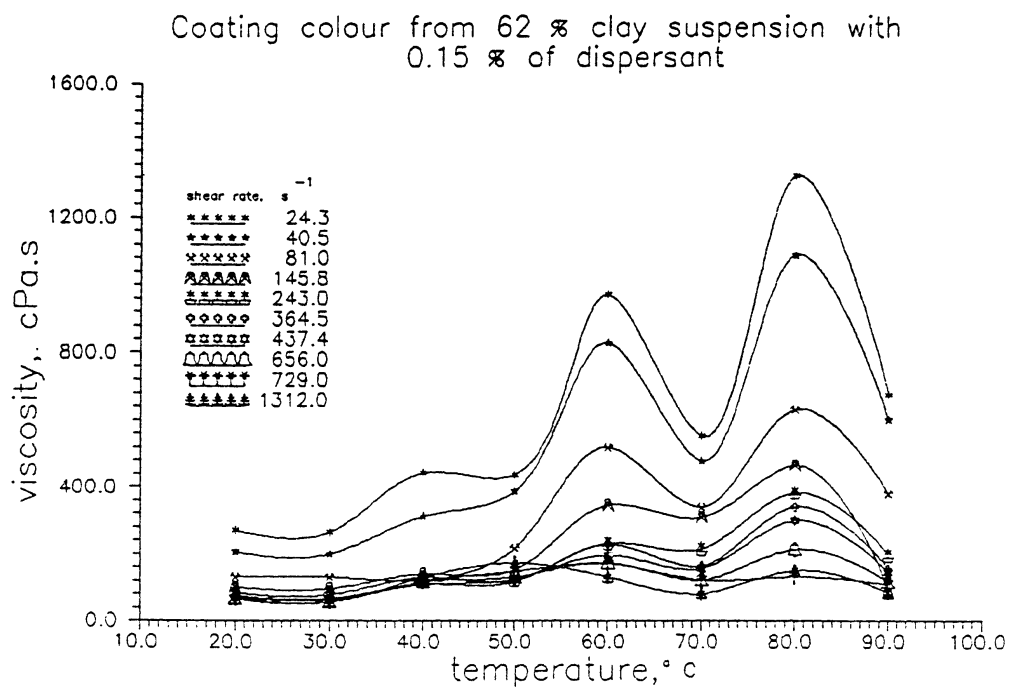


Fig. 8 Dependence of viscosity coefficient upon temperature at different shear rates for coating colour from 62 % clay suspension with 0.15 %

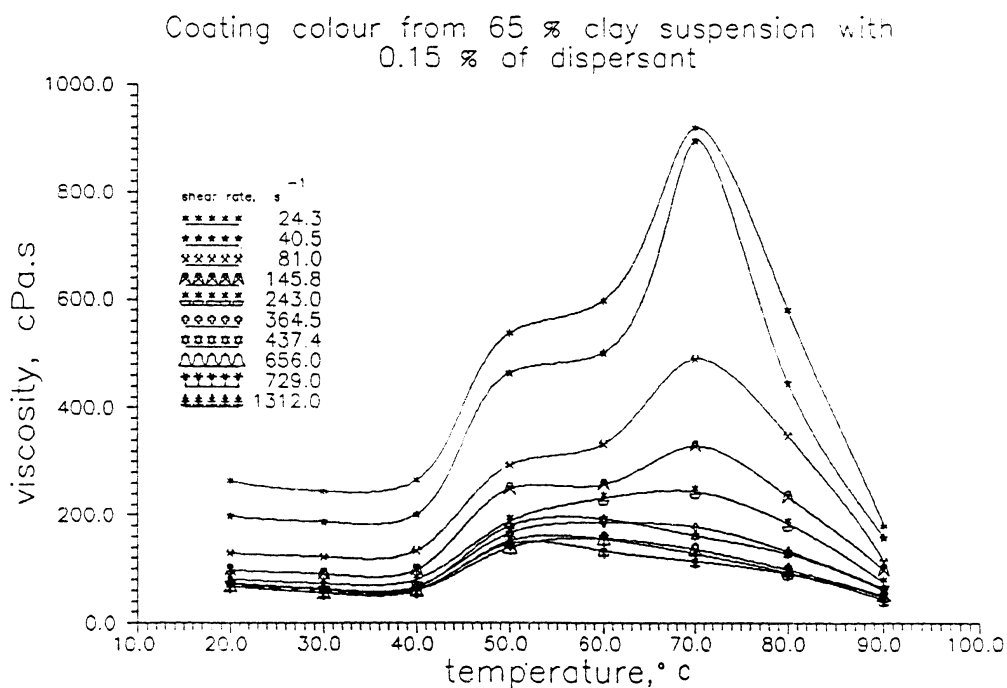


Fig. 9 Dependence of viscosity coefficients upon temperature at different shear rates for coating colour from 65 % clay suspension with 0.15 % dispersant

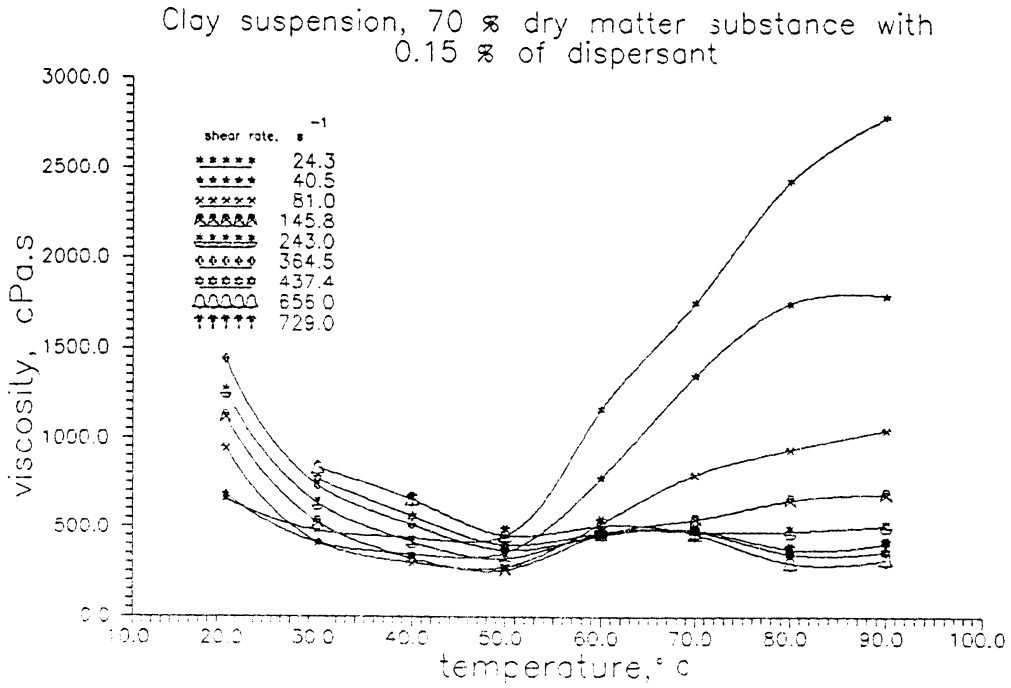


Fig.10 Dependence of viscosity coefficients upon temperature at different shear rates for coating colour from 70 % clay suspension with 0.15 % dispersant

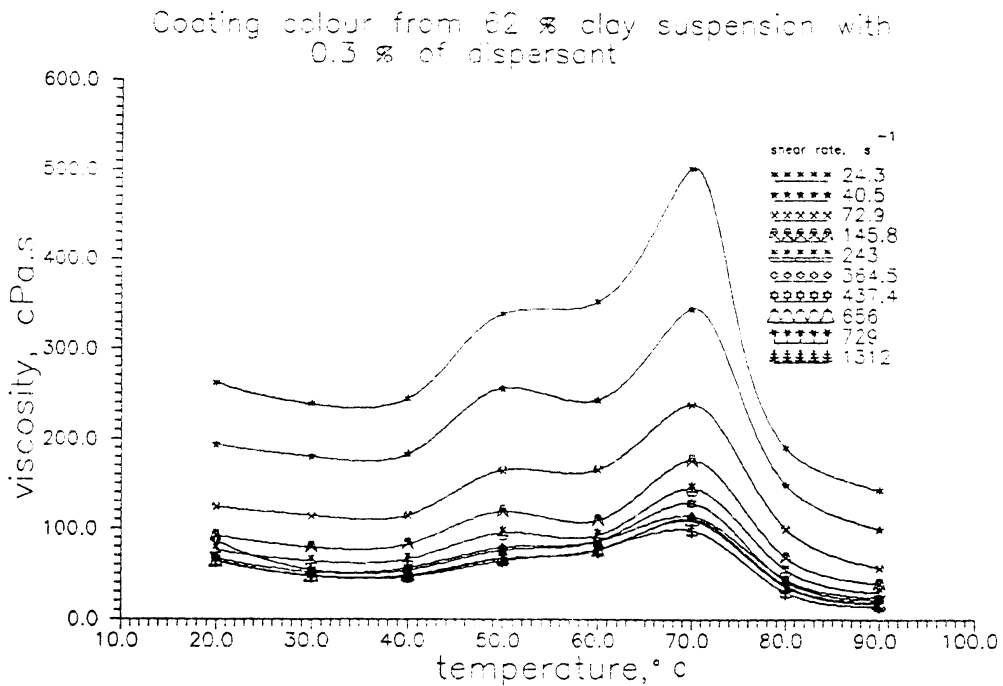


Fig.11 Dependence of viscosity coefficients upon temperature at different shear rates for coating colour from 62 % clay suspension with 0.30 % dispersant

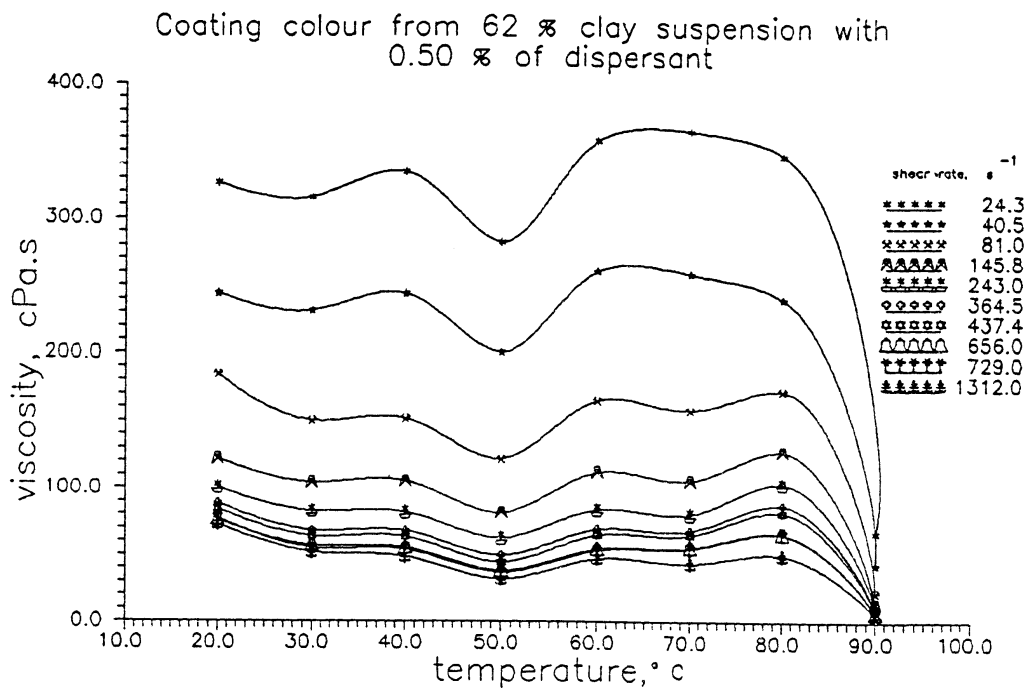


Fig.12 Dependence of viscosity coefficients upon temperature at different shear rates for coating colour from 62 % clay suspension with 0.5 % dispersant

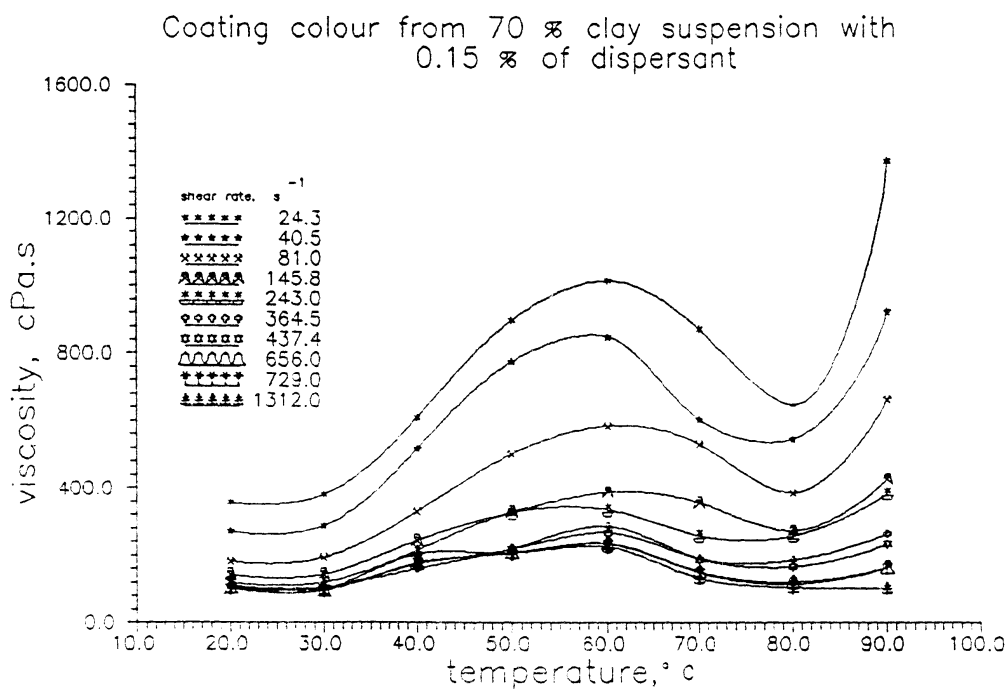


Fig.13 Dependence of viscosity coefficients upon temperature at different shear rates for 70 % clay suspension with 0.15 % dispersant

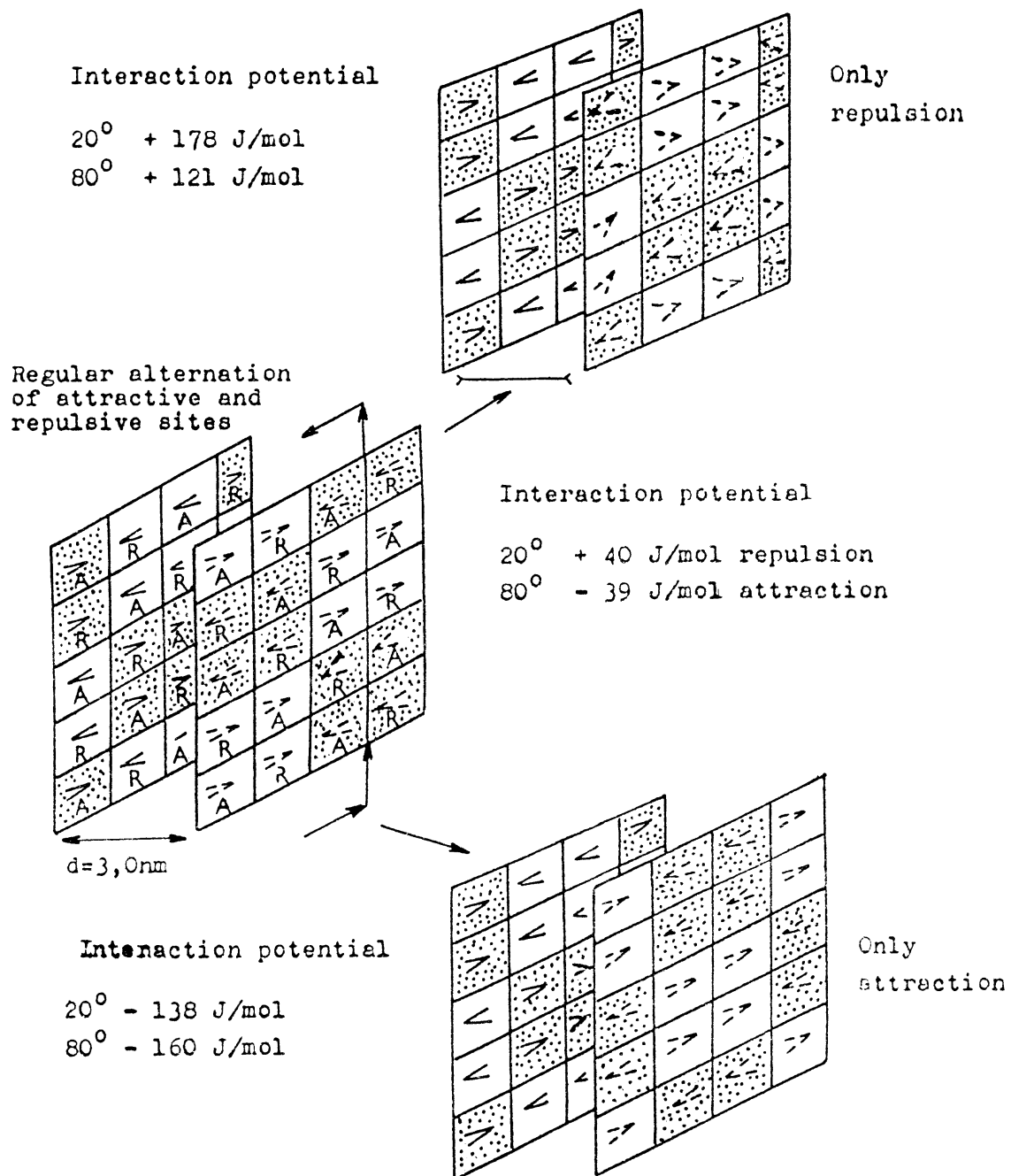


Fig.14. Graphical description of interaction of two parallel flat formations with regular alternation of interacting sites (mosaic type). These are qualitatively different and quantitatively equal

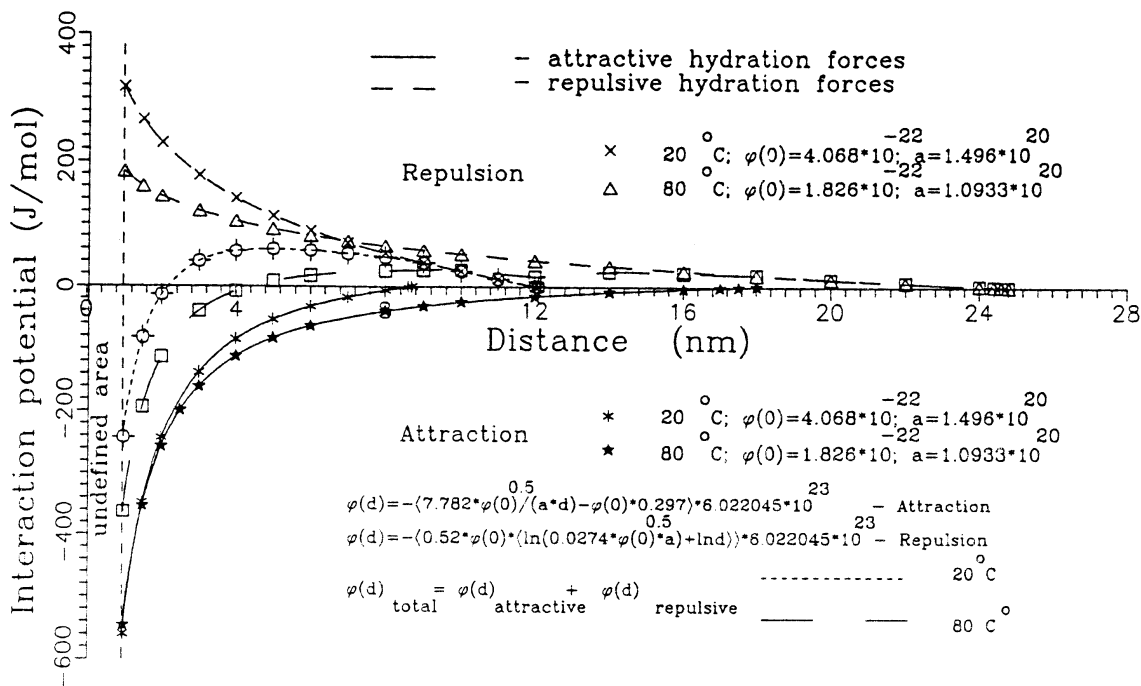


Fig.15. Dependence of interaction potentials $\phi(d)$ upon distance d of interacting quantitatively equal flat formations of mosaic type¹⁶

Attraction

$$\varphi(d) = - \left[7.782 \varphi(0)^{0.5} / (a \cdot d) - 0.297 \varphi(0) \right] N_A$$

Repulsion

$$\varphi(d) = - 0.52 \varphi(0) \left[\ln(0.0247 a \varphi(0)^{1/2}) + \ln d \right] N_A$$

Where $\varphi(0)$ - interaction potential at distance $d = d_0$ according to

$$\varphi(0) = \left(\sigma_{s,1} \delta x / a \right)^{2/3} \text{ is}$$

$$\varphi(0) = 4.068 \times 10^{-22}, \text{ at } 293 \text{ K}$$

$$\varphi(0) = 1.826 \times 10^{-22}, \text{ at } 353 \text{ K} \quad \text{and parameter}$$

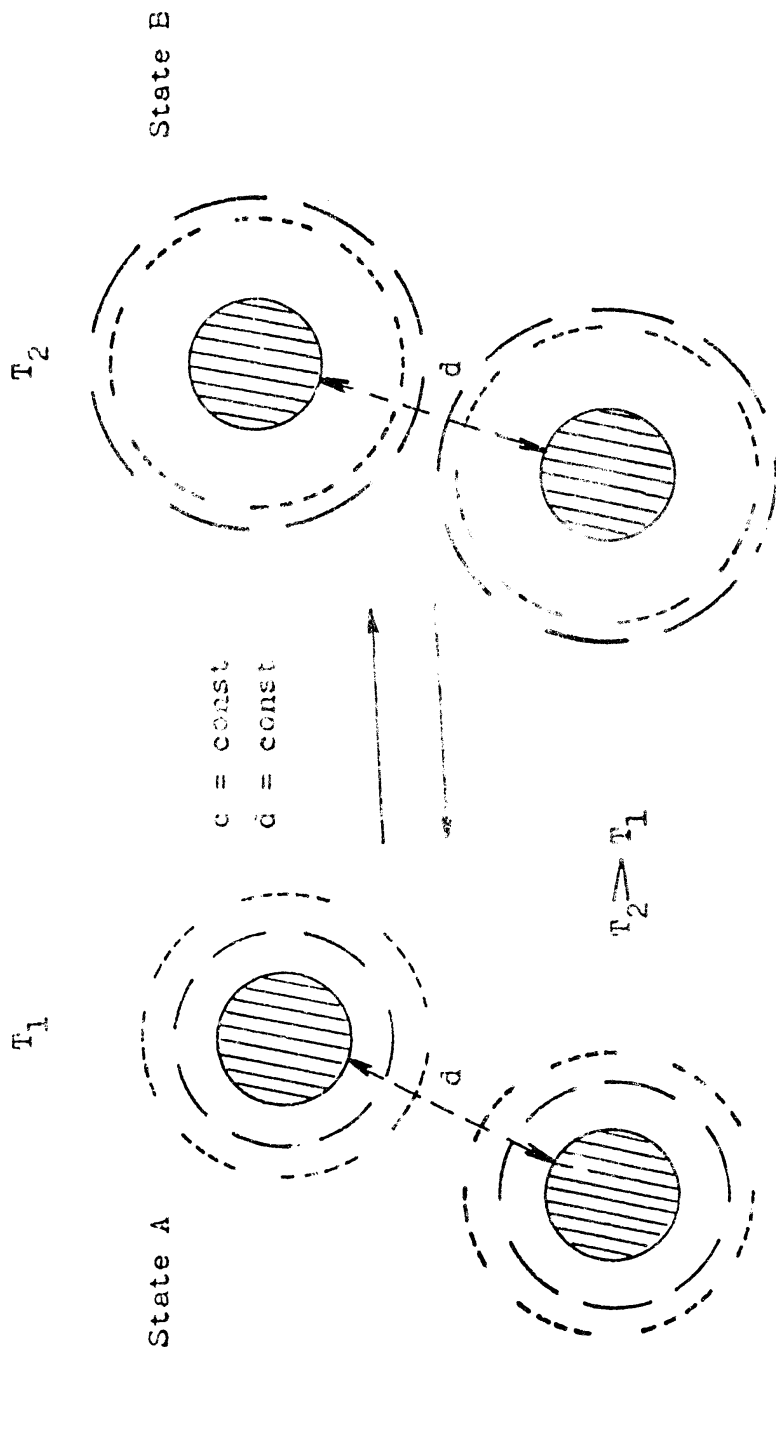
$$a = \left(\sigma_1 - \sigma_{s,1} \right)^{1/2} \quad 3kT \quad \text{is}$$

$$a = 1.496 \times 10^{20}, \quad N^{-1/2} \text{ m}^{-3/2} \quad \text{at } 293 \text{ K};$$

$$a = 1.093 \times 10^{20}, \quad N^{-1/2} \text{ m}^{-3/2} \quad \text{at } 353 \text{ K};$$

N_A - Avogadro's number, δx - distance between two O-atoms of interacting water molecules at phase interface ($\delta x = 0.3 \text{ nm}^{13,16}$).

Both $\varphi(0)$, $\varphi(d)$ are in J/molecule and J/mol, respectively, of water in the first adjacent layer. Both $\sigma_1, \sigma_{s,1}$ are surface tension where σ_1 - hypothetical tension in bulk of water ($\sigma_1 = 3.3 \text{ N m}^{-1}$ - Ref.^{13,16}) and $\sigma_{s,1}$ - surface tension solid - liquid, e.g. $\sigma_{s,1}(T) = 1.91 \times 10^{-2} - 5.12 \times 10^{-5} T$ in N m^{-1} - Ref.¹⁶, T - temperature in K, k - Boltzman's constant



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

Fig.16. Schematic representation of isopotentials around particles of heterogeneous character (mosaic type)

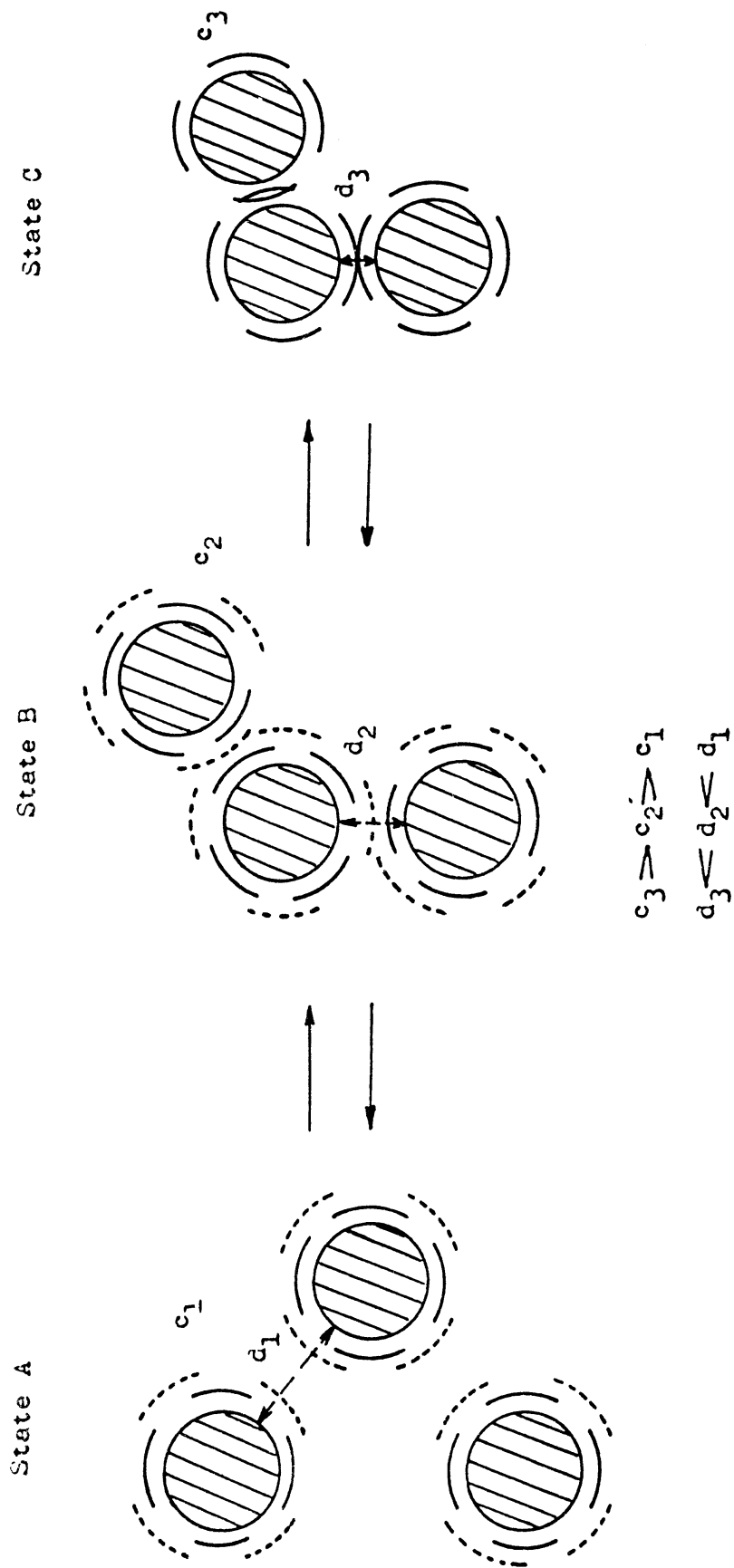
$T = \text{const}$


Fig.17. Schematic representation of interacting particles with heterogeneous character (mosaic type) upon their concentration

References

1. Kurath S.F., Larson W.S.: Tappi J. 73, 23 (1990).
2. Metzner A.B.: Trans. Soc. Rheology 29, 735 (1985).
3. Fadat, G., Rigdahl M.: Nord. Pulp Pap. Res. J. 2, 30 (1987).
4. Fadat G., Engström, G. Rigdahl M.: Rheologica Acta 27, 289 (1988).
5. Engström G. Rigdahl M.: Nord. Pulp Pap. Res. J. 3, 25 (1989).
6. Kurath S. F. G., Larson W.S.: Tappi J. 54, 1509 (1971).
7. Andrade E.N.: Nature 125, 582 (1930).
8. Kruyt H.R.: Colloid Science, Vol. 1, Chap. V - VI, Elsevier, Amsterdam 1952.
9. van de Ven T.G.M.: Colloid Hydrodynamics, p.1 - 200, Academic Press, London 1989.
10. Cross M.M.: Colloid and Interface Sci. 20, 417 (1965)
11. Gillespie T.J. : Colloid and Interface Sci. 22, 554 (1966).
12. Poppel E.: Rheologie und Elektrokinetische Vorgänge in der Papiertechnologie, Chap. 2, Fachbuchverlag, Leipzig 1977.
13. Milichovský M.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice 51, 71 (1988).
14. Milichovský M.: Tappi J. 73, 221 (1990).
15. Milichovský M.: Przegląd papierniczy 46, 418 (1990).
16. Milichovský M.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice 55, (in press).
17. Sandas S.E. Salminen P.J.: Tappi J. 74, 179 (1991).

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