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**Investigation of Aqueous Kaolin Suspensions:
a Rheological and Sedimentation Volume Study**

Ying Li

A Thesis

in the Department of

Mechanical Engineering

Faculty of Engineering and Computer Science

Presented in Partial Fulfillment of the Requirements

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Abstract

Investigation of Aqueous Kaolin Suspensions: a Rheological and Sedimentation Volume Study

Ying Li

Coating colors are very complex colloid systems of which stability and rheological behaviors are of importance in the coating process and in the mechanical, optical properties of the coated layer. Clay is one of the main ingredients of coating colors in the paper industry. There can be very complicated colloid interactions that control the stability and rheological properties of the coating colors. The main purpose of this work is to get a better understanding about the role of the colloid interactions in the rheological behavior of suspensions which are composed of materials having significant meanings in coating color formulations (kaolin, sodium carboxymethyl cellulose, and sodium chloride). For practical applications in many cases, suspensions with a high solid content are required which show low viscosity, significant elasticity, and thixotropy as well. The aim of this investigation is to find such a composition of above components which show the above mentioned rheological properties.

The colloid interactions were studied by the rheological and sedimentation volumes investigations. The results showed that lv (low viscosity) NaCMC was a better stabilizing and thinning agent than mv (medium viscosity) NaCMC; NaCl increased the viscosity of CMC added suspensions. 0.01% mv NaCMC increased the viscosity of 0.5% lv NaCMC added kaolin suspension supposedly due to bridging flocculation. This is in a good agreement with the results of sedimentation volume investigations. 0.1% lv NaCMC, 0.002% mv NaCMC and 0.5% NaCl together caused the most significant thixotropy; without of NaCl, the suspension shows anti-thixotropy. Real-elasticity was only found in the presence of mv NaCMC. The samples, prepared from the mixture of low and medium viscosity NaCMCs, were found to be the best composition for getting low viscosity, significant thixotropy and elasticity.

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LIST OF ABBREVIATIONS AND NOMEMCLATURES

MW	medium weights
LW	low weights
G'	storage modulus
G''	loss modulus
G^*	complex shear modulus
γ_0	residual viscosity
G_{ii}	instantaneous shear modulus
$S(Q)$	structural factor
NaCMC	sodium carboxymethyl cellulose
NaCl	sodium chloride
Kaolin (K)	kaolin
CR	controlled shear rate
CS	controlled shear stress
OSC	oscillation
τ	shear stress
γ	deformation
η	viscosity
M	torque
A	area
Ω	rotational speed
lv	low viscosity

mv	medium viscosity
k	viscosity parameter
$\dot{\gamma}$	shear rate
τ_{HB}	Herschel-Bulkley yield stress
τ_B	Bingham yield stress
η_p	plastic viscosity
V_s	sedimentation volumes
Na^+	sodium ion
CMC	carboxymethyl cellulose iron

CHAPTER 1

INTRODUCTION

1.1) Introduction

The aqueous clay suspensions are of great importance in many fields of industrial applications (e.g. ceramics production, drilling fluids, paper coating [1-3]). Neutral polymers or polyelectrolytes are frequently used as dispersant or flocculant agents. The combination of different polymers can cause synergetic effects. Due to the practical and theoretical importance, the competitive adsorption of neutral (Csempesz and Rohrsetzer, 1984; Csempesz et al., 1987; Csempesz and Csáki, 2000)[4-6] and ionic (Tanaka et al., 1997; Swerin et al., 1996; Swerin et al., 1997)[7-9] macromolecules was intensively studied in the past decades. Macromolecules can cause bridging flocculation if the molecular weight is great enough and the adsorption layer is not saturated. The efficacy of flocculation can be improved, adding simultaneously a lower and a higher molecular weight polymer (Tanaka et al., 1997; Swerin et al., 1996; Swerin et al., 1997)[7-9] in the suspension. In most cases cationic (Tanaka et al., 1997; Swerin et al., 1996; Swerin et al., 1997)[7-9] or oppositely charged (Aksberg and Ödberg, 1990)[10] polyelectrolytes are used for initiating flocculation resulting in strong floc structure. In the first case, the lower molecular weight polymer enhances the possibility of bridging formation of its higher molecular weight counterpart, blocking the active adsorption sites. Strong floc structure is required e.g. in papermaking (Main and Simonson, 1999) [11] relating to the high speed paperboard processing. The usage of the mixtures of cationic polymers has been suggested for this purpose (Tanaka et al., 1997; Swerin et al., 1996; Swerin et al., 1997) [7-9].

In paper coating liquids, including kaolin, NaCMC is a commonly used addition (Jamström et al., 1987; El-Saied et al., 1996; Mäkinen and Eklund, 1996; Persson et al., 1997; Wang et al., 1996)[12-16]. There are many conflicting requirements for the coating color. High solid content, for example, but low shear viscosity and a certain degree of thixotropy and elasticity are required. It means that strong flocculation of the pigments should be avoided in the coating colors. That is why the site-blocking based flocculation, concerning the coating colors, has not been studied, yet. But a weak flocculation of pigments can result in an advantageous optical properties of the coating layer (Persson et al., 1997).

The main purpose of this work is to show that these advantageous rheological properties are feasible in the aqueous kaolin suspensions using the mixture of a lower and a higher molecular weight NaCMC and in certain cases in inorganic electrolyte, NaCl. Due to the positively charged edges of kaolinite particles, the anionic polyelectrolytes can cause a weak flocculation based on the site-blocking mechanism. The rheological properties are examined by cone-plate viscometry. In order to get a better understanding of the rheological results, the results of sedimentation volume investigations are compared.

1.2) Colloid chemical background of the coating color formulation

1.2.1) Structure of concentrated suspensions

In the concentrated suspension, forces between the particles play an important role in determining the overall properties of dispersion. Types of particle-particle interaction are: the hard-sphere interaction, the electrical double layer repulsion, the Van der Waals

attraction and the steric interaction. The maintenance of particles in suspension as individual primer units or their combination into aggregates depends on the balance of interaction forces that operates between them. By controlling the interaction forces, one is able to arrive at the desired units, i.e. primer particle or various types of aggregates.

Various forms of aggregates may form depending on the range and magnitude of attractive forces. For example, a tight cluster of particles, strongly held together by Van der Waals forces may form (usually referred to as coagulation) and these aggregates cannot be separated under the normal shear field applied to the suspension. On the other hand, loose metastable structures (usually referred to as flocs or floccules) may form. Such flocs may be destroyed to a greater or lesser extent, by application of stresses, and reform, under certain conditions. When the stresses are removed, it may be possible to distinguish between weak, open structures or floccules and tight but weak structures or agglomerates.

1.2.2) Effect of polymer addition on behavior of suspensions

Many polymers have a tendency to adsorb on the surface of dispersed particles. Polymer adsorption may lead to colloid stability or to particle flocculation. Which occurs depends on factors such as the concentration, the charge density and chemical structure of polymer, the nature of the particle surface and so on. At low polymer concentration the predominant effect is bridging flocculation. Bridging flocculation is favored when the adsorbed polymer has long chains (tails) dangling into the dispersed phase and the amount adsorbed is below saturation coverage. Under these conditions the flocs are held together by individual molecules. At higher polymer concentration for which particles are fully coated with a

polymer layer, the steric stabilization may occur. When the sterically stabilizing layer is thin, the effect of the short-range Van der Waals interparticle attraction may lead to weak coagulation. When the particles are large, or the solvent quality is reduced to poorer than theta condition, sterically stabilized particles may exhibit secondary minimum-type flocculation. The flocculation may also be induced by non-adsorbing (free) polymers too. It is usually referred to as depletion flocculation. A large concentration of non-adsorbing polymers may lead to depletion (re)stabilization.

In systems where polymer molecules have opposite net charges to that of the particle surface, the flocculation or stabilization is adequately described by a charge neutralization or charged reversal mechanism. In such a case, Mabire et al. [17] were able to explain in a semiquantitative way the effects of molecular weight of polymer and polymer charge density on settling rate and clarification of silica suspensions by using a “electrostatic patch” model.

The flocculation or stabilization processes can be very complicated in suspensions with two or more polymers. Two-component flocculant systems are commonly used nowadays [18]. The polymer and particles will interact with the added second polymer in either a more or less complex way. Mixing of oppositely charged polyelectrolytes may result in complex coacervation or polyelectrolyte complex formation. The latter may be in the form of dissolved complexes, colloidal dispersion or macroscopic precipitates. The polymer-particle or polymer-polymer interaction may cause problems, for example; restrictions in flocculant efficiency and floc properties. However, it can be used as an advantage as in the case of the dual polymer retention system used in papermaking. In this technique, one combines the

strong adsorption of highly cationic polyelectrolytes of low molecular weight with the bridging effect of high-molecular-weight anionic polyelectrolytes [19].

In the case of more than one polymer in suspension, one must take into account the effect of competitive adsorption of polymers. Theoretical investigations of non-ionic polymers have predicted the preferential adsorption of the higher molecular weight (MW) component and displacement of lower polymers by polymers of higher MW. Experimental investigations are consistent with this theory.

For polyelectrolytes, the situation is more complicated because of strong interrelations between electrostatic and conformational effects. Tanaka et al. [19] have studied the individual and competitive adsorption of two cationic polyacrylamides with different molecular weights but with very similar charge densities onto oppositely charged surfaces (polystyrene latex, cellulose beads and cellulose fibers).

Swerin et al. [20] studied the adsorption of two cationic polymers with different molecular weights (low and medium MW) and of cationic polyacrylamide with high MW onto microcrystalline cellulose and the flocculation of the suspension. The two polymers were added in sequence or simultaneously. The combination of two polymers gave a site-blocking effect by the low MW polymer which gave a charge reversal at a lower total amount of added polymer. The bridging efficiency by the high MW polymer was still maintained. The results indicated that the simultaneous addition mode could be beneficial.

1.2.3) Methods to control the network structure in concentrated suspensions

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In industrial applications, it is often necessary to control the properties of a suspensions for adequate shelf life, on the one hand, and for ease of application, on the other. For these reasons, it is necessary to control the physical stability and the flow characteristics of the suspension. For the most concentrated suspensions encountered in practice, it is necessary to have a three dimensional network structure (gel structure) in the suspension to avoid sedimentation and such a structure could be broken down by shear in a manner that is dictated by application. Moreover, it is necessary for the “gel structure” to form after application to avoid rapid flow.

Below some methods are shown for forming a network structure in suspensions.

1.2.3.1) Controlled flocculation (self structured systems)

In an electrostatically stabilized suspension, the structure may be controlled by the particle size and shape, and the charge on particles and electrolyte concentration. In this manner, weak flocculation of the suspension in the secondary minimum is possible and a three dimensional network of suspension may be produced. In a sterically-stabilized dispersion, the secondary minimum-type flocculation is also possible by controlling the adsorbed layer thickness.

1.2.3.2) Addition of polymeric thickeners

Macromolecules of nonionic or ionic type with high molecular weight at moderate concentration produce thixotropic systems. Such materials are, therefore, ideal for controlling the rheology of suspensions.

1.2.3.3) Addition of particulate-type thickeners

Sodium montmorillonite and oxides (silica or alumina) can form, under specified conditions (pH, electrolyte concentration, phase volume concentration) a “three dimensional gel network”. With sodium montmorillonite, the mechanism by which such a gel-structure is formed is usually attributed to a combination of double layer repulsion and edge-to-face flocculation [21]. With silica, the “gelation” may take place as a result of double layer repulsion or formation of chain aggregation (depending on the pH) [22].

1.2.3.4) Use of mixture of polymers and particulate solids

By using a combination of sodium montmorillinate and an oxide with polymers, it is possible to form a three dimensional structure. The solid particles act as centers connecting the polymer chains. In other words, the polymer chains act as “bridges” or “links” between the particles (bridging flocculation) [23].

1.2.3.5) *Heteroflocculation*

By addition of small oppositely charged particles to a coarse suspension, it is possible to form a network structure by bridging with small particles. The degree of flocculation and its “strength” can be controlled by controlling the polymer layer and electrolyte concentration [24].

1.2.3.6) *Flocculation by addition of free polymer (depletion flocculation)*

The addition of a free (i.e. non-adsorbing) polymer to a sterically stabilized dispersion may, under specific conditions of polymer molecular weight and concentration, produce a weakly structured suspension. Such a suspension showed marked viscoelasticity indicating the build-up of a “structure” in the suspension [25].

1.2.4) Methods for study of interactions and behaviors of flocs and network

1.2.4.1) *Measurement of sedimentation rate and volume*

In a structured suspension, the flocs settle at a rate depending on the size and porosity of the aggregated mass. Michael and Bolger [26] suggested a relationship to calculate the average size of the aggregates and the water-solid ratio within the aggregates from the sedimentation curves. The equilibrium sedimentation volume may provide qualitative information on its structure (close-packed or open structure). From the redispersion experiments, information on strength of the interaction between the particles can be obtained.

1.2.4.2) *Rheological measurements*

This is by far the best quantitative method available to obtain information on the properties of concentrated suspension. In general one may distinguish between two types of measurement. Measurement during which the network structure is not disturbed i.e. at small deformations, and measurement during which the network structure is broken down, i.e. at large deformation. Below, a brief account is given of the possible methods of measurement available at present:

The steady-state flow curve (shear stress vs. shear rate) of concentrated suspensions can be characterized by three distinct parameters: the shear rate, the plastic viscosity, and the Bingham yield value. Various theories have been put forward to explain the flow behavior of flocculated and structured suspensions [27]. However, the relationship between interparticle interactions and rheological characteristics of concentrated suspensions is far from being adequately determined. There are several rheological models which can be used to fit the measured viscosity vs. shear rate data.

In dynamic measurement, an oscillating deformation / stress with an angular frequency is applied to the system. It is possible to measure the storage modulus G' (i.e. a measure of the elastic component) and the loss modulus G'' (i.e. a measure of the viscous component). The complex shear modulus $G^* = G' + iG''$. The limiting value of G^* depends on the second differential with respect to distance of the equilibrium interaction potential.

There are two methods for performing static (transient) deformation measurements on concentrated suspensions: by measuring the change of the stress with time at constant strain (transient stress response) or measuring the change of strain with time at constant stress (creep curve). The zero shear viscosity (“residual viscosity”) γ_0 and the instantaneous shear modulus $G_0 = \tau / \gamma_0$ obtained from creep curves can be used to obtain information on the interaction forces between the particles in a concentrated suspension. The thixotropy and creep- recovery investigations can provide useful information about the time dependence of structure management in concentrated systems.

1.2.4.3) Neutron scattering studies of floc structure

Application of the small-angle neutron scattering technique is based on the fact that the interference pattern of scattered radiation is determined by the distribution of separation between particles centered in the floc. Information on floc structure is contained in the structure factor $S(Q)$. Cabane and coworkers [28] have investigated the structure of monodispersed silica particles flocculated by polymers of variable charge density. The neutron scattering experiments indicate two types (I and II) of aggregates. Type I Aggregates (produced by uncharged or low-charged polymers of high molecular weight) were formed by bridging mechanism without full neutralization or screening of the charges on the silica surface. The residual electrostatic repulsion allowed spheres to reorganize themselves into lower potential energy states and resulted in a short-range liquid-liquid order in the floc. Type II Aggregates (produced by intermediate or high-charged polymers near the isoelectric point of silica, or high ionic strength) formed by electrostatic patch neutralization have a rigid, branched tenuous structure.

1.2.4.4) *Computer simulation of floc structure*

At a very simple level, a system of polymer and particles can be modeled as a binary mixture of small and large spheres interacting with a square-well potential. The equilibrium properties can be determined by Monte Carlo simulation [29]. Calculation from simple algebraic expressions shows [29] that relatively weak attractive interactions (1 or 2 kT) may cause extensive, weak, reversible bridging flocculation (and gelation) in a concentrated dispersion. Further work on this sort of simulation model is required to examine more complex types of particle-particle, particle-polymer and polymer-polymer interaction.

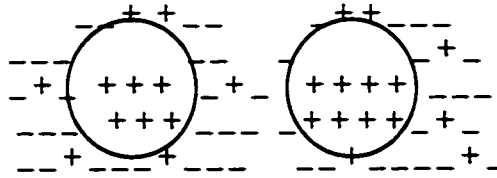


Figure 1.2.1. Positively charged particles with negatively charged counter ion cloud in the electrostatically stabilized suspension (this is the result of electrical double layer repulsion).

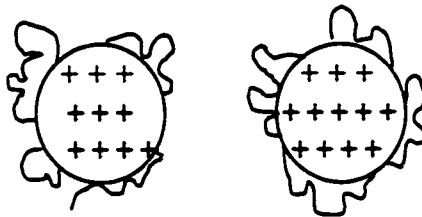


Figure 1.2.2. Polymer molecules (macromolecules) in the sterically stabilized suspension (this is the result of the sterical barrier).

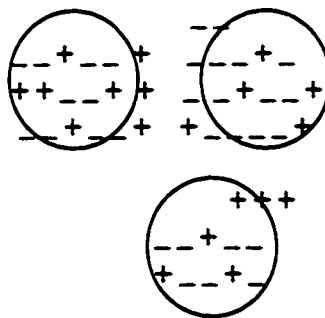


Figure 1.2.3. Screening of charges in aggregated form in a non-stable (coagulated) suspension resulting in increase of viscosity.

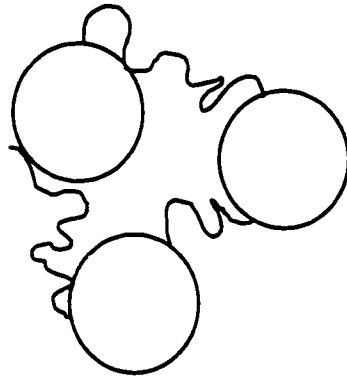


Figure 1.2.4. Low concentrated and adsorbed polymer chains act as “bridges” or “links” in aggregated form in a non-stable (flocculated) suspension resulting in increase of viscosity.

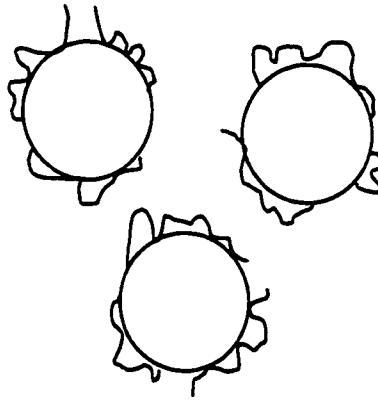


Figure 1.2.5. High concentrated and adsorbed polymers in the steric stabilization suspension resulting in no increase of viscosity.

1.3) Rheological behavior of coating colors

Rheology is the science of understanding the flow and deformation of materials. Rheology plays a very important role during the coating process. In high solid content kaolin suspensions, viscosity varies with shear rate. Such non-Newtonian fluids exhibit several types of complex rheological flow behaviors — shear thinning, yield stress, thixotropy, dilatancy, viscoelasticity, *etc.* By controlling the rheological properties, a satisfactory performance during high speed coating can be obtained [30]. In addition, the rheology of coating colors has been found to affect the quality of coated and printed papers [31].

In application of the coating, ease of spreading and leveling to a thin layer on the paper requires a high degree of fluidity of the color, despite the rather high solids concentration. In the modern coating technique there is an exact requirement for thixotropy of coating colors. Thixotropy is a very time dependent property. Thixotropic substances are colloidal gels when solid and sols when liquefied. Clay suspensions which are more or less flocculated show the phenomenon of thixotropy. In the coating process, highly thixotropic coatings usually have better runnability on blade coaters [32]. Yield stress is the characteristic stress above which some materials will flow. Above the yield stress, the stress and strain rate are nearly linearly related. Suspensions of flocculated particles often show plastic behavior. These suspensions do not flow until the yield stress has been exceeded. Yield stress has a great relevance in the coating process [33]. In the paper coating process, the yield stress is an important parameter for hydrodynamic instability phenomena in the flow under the blade [34]. In the determination of yield stress of a kaolin suspension with CMC, Davis [35] related the value of yield stress to the adsorption of CMC, due to hydrogen bonding on kaolin

particles using the Casson equation. Lepoutre et al. [36] have also shown that the addition of electrolytes increases the suspension viscosity, the yield stress value and the shear-thinning character. Obviously, this confirms the important role of the ionic strength in the aggregation of kaolin suspensions.

Viscoelastic properties of coating colors have been found to have a bearing on the performance or runnability of the colors in blade coating [37,38]. The relationship between viscoelasticity and high shear viscosity of coatings was studied in connection with the short dwell runnability. In the latex-based paper coating processes, the film-forming behavior of the latex and the coating's compressive response to calendaring depend on the viscoelastic properties of the latex binder and the coating. In the printing process - coating strength, rotogravure printability, stiffness, cracking resistance, folding endurance, blister resistance – are all properties that are affected by the viscoelastic properties of the latex and coating [38].

The rheological properties mostly depend on the colloidal chemical interactions between the coating colour components [3]. As is well known, the coating colour is a very complex colloid system (mainly composed of a very dense suspension of pigment microparticles, e.g. kaolin, titanium-dioxide, calcium-carbonate, latex binders and different additions like extender nanoparticles and stabilizing polyelectrolytes). By controlling the colloidal chemical interactions, the rheological properties of coating colours can be controlled.

1.4) The role of NaCMC in the formulation of coating colors

The formulation of coating colors using clay, latex and sodium carboxymethyl cellulose (NaCMC) has received more and more attention in recent years [39]. Some researchers [40] compared the colloidal stabilizing effect of NaCMC and starch: they showed that flocculation of latex by NaCMC occurred after centrifuging the coating colors but not by the starch. The other researchers [41] compared the rheological behavior of a NaCMC containing color with those of a starch containing color. They have demonstrated that 1 wt% of NaCMC conferred about the same elastic character on the colors as oxidized starch added at a level of 6 wt%. They showed that there was a change in suspension structure when either polymer was added, which they interpreted as an aggregation process. Zaman, et al. [42] emphasized that the flow properties of silica suspensions are highly affected by the pH of the suspending media and concentration of the added salt.

CHAPTER 2

EXPERIMENTAL

2.1) Materials

Kaolin powder (K-7375, hydrated aluminum silicate), was purchased from Sigma Chemical Company, St. Louis, Missouri U.S.A. The particle size of this kaolin is in the range of 0.1-4.0 μm , containing 90% by weight of kaolinite particles < 2 μm . The particles are platelet-shaped but form larger stacks. Below pH = 8, the edges of particles are positively charged and the faces are negatively charged. In this study, kaolin powders were dispersed with distilled water to get 40% & 50% concentrations at room temperature by an overhead stirrer for the rheological investigations; while 10% concentration kaolin suspension was made using scaled glass tubes for the sedimentation volume study. The pH of the prepared samples was found to be between 5 and 6. The approximate measurements were carried out by indicator paper.

Sodium Carboxymethyl Cellulose, NaCMC powder of two viscosities: low (No.C-8758) and medium (No.C-4888) viscosity were ordered from Sigma. Their solutions were prepared with distilled water for examining flow properties and for the composition with kaolin suspensions at room temperature, depending on the concentration, sufficient time was given to achieve the homogeneity of the solutions without mixing or any external source of heat or power to avoid any decomposition of the polymer molecules. CMC normally acts as thickening agent [43], and most CMC solutions show pseudoplastic behavior, that is, viscosity is decreased by shearing [44]. In this study, low (lv) and medium (mv) viscosity NaCMC powders and solutions were added at different concentrations into kaolin

suspensions as thinning agent. NaCl (sodium chloride, BDH, analytical reagent), is water-soluble and ionizes easily. The NaCl in solution accommodates both positively (Na^+) and negatively charged (Cl^-) ions. Distilled water, pH-value around 5~6, was used for preparation of samples.

2.2) Instruments for rheological measurements

Rheological measurements of our samples were carried out using a rotational controlled Rheometer (Rheostress RS100), equipped with a cone and plate sensor. The RS100 is an air-bearing rheometer allowing characterization of sensitive structures which can be applied to low and medium viscosity materials using low stresses and low shear rates. It is designed with a frame which is especially stiff to allow precise strain and normal force measurements; the motor is the most powerful drag cup with an excellent dynamic response and low current to minimize heat generation; the frictionless air-bearing design allows a high axial and radial force together with a small mechanical start-up torque. At a pressure of 2.5 bar and a flow rate of 6 l/min [45], it starts rotating with a torque of less than $1\mu\text{Nm}$; the sensor design, cone and plate is preferred when cleaning is a problem or only a limited sample volume is available; it is controlled by a sophisticated application software package which contains all the routines desired and required in only one rheometer; The resulting shear rate registered into the sensor system is detected with a stable and precise digital encoder with up to 10 million impulses for one revolution which is able to measure a small yield value and low strain or shear rates. The air bearing with the highest specifications available with respect to start up torque, friction and stability for precisely applying stress. The resulting strain is detected digitally with 10 million impulses for 360° . There are more special features

in RS100 for example torque calibration; autogap/thermogap controls; microstress control; compliance correction; and inertia correction, etc..

While the Rheometer is running, there is a gap between the cone and the plate to ensure no damage to either surface, and the gap is designed small enough to keep the angle 'θ' between the cone and plate as small as 4 degrees for keeping the ratio of angular speed and distance to the plate constant. That is, for any point within the gap, a constant shear rate 'γ̇' can be assumed. Some operating modes such as controlled rate (CR) mode, controlled stress (CS) mode, and oscillation (OSC) mode which are conducted alternatively and interchangeably in the RS 100 are performed easily using the computer control. In CR mode, the torque is measured at a certain preset speed, and both steady flow curves and thixotropy behavior can be perfectly determined; In CS mode, the speed is measured at a certain preset torque, and both yield point of samples, which is measured within a loop composed by an up and down curves with the increase of stress from zero to a fixed value, and the creep-recovery behavior, where a constant stress is applied on samples and the corresponding strain is obtained, can be measured. In OSC mode, the torque is applied as a sine wave at varying frequencies; when it is operating, there is no destruction of samples and no destroying the structure of samples. In this mode, both the stress and frequency sweeps can be measured.

Geometrical factors convert physical quantity into rheological quantity as below:

$$\tau = A_{\text{factor}} * M_{\text{torque}} \text{ (in CS mode)} \quad (1)$$

$$\gamma = M_{\text{factor}} * \Omega_{\text{rotational speed}} \text{ (in CR mode)} \quad (2)$$

$$\eta = M_{\text{torque}} * \tau_{\text{factor}} / \Omega_{\text{rotational speed}} * \gamma_{\text{factor}} \text{ (in CR mode)} \quad (3)$$

2.3) Preparation of samples

2.3.1) Preparation of samples for rheological study

Using an analytical balance with a four digital resolution, kaolin powder, NaCMC low and medium viscosity powders, and sodium chloride NaCl powder were exactly measured to make samples with the content of 40% & 50% kaolin suspensions. Stock solutions of NaCMC and NaCl were prepared as well. During the preparation, the components for every sample were introduced simultaneously. In this work, 40% and 50% kaolin suspensions were prepared by adding one and half weight of distilled water, and half weight of distilled water to kaolin powders. Dispersed at room temperature was performed firstly using a glass rod by hand, then by an overhead stirrer at 1500rpm for five minutes for rheological investigations. A 10% concentration kaolin stock suspension was dispersed with a glass rod and stored in the scaled glass tubes for the further study of sedimentation volumes. The CMC solutions were prepared by adding distilled water at the specific concentrations for low and medium viscosities respectively at room temperature.

2.3.1.1) *Preparation of aqueous solutions of low (lv) and medium (mv) viscosity NaCMCs*

For a total 50g weight of solution for each sample, the calculated amount of lv NaCMC and mv NaCMC powders were put in each glass beaker, distilled water was added to get different concentrations from 1% ~ 5%. The solution of 1% mv NaCMC and 1% NaCl was made the same way. The compositions of samples are shown in Table 2.3.1.1.

2.3.1.2) Preparation of 40% kaolin suspensions (additions: mv NaCMC powder and NaCl)

For a total 50g weight for each sample, 4 kinds of samples of 40% kaolin suspensions were prepared. The compositions of samples are shown in Table 2.3.1.2.

2.3.1.3) Preparation of 50% kaolin suspensions (additions: lv NaCMC, mv NaCMC and NaCl)

For a total 60g for each sample, 10 kinds of different composites were prepared in two groups (Tables 2.3.1.3 & 2.3.1.4). In Table, 2.3.1.3, 0.25% and 0.5% solutions were prepared from 5% lv NaCMC stock solution, while 0.25% and 0.5% solutions were prepared from 3% mv NaCMC stock solution. In Table, 2.3.1.4, 0.1% and 0.5% solutions were prepared from 5% lv NaCMC stock solution, while 0.01% and 0.002% solutions were prepared from 1% mv NaCMC stock solution.

2.3.2) Preparation of samples for sedimentation volume study

For a total volume of 10ml, the samples were prepared from suitable amounts of the stock solutions (kaolin, NaCMC and NaCl). In this study, 2.5% kaolin suspension was prepared from 10% kaolin stock suspensions, different concentrations of lv NaCMC solutions were prepared from 0.25% lv NaCMC stock solution and different concentrations of mv NaCMC solutions were prepared from 1% mv NaCMC stock solution. Different concentrations of NaCl solutions were prepared from 10% NaCl stock solutions. All the samples were made by adding the necessary amount of distilled water in scaled tubes, and homogenized by shaking the tubes thoroughly. For practical reasons, we prepared more diluted (2.5%) kaolin

suspensions for the sedimentation volume investigations. During the same observation periods (after 3, 21, 27 and 72 hours), three groups of experiments were carried out. The compositions of prepared samples are given in Tables 2.3.2.1 to 2.3.2.3.

Table 2.3.1.1**The compositions of prepared low (lv) and medium (mv) viscosity NaCMC solutions****lv: low viscosity; mv: medium viscosity**

Samples	Content of NaCMC solution			
	lv NaCMC	mv NaCMC	NaCl	Distilled water
NaCMC/1	5%	-	-	95%
NaCMC/2	-	1%	-	99%
NaCMC/3	-	2%	-	98%
NaCMC/4	-	3%	-	97%
NaCMC/5	-	4%	-	96%
NaCMC/6	-	5%	-	95%
NaCMC/7	-	1%	1%	98%

Table 2.3.1.2**The compositions of samples prepared from 40% kaolin suspensions (addition: mv NaCMC or NaCl)****mv: medium viscosity**

Samples	Content of different components			
	Kaolin	mv NaCMC	NaCl	Distilled water
K40/1	40%	-	-	60%
K40/2	40%	1%	-	59%
K40/3	40%	-	1%	59%
K40/4	40%	1%	1%	58%

Table 2.3.1.3

The compositions of samples prepared from 50% kaolin suspensions (additions: NaCMC or NaCl) Group I

lv: low viscosity; mv: medium viscosity

Samples	Content of different components				
	Kaolin	lv NaCMC (5%)	mv NaCMC (3%)	NaCl	Distilled water
K50/(I)1	50%	-	-	-	50%
K50/(I)2	50%	0.5%	-	-	50%
K50/(I)3	50%	-	0.5%	-	50%
K50/(I)4	50%	0.25%	0.25%	-	50%
K50/(I)5	50%	0.5%	-	1%	49%
K50/(I)6	50%	-	-	1%	49%

Table 2.3.1.4

The compositions of samples prepared from 50% kaolin suspensions (additions: NaCMC or NaCl) Group II

lv: low viscosity; mv: medium viscosity

Samples	Content of different components				
	Kaolin	lv NaCMC (5%)	mv NaCMC (1%)	NaCl	Distilled water
K50/(II)1	50%	0.5%	0.01%	-	49.5%
K50/(II)2	50%	0.1%	-	-	49.9%
K50/(II)3	50%	0.1%	0.002%	-	49.9%
K50/(II)4	50%	0.1%	0.002%	0.5%	49.4%

Table 2.3.2.1

The compositions of samples prepared from 2.5% kaolin suspension (additions: NaCMC)

lv: low viscosity; mv: medium viscosity

Samples(I)	Content of different components			
	Kaolin (10%)	lv NaCMC (0.25%)	mv NaCMC (1%)	Distilled water
Tube (I)1	2.5%	0.04%	-	97.5%
Tube (I)2	2.5%	-	0.04%	97.5%
Tube (I)3	2.5%	0.02%	-	97.5%
Tube (I)4	2.5%	-	0.02%	97.5%
Tube (I)5	2.5%	0.01%	0.01%	97.5%
Tube (I)6	2.5%	0.02%	0.02%	97.5%
Tube (I)7	2.5%	0.01%	-	97.5%
Tube (I)8	2.5%	-	0.01%	97.5%
Tube (I)9	2.5%	-	-	97.5%
Tube (I)10	2.5%	-	0.005%	97.5%

Table 2.3.2.2

The compositions of samples prepared from 2.5% kaolin suspension (additions: lv and mv NaCMC) and NaCl

lv: low viscosity; mv: medium viscosity

Samples(II)	Content of different components				
	Kaolin (10%)	lv NaCMC (0.25%)	mv NaCMC (1%)	NaCl (10%)	Distilled Water
Tube (II)1	2.5%	-	0.01%	1%	96.5%
Tube (II)2	2.5%	-	0.02%	1%	96.5%
Tube (II)3	2.5%	-	0.04%	1%	96.5%
Tube (II)4	2.5%	0.01%	-	1%	96.5%
Tube (II)5	2.5%	0.02%	-	1%	96.5%
Tube (II)6	2.5%	0.04%	-	1%	96.5%

Table 2.3.2.3**The compositions of samples prepared from 2.5% kaolin suspension (addition: NaCl)**

Samples(III)	Content of different components		
	Kaolin (10%)	NaCl (10%)	Distilled water
Tube (III)1	2.5%	-	97.5%
Tube (III)2	2.5%	0.2%	97.3%
Tube (III)3	2.5%	0.4%	97.1%
Tube (III)4	2.5%	0.6%	96.9%
Tube (III)5	2.5%	0.8%	96.7%
Tube (III)6	2.5%	1.0%	96.5%

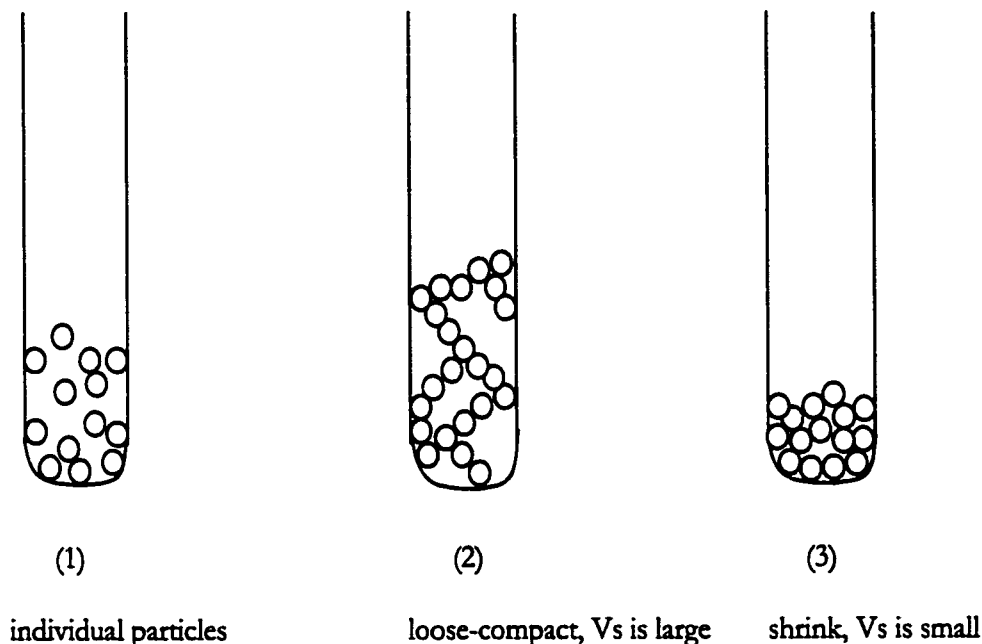
CHAPTER 3

METHODS

3.1) Sedimentation volume investigation

To get qualitative information about the effect of different additions on the colloidal interactions of kaolin particles and structure formation, sedimentation volume investigations were performed. This method provides information about the particle-particle interactions (p-p adhesion). As is well known, the bigger the sedimentation volume, the stronger the particle-particle adhesion. The explanation can be given as follows (the figures are shown below):

- if the system is stable, there are only individual particles and aggregation does not happen. They settle down in the bottom of the tube individually, and the forming sediment is very dense. There is no attraction between the particles.
- if the system is unstable, the particle-particle adhesion is strong and the particles aggregate. The structure of the aggregate is usually loose. Due to the strong particle-particle attraction, they can not shrink in the sediment, so the structure of sediment is also loose, that is, the sedimentation volume is large.
- if the system is unstable, but the particle-particle adhesion is weak, the particles aggregate but they can shrink in the sediment due to the gravity. Hence, the sedimentation volume in this case is small.



The sedimentation volumes were measured at ambient temperature (23 ± 1 °C). The entire homogenization was obtained by a standard shaking method after preparation. The equilibrated values were recorded after shaking (homogenization), at 3 hours, 21 hours, 27 hours and 72 hours. The apparent sedimentation volumes were examined by reading the value in each tube. In order to check the equilibration, reading the near constant values of volumes, the samples were homogenized again and measured the sedimentation volumes.

3.2) Rheological property investigation

Using the Rheostress RS100, the properties of kaolin suspensions for different compositions were obtained quantitatively by measuring four kinds of curves in CS & CR modes. These curves are: 1) steady-state flow curve; 2) thixotropy loop; 3) yield stress loop; 4) creep-recovery curve.

The rheological properties were measured at ambient temperature (23 ± 1 °C) using a cone-plate (Rheometer RS100). Both the viscous and elastic properties were studied. The apparent and plastic viscosities, the Bingham yield stresses, the Herschel-Bulkley yield stresses, and thixotropy were examined by measuring the steady-state flow curves and thixotropy loops “area”. The elastic behaviour was investigated by measuring and analysing the creep-recovery functions.

3.3) Analysis of rheological results

3.3.1) Analysis of flow curves

Observing flow behaviors of the investigated samples and measuring viscosity values at different shear rates were performed with the steady-state flow curves. There is a relationship between the assigned shear stress and the resulting shear rate in CS mode, or between the assigned shear rate and the resulting shear stress in CR mode. In this study, the CR mode was chosen in order to get a high shear rate. A constant shear rate was applied through the flow field in each measurement to study the deformation of the sample as a function of shear rate. By choosing a minimum value for the start point of shear rate to a maximum value for the end point of shear rate, a series of data from which one shear rate corresponded to one shear stress were obtained.

The flow and viscosity curves were fitted to the Ostwald-de-Waele equation for the CMC solutions, and the flow and viscosity curves were fitted to the Herschel-Bulkley and Bingham equations for the kaolin suspensions. The flow curves of the kaolin samples can be separated

into two main parts manually suitable for the analysis. The Herschel-Bulkley equation fits well for the first part since the flow curve is non-linear at low shear rate, and the Bingham equation is related to the second part since the flow curve in this part shows nearly linear behaviors at high shear rate. Regression calculations for the power law and linear model were carried out for the suspensions and solutions. All the slopes of the straight lines in the flow curves indicate the degree of deviation from Newtonian behavior. All the kaolin samples showed plastic (shear-thinning) behavior with $n < 1$ (n reflects the degree of deviation from the Newtonian behavior. The greater the deviation from 1, the greater the deviation from the Newtonian behavior.). All the NaCMC solutions showed pseudoplastic behavior with $n < 1$ as well. The power law model can be presented by:

Ostwald-de-Waele equation for solutions

$$\tau = k\dot{\gamma}^n \quad (4)$$

wherein k is viscosity parameter.

Herschel-Bulkley equation for suspensions

$$\tau = \tau_{HB} + k\dot{\gamma}^n \quad (5)$$

wherein τ_{HB} is the Herschel-Bulkley yield stress.

The linear model can be presented by the Bingham equation for suspensions

$$\tau = \tau_b + \eta_p \dot{\gamma} \quad (6)$$

wherein τ_b is the Bingham yield stress, η_p is the plastic viscosity.

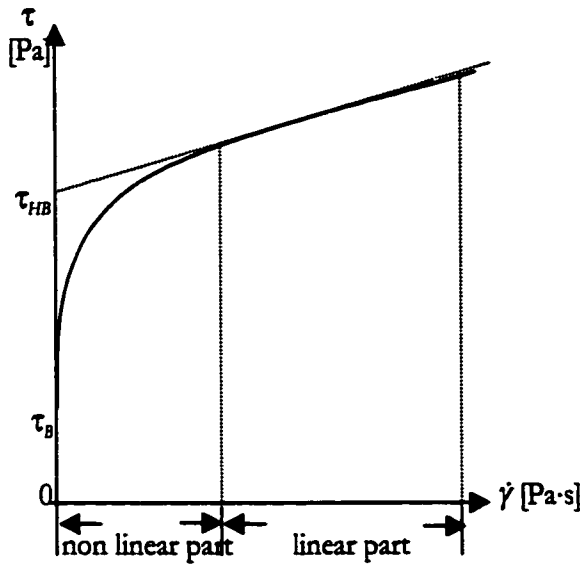


Figure 3.3.1. Diagram of flow curve of suspensions in the shear stress versus shear rate coordinate system. τ_{HB} : Herschel-Bulkley yield stress; τ_B : Bingham yield stress.

3.3.2) Analysis of yield stress curves

The yield stresses (τ_{HB} and τ_B) of the investigated samples can be determined from the above flow curve. Suspensions of flocculated particles often show plastic behavior. These suspensions do not flow until an initial stress level has been exceeded. This stress is called the yield stress. Above the yield stress, the stress and shear rate are linearly related for the ideally plastic behavior. The Bingham equation describes the shear stress/shear rate behavior of many shear-thinning materials at high shear rates. The intercept of the linear portion of the flow curve gives the Bingham yield stress and the slope gives the plastic viscosity of the suspensions. Hence, by choosing the nearly linear range of the second part of the flow curves, the Bingham yield stress (τ_B) and plastic viscosity (η_p) of different samples can be compared with each other. The Herschel-Bulkley (τ_{HB}) yield stress, can be determined from

the Herschel-Bulkley equation. These two yield stresses should be in a good agreement with each other, although the Bingham yield value should always be higher than the other one.

The Herschel-Bulkley (τ_{HB}) yield stress of the investigated samples was performed by forming a hysteresis loop in stress ramp measurements of CS mode. In this test, the controlled stress was applied and controlled, the start shear stress was set to zero. However it will not measure any meaningful shear rate as long as the end stresses were not high enough to cause the fluid to flow. For the 50% kaolin suspension, the end shear stress is much higher than lv NaCMC added kaolin suspension since its low viscosity. If you increase the shear stress, you might increase the time, in order to keep the velocity of elevation of the stress ramp constant. Therefore, the meaningful tests should be carried out under the same rate of velocity elevation during the yield stress measurements. The corresponding results of samples can be compared with each other.

Apparent viscosity of fluid gives much useful behavioral and predictive information for various products, as well as knowledge of the effects of processing, formulation changes, aging phenomena, etc. Flow behavior is used as an indirect measure of product consistency and quality, and flow behavior studies are also deemed as a direct assessment of processability. For example, a high viscosity liquid requires more power to pump than a low viscosity one. Knowing its flow behavior, is useful when designing pumping and piping systems [46].

Modelling clay, drilling muds and certain pigment dispersions are examples of plastic dispersions. Suspensions of carbon black in hydrocarbon oil often acquire a yield value on standing and become conducting, owing to the contact between the carbon particles which is

developed throughout the system. Above the yield stress the interparticle contacts break in the floc. Once these contacts are broken, the suspension behaves as though the particles were dispersed. The concept of the yield stress is very useful for practical purposes, for example, in characterizing the ability of a grease to resist slumping in a roller bearing, in determining the stability of suspensions and the appearance of coated material, etc. [47].

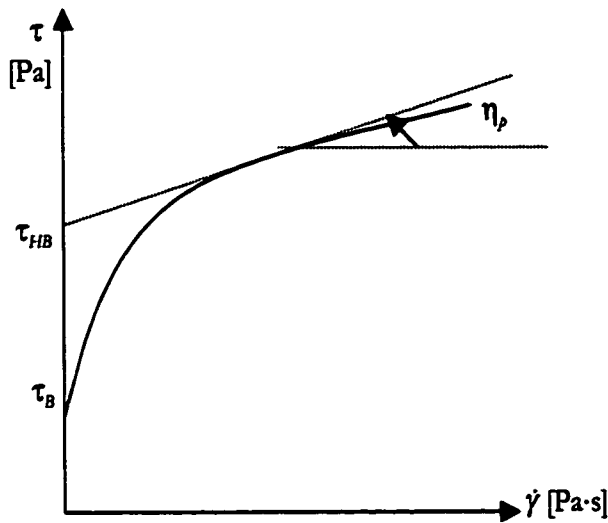


Figure 3.3.2. Diagram of yield stress analysis of suspensions in the shear stress versus shear rate coordinate system. τ_{HB} : Herschel-Bulkley yield stress; τ_B : Bingham yield stress. η_p : plastic viscosity.

3.3.3) Analysis of thixotropy curves

Clay suspensions which are more or less flocculated show the phenomenon of thixotropy. Thixotropic property of materials is defined as a gradual decrease of the viscosity under shear stress followed by a gradual recovery of structure when the stress is removed. The opposite type of behavior, involving a gradual increase in viscosity, under stress, followed by recovery, is called 'negative thixotropy' or 'anti-thixotropy'. The anti-thixotropy materials frequently show dilatancy. A dilatant substance is one that develops increasing resistance to

flow as the rate of shear increases. A household example of a dilatant material is a thick dispersion of cornstarch in water. This appears to be a free-flowing liquid when poured, but when it is stirred, it becomes very firm. The thixotropic behavior is reversible when the shearing is stopped, the viscosity is recovered over a reasonable period of time. Various mechanisms can cause thixotropic behavior. For a gel system, agitation disrupts the three-dimensional structure that binds the system into a gel. Agitation might also introduce order into the system. In a system containing long polymeric molecules, these molecules can be disordered in the gel. When the gel is agitated, the molecules can align in the direction of flow, reducing the resistance to flow [48].

The thixotropy tests were conducted in CR mode of RS100, the hysteresis loop was formed with the up curve which was started at shear rate 0.15 s^{-1} continuously increased to the ended value at shear rate 749.79 s^{-1} , and the down curve which was immediately started at the maximum ended shear rate decreased continuously to the minimum shear rate value as quickly as possible (Green-method). During this study of thixotropy, all the up curves were obtained in the period of 450s (steady-state condition), while all the down curves were obtained in the period of 60s (not steady-state condition). Since the thixotropy is very time-dependent, the up curve is set in a sufficient time for each test to let the network structure of samples break down to reach an equilibrated situation causing reduction in viscosity. When plotting shear stress versus shear rate, the area between the up and down curves defines the degree of the thixotropy. It has the dimension of energy related to volume of the sheared sample indicating the energy required to break down the thixotropic structure [49]. If the fluid is anti-thixotropic, the down curve will be above the up curve. In case of time independent fluids, the upper and lower curves will be identical.

Thixotropy is favorable in certain applications such as paint, ink and coating. Paint that thins fast by strokes of brush can be easily painted. When the applied paint layer rethickens fast, it prevents sagging. In coating mills, highly thixotropic coatings usually have better runnability on blade coaters [32]. In pharmaceuticals, additions are added to drugs to get a thixotropic syrup that prevents dissolving or separation of drugs from the syrup base. In the application of process control design, when a thixotropic fluid enters a long pipe from a large vessel where it has been allowed to rest, the development of the velocity and pressure field in the pipe is very complicated [50].

3.3.4) Analysis of creep-recovery curves

The creep-recovery test is the static method which is used to determine linear viscoelastic behavior of materials. When a typical elastic solid is stressed, it immediately deforms by an amount proportional to the applied stress and maintains a constant deformation as long as the stress remains constant. On removal of the stress, the elastic energy stored in the solid is released and the solid immediately recovers its original shape. Newtonian liquids, on the other hand, deform at a rate proportional to the applied stress and show no recovery when the stress is removed, the energy involved having been dissipated as heat in overcoming the internal frictional resistance. When viscoelastic materials are stressed, some of the energy involved is stored elastically; various parts of the system being deformed into new non-equilibrium positions relative to one another. The remainder is dissipated as heat; various parts of the system flowing into new equilibrium positions relative to one another. If the relative motion of the segments into non-equilibrium positions is hampered, the elastic deformation and recovery of the materials is time-dependent (retarded elasticity) [51].

Static test involves the imposition of a step change in stress (or strain) and the observation of the subsequent development in time of the strain (or stress). While the dynamic test method involves the application of a harmonically varying strain. Whatever method is applied, the very important point is that, the measurements are made in the linear viscoelastic range. Otherwise, the results will be dependent on experimental details and will not be unique to the material. The test for linearity is to check that the computed viscoelastic functions are independent of the magnitude of the stresses and strains applied.

The determination of the linear viscoelastic response is very meaningful for the properties of materials. There is the possibility of elucidating the molecular structure of materials from the linear viscoelastic response; The material parameters and functions measured in the relevant experiments sometimes prove to be useful in the quality-control of industrial products; A background in linear-viscoelasticity is helpful before proceeding to the much more difficult subject of non-linear viscoelasticity; Finally, a further motivation for some past studies of viscoelasticity came from tribology, where knowledge of the steady shear viscosity function η was needed at high shear rates. Measurements of this function on low-viscosity “Newtonian” lubricants at high shear rates were made difficult by such factors as viscous heating, and this led to a search for an analogy between shear viscosity and the corresponding dynamic viscosity [52].

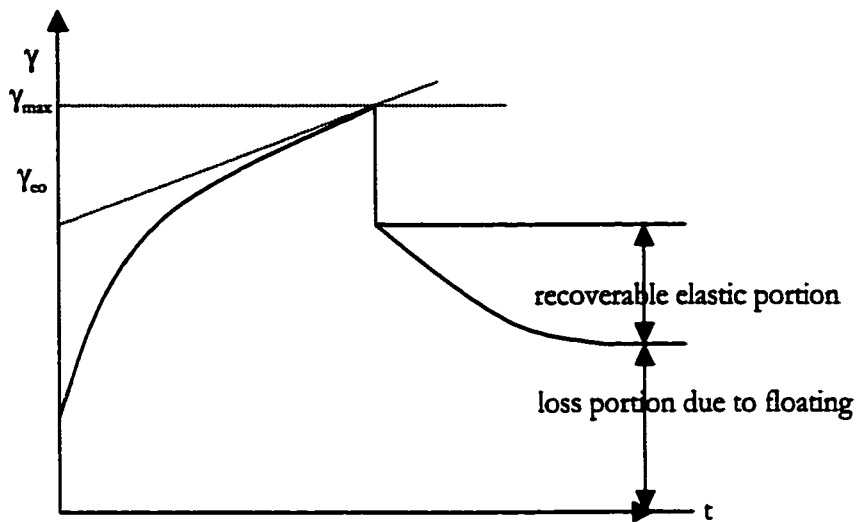


Figure 3.3.4. Diagram of creep-recovery analysis of viscoelastic materials.
 γ_{max} : maximum deformation; γ_{eo} : elastic deformation.

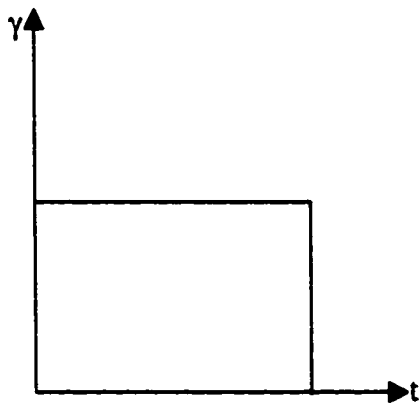


Figure 3.3.5. Diagram of creep-recovery analysis of elastic solid materials

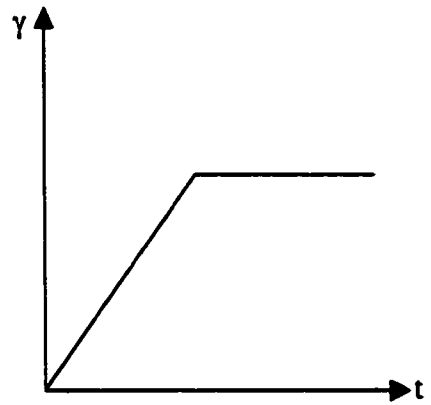


Figure 3.3.6. Diagram of creep-recovery of analysis of Newtonian liquids materials

CHAPTER 4

RESULTS AND DISCUSSION

4.1) Results of preparation technique

In order to check the effect of the technique of NaCMC addition to the kaolin samples, the rheological and sedimentation volume investigations were carried out. Concerning the rheological investigations of samples for 40% kaolin suspensions, the time-dependence of viscosity was found in samples prepared from mv NaCMC powder. The time-dependence was also found in viscosity of samples for 50% kaolin suspensions, in the case of the samples prepared from (l-m)v NaCMC powders. Moreover, from the observation and viscosity measurements, it was also shown that the lv NaCMC-added 50% kaolin suspensions were significantly thinner than that of mv NaCMC-added suspensions. However, the time-dependence was not found in the viscosity of some 50% kaolin suspensions, of which the samples were prepared from (l-m)v NaCMC solutions. To reach a near-equilibrated situation for macromolecules at a solid-liquid interface takes more time if one prepares the samples from NaCMC powders than NaCMC solutions. It also takes more time to reach an equilibrated situation in adsorption and in the conformation. In Table 4.1.1, the viscosity of some 50% kaolin suspensions samples prepared directly from (l-m)v NaCMC powder was measured and recorded after one day of preparation and after two weeks of preparation at room temperature. The viscosity of these samples decreased after two weeks. However, in Table 4.1.2, there was no change at all during the kinetic study of viscosity for 50% kaolin suspensions prepared from NaCMC solution. The viscosity were constant during the investigation period.

Concerning the sedimentation volumes investigations of samples for 2.5% kaolin suspensions, the time-dependent property was even found for samples prepared from NaCMC solutions. In Table 4.1.3, 10 kinds of samples were prepared and measured at equilibrated state after 3 sets of shaking; for each shaking, the sedimentation volumes (V_s) were recorded. Corresponding to each sample, the V_s decreased with time, which showed significant time-dependence. This is not in a good agreement with the rheological results that can be interpreted as follows. In the rheological investigations, by applying a stronger force than the gravitational force, one can destroy every structure independently of the structural strength provided that the structural strengths are not too high. Hence, the cone-plate viscometry does not make any difference between the samples.

Table 4.1.1

Viscosity [Pa·s] of samples prepared from NaCMC powder

lv: low viscosity; mv: medium viscosity

Sample			Viscosity range [Pa·s]
50% K with 0.5% lv NaCMC and 0.5% mv NaCMC	Time	After 1 day	0.4 ~ 3.6
		After 2 weeks	0.09 ~ 3
50% K with with 0.5% lv NaCMC and 0.5% mv NaCMC and 1% NaCl	"	After 1 day	0.5 ~ 13
		After 2 weeks	0.1 ~ 1.3
50% K with 1% lv NaCMC and 1% NaCl	"	After 1 day	0.25 ~ 2.1
		After 2 weeks	0.16 ~ 1.7

Table 4.1.2

Viscosity [Pa·s] of 50% kaolin suspensions prepared from NaCMC solution

lv: low viscosity; mv: medium viscosity

Shear rate: 26.09[1/s]

Sample	2nd day	7th day	11th day	18th day	21st day
50% K with 0.5% lv NaCMC	0.58	0.58	0.52	0.58	0.56
50% K with 0.5% mv NaCMC	2.52	2.56	2.6	2.56	2.46
50% K with 0.5% lv NaCMC and 1% NaCl	4.7	4.68	4.55	4.68	4.55
50% K (washed) with 0.5% lv NaCMC	0.28	0.31	0.28	0.31	0.3

Shear rate: 362.0[1/s]

Sample	2nd day	7th day	11th day	18th day	21st day
50% K with 0.5% lv NaCMC	0.12	0.14	0.13	0.12	0.12
50% K with 0.5% mv NaCMC	0.41	0.44	0.42	0.43	0.41
50% K with 0.5% lv NaCMC and 1% NaCl	0.37	0.37	0.45	0.33	0.32
50% K (washed) with 0.5% lv NaCMC	0.07	0.09	0.09	0.08	0.09

Table 4.1.3

Sedimentation volumes of 2.5% kaolin suspensions in mL [equilibrated data, after dispersing again] (* without additions)

lv: low viscosity; mv: medium viscosity.

Sample	After the first shaking	After the second shaking	After the third shaking
1. 0.04% lv NaCMC	0.9	0.65	0.5
2. 0.04% mv NaCMC	1.3	1	0.8
3. 0.02% lv NaCMC	0.9	0.6	0.55
4. 0.02% mv NaCMC	2.6	1.5	1.2
5. 0.01% lv NaCMC and 0.01% mv NaCMC	2.5	1.1	0.95
6. 0.02% lv NaCMC and 0.02% mv NaCMC	1	0.75	0.6
7. 0.01% lv NaCMC	0.9	0.55	0.5
8. 0.01% mv NaCMC	3.3	2	1.6
9. - *	2.5	2.5	2.5
10. 0.005% mv NaCMC	3.2	2.4	1.9

4.2) Results of sedimentation volume investigations

The results of sedimentation volumes (V_s) are presented in Tables 4.2.1 to 4.2.3 and Figures 4.2.1 to 4.2.3. In Table 4.2.1, at 10 and 20 minutes after homogenization (shaking), V_s can not be recorded due to the very milky-like nature of the suspensions. This phenomenon was also found for some tubes after 3 hours. As can be seen in Table 4.2.1 and Figure 4.2.1, the lv NaCMC shows a stabilizing effect in the whole concentration range. This means that the V_s values significantly decrease with increasing concentration of polymer. In the case of the mv NaCMC, however, a maximum V_s appears at the lowest polymer concentrations due to the bridging flocculation. The mv polymer can form bridges between the positively charged edges of different particles. The simultaneous addition of the lv and mv polymers in the suspension leads to intermediate sedimentation volumes, indicating that beside the adsorption of lv NaCMC the bridge forming adsorption of mv NaCMC also occurs (site-blocking effect).

The simultaneous addition of NaCl and NaCMC in the kaolin suspensions resulted in interesting observations. As can be seen in Figure 4.2.2, the NaCl diminishes the stabilizing capability of lv NaCMC, especially at the lower concentrations of the lv polymer (also see in Figure 4.2.1). This effect can be attributed to screening of the electrostatic forces by the sodium chloride. The NaCl can decrease the adsorption capability of the negatively charged polymers on the positively charged edges on the one hand; On the other hand, the sodium-ions can also screen the electrostatic repulsion between the polymer-covered particles. An opposite effect can be observed for the mv NaCMC. The NaCl improves the stabilizing capacity of the polymer, supposedly due to the hindered bridge forming adsorption.

In Figure 4.2.3 and Table 4.2.3, the results of V_s of 2.5% kaolin suspension in the presence of NaCl are presented. The study of sedimentation volumes in the presence of NaCl is of great importance because we can get indirect information about the amphoteric character of the surface charges of kaolin particles. As can be seen in Figure 4.2.3, the V_s values are decreasing with increasing concentration of the NaCl up to 0.6 cm^3 , then remaining at a constant value. The particle-particle adhesion in this case becomes weaker after adding NaCl into kaolin suspension which can be explained in terms of screening the face-edge electric attractions. The NaCl hinders the adsorption (screening effect) and also screens the repulsion among the NaCMC-covered particles. The NaCl mostly hinders the bridge forming adsorption of mv NaCMC resulting in a more stable suspensions.

Table 4.2.1

Vs (Sedimentation Volumes) of 2.5% kaolin suspension with the addition of lv and mv NaCMC. For a total volume of 10mL after shaking thoroughly.

lv: low viscosity; mv: medium viscosity

Unit: mL

Composition\Sample		after shaking		after 3 hours	after 21 hours	after 27 hours	after 72 hours
		10 min.	20 min.				
1	2.5% Kaolin + 0.04% lv NaCMC	0	0	0	0.9	0.8	0.9
2	2.5% Kaolin + 0.04% mv NaCMC	0	0	0	1.0	1.4	1.3
3	2.5% Kaolin + 0.02% lv NaCMC	0	0	0	0.9	1.0	0.9
4	2.5% Kaolin + 0.02% mv NaCMC	0	0	3.1	2.5	2.6	2.6
5	2.5% Kaolin + 0.01% lv NaCMC + 0.01% mv NaCMC	0	0	3.0	2.6	2.5	2.5
6	2.5% Kaolin + 0.02% lv NaCMC + 0.02% mv NaCMC	0	0	0	1.3	1.2	1.0
7	2.5% Kaolin + 0.01% lv NaCMC	0	0	0	0.9	0.9	0.9
8	2.5% Kaolin + 0.01% mv NaCMC	0	0	3.7	3.4	3.4	3.3
9	2.5% Kaolin	0	0	2.9	2.6	2.5	2.5
10	2.5% Kaolin + 0.005% mv NaCMC	0	0	3.5	3.3	3.3	3.2

Table 4.2.2

Vs (Sedimentation Volumes) of 2.5% kaolin suspension with the addition of NaCMC. For a total volume of 10mL after shaking thoroughly [1% NaCl in each tube]

lv: low viscosity; mv: medium viscosity

Unit: mL

Composition\Sample		after shaking	after 3 hours	after 21 hours	after 27 hours	after 72 hours
1	2.5% Kaolin + 0.01% mv NaCMC	2	2	2	2	2
2	2.5% Kaolin + 0.02% mv NaCMC	1.4	1.4	1.5	1.5	1.5
3	2.5% Kaolin + 0.04% mv NaCMC	0.5	0.5	1	1	1
4	2.5% Kaolin + 0.01% lv NaCMC	2.5	2.5	2.3	2.3	2.3
5	2.5% Kaolin + 0.02% lv NaCMC	0.7	0.7	1.2	1.2	1.2
6	2.5% Kaolin + 0.04% lv NaCMC	0.4	0.4	0.6	0.6	1.0

Table 4.2.3

Vs (Sedimentation Volumes) of 2.5% kaolin suspension with the addition of NaCl. For a total volume of 10mL after shaking thoroughly.

Unit: mL

Composition\Sample		after shaking	after 3 hours	after 21 hours	after 27 hours	after 72 hours
1	2.5% Kaolin	3.5	2.5	2.5	2.5	2.4
2	2.5% Kaolin + 0.2% NaCl	3	2.4	2.2	2.2	2.1
3	2.5% Kaolin + 0.4% NaCl	3	2.4	2.2	2.2	2.1
4	2.5% Kaolin + 0.6% NaCl	2.9	2.4	2	2	2
5	2.5% Kaolin + 0.8% NaCl	3	2.2	2	2	2
6	2.5% Kaolin + 1.0% NaCl	3	2.1	1.9	1.9	2

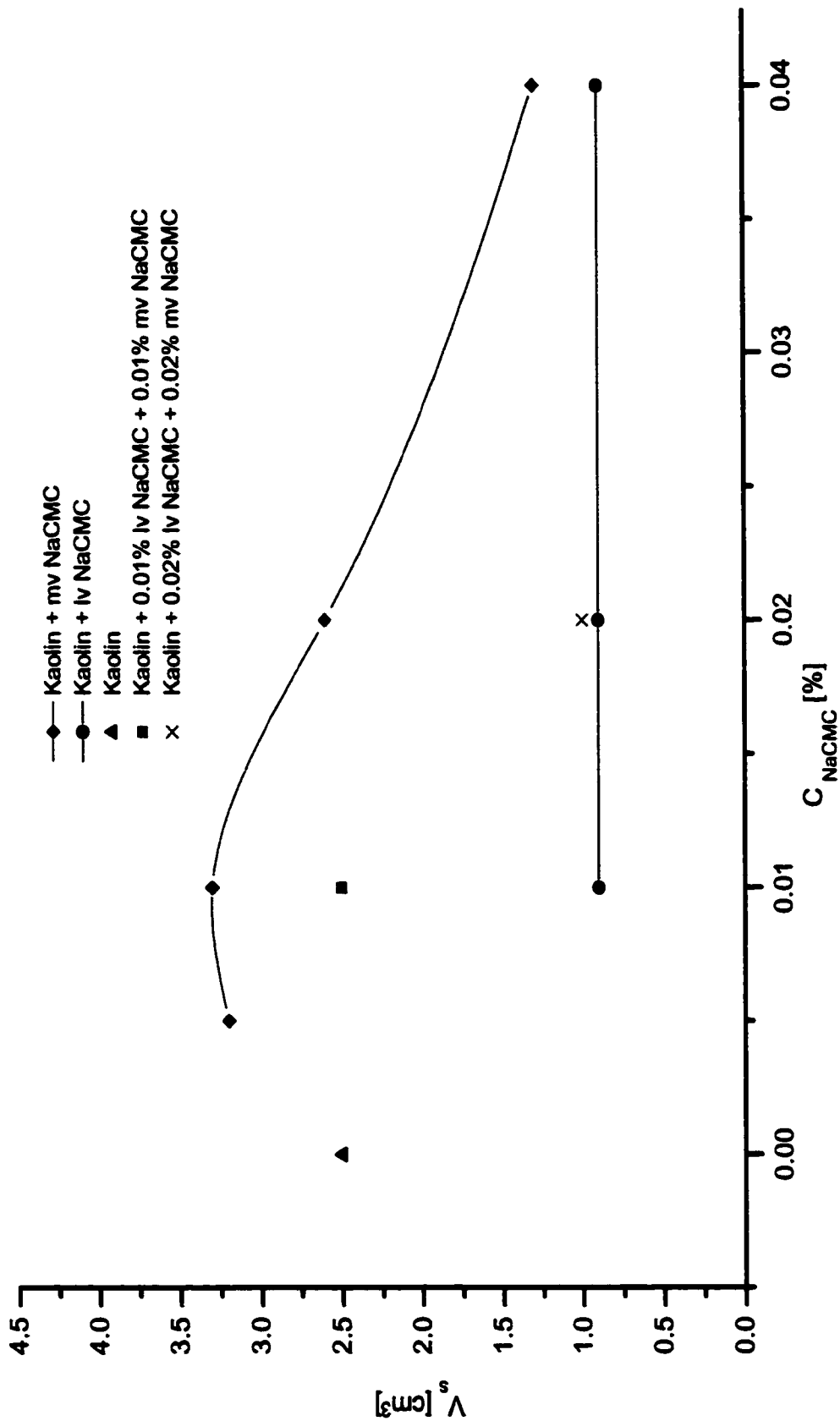


Figure 4.2.1. Sedimentation volumes (V_s) of 2.5% kaolin suspensions as a function of NaCMC concentration (C_{NaCMC}). lv: low viscosity; mv: medium viscosity.

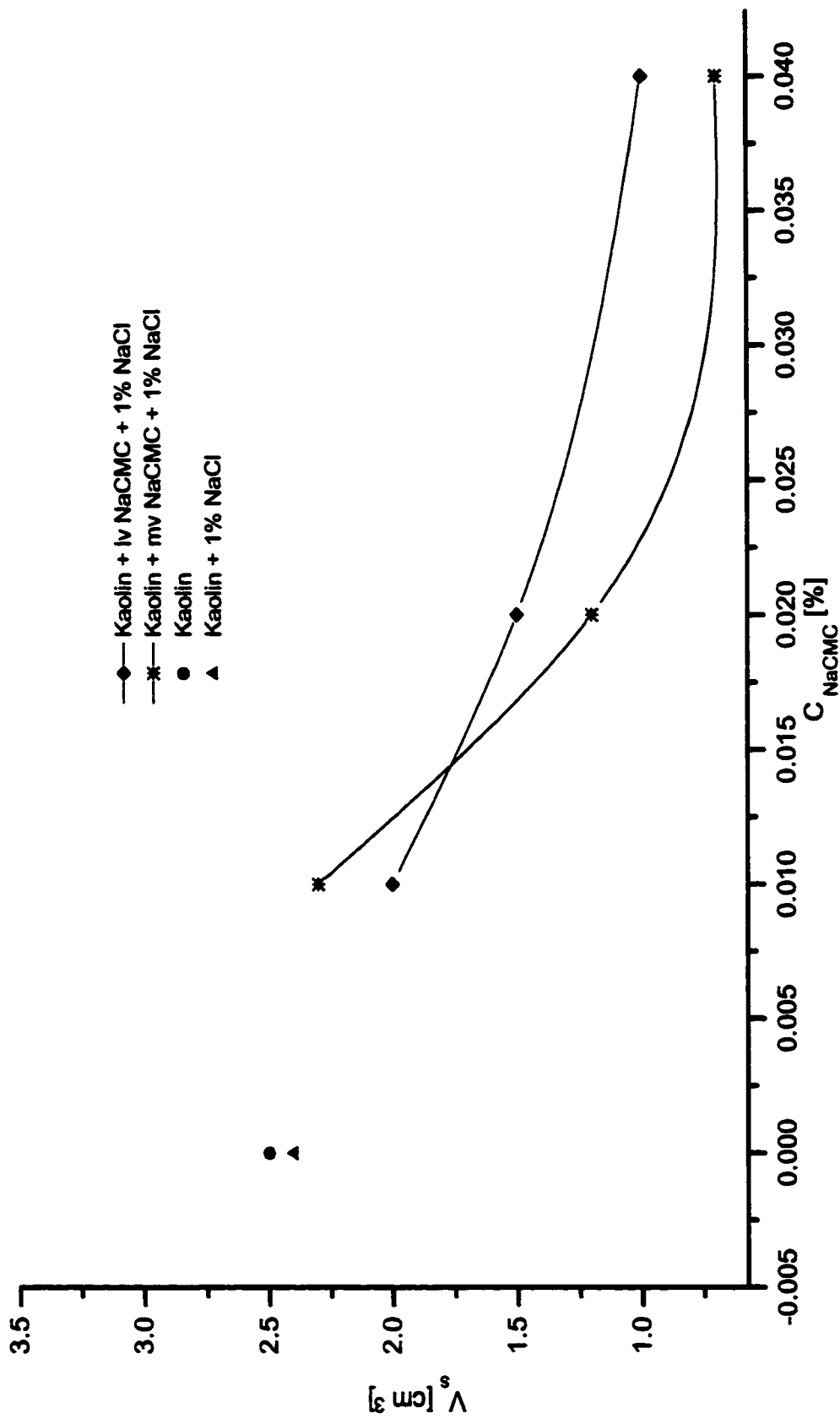


Figure 4.2.2. Sedimentation volumes (V_s) of 2.5% kaolin suspensions as a function of NaCMC concentration (C_{NaCMC}) in the presence of 1% NaCl. lv: low viscosity; mv: medium viscosity.

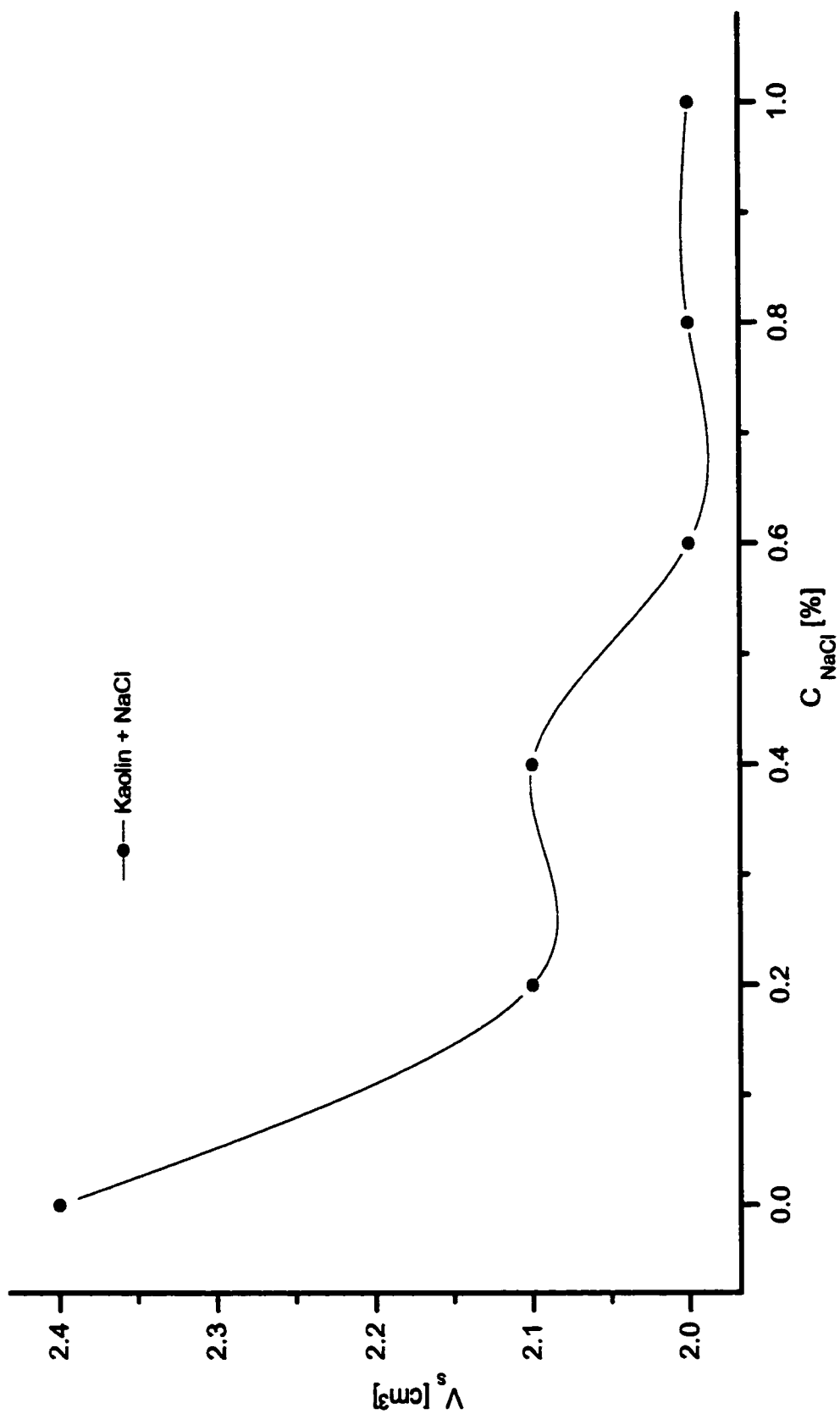


Figure 4.2.3. Sedimentation volumes (V_s) of 2.5% kaolin suspensions as a function of NaCl concentration (C_{NaCl}).

4.3) Results of rheological investigations

The results of rheological investigations in this study were examined for the aqueous NaCMC solutions and for the 40% and 50% kaolin suspensions. Every investigated sample showed non-Newtonian, mostly plastic behaviour. The viscosity curves and flow curves for the aqueous NaCMC solutions can be seen in Figures 4.3.1.1 and 4.3.1.4. The viscosity curves and flow curves for the 40% kaolin samples can be seen in Figures 4.3.1.2 and 4.3.1.5. And the viscosity curves and flow curves for the 50% kaolin samples can be seen in Figures 4.3.1.3 and 4.3.1.6. The determined rheological parameters (the range of apparent viscosities, plastic viscosity, Herschel-Bulkley and Bingham yield stress, area of the hysteresis loop for thixotropy and elasticity ratio for creep-recovery tests) for both the 40% and 50% kaolin suspensions are given in Tables 4.1 and 4.2, respectively. The yield stresses of samples prepared from 40% and 50% kaolin suspensions are shown in Tables 4.3.2.1 and 4.3.2.2. The characteristic results of thixotropy measurements appear in Figures 4.3.3.1 (for the 40% kaolin suspensions) and Figures 4.3.3.2 ~ 4.3.3.4 (for the 50% kaolin suspensions). In the meantime, the characteristic creep-recovery functions are given in Figures 4.3.4.1 ~ 4.3.4.4 (for the 40% kaolin suspensions) and Figures 4.3.4.5 ~ 4.3.4.7 (for the 50% kaolin suspensions).

4.3.1) Results of viscosity analysis

4.3.1.1) *Viscosity curve analysis of NaCMC aqueous solutions*

The viscosity curves for (l-m)v NaCMC {(l-m)v: low and medium viscosity} are shown in Figure 4.3.1.1. As can be seen, there is an increase in viscosity with the increase of the concentration of mv NaCMC. Comparing the viscosity of 1% mv NaCMC with 1% NaCl added 1% mv NaCMC solution, the addition of 1% NaCl results in approximately 10% decrease, supposedly due to the screening effect. It can screen the repulsion between the chains of segments of (CMC) macromolecules. Hence, the macromolecules become smaller (reaching a more coiled conformation) in the solution leading to the decrease of viscosity. The Ostwald-de-Waele parameters for the investigated aqueous NaCMC solutions are given in Table 4.3.1.1. All the slopes of the straight lines in the flow curves indicate the degree of deviation from Newtonian behavior, and all the samples show pseudoplastic (shear-thinning) behavior with $n < 1$. 1% mv NaCMC has the largest value of n among all of them, it shows the most Newtonian-like behavior. 1% mv NaCMC and 1% NaCl together also has the largest value of n among all of them; it shows almost Newtonian behavior as well. 5% mv NaCMC has the smallest value of n among all of them showing a very shear-thinning behavior. The flow behavior curves of the above solutions are presented in Figure 4.3.1.4.

4.3.1.2) Viscosity curve analysis of samples of 40% kaolin suspensions

As can be seen in Figure 4.3.1.2, the curve of 40% kaolin suspension presented the highest viscosity value corresponding to the shear rate. 1% NaCl added sample presented the lowest value. 1% NaCl was a better thinning agent than 1% mv NaCMC in this case. The viscosity for the 1% mv NaCMC and 1% NaCl added together sample was also lower than just the 40% kaolin suspension; they act as thinning agents here as well.

NaCMC is a polyelectrolyte, it can dissociate in water. The negatively charged (CMC) molecules can adsorb on the positively charged surface of kaolin particles: the card-pack structure breaks down. At a sufficient level of polymer concentration, the adsorption results in the steric and elastic stabilization of suspension (viscosity decrease). When NaCl is added to the aqueous kaolin suspension, the electrostatic interaction (attraction) between the oppositely charged particle surfaces is reduced (screening effect). This results in a weaker structure i.e. it decreased the viscosity of the sample. The results can be supported by the sedimentation volumes study (see Tables 4.2.1 and 4.2.3). When the two additions are put into the kaolin suspension together, the viscosity decreased as well (in Figure 4.3.1.2 comparing to the 40% kaolin suspension). In the sedimentation volume study, you can see the obvious decrease in the V_s value (Table 4.2.2). The electrolyte decreases the electrostatic repulsion between the macromolecule covered particles (screening effect). That is, the addition (Na^+) can decrease the stabilizing effect of (CMC) in comparison with the viscosity of the 1% mv NaCMC-added kaolin suspension. The flow property of these curves are presented in Figures 4.3.1.5 and 4.3.1.6. The flow parameters for the samples with 40% kaolin content are shown in Tables 4.3.1.2 and 4.3.1.3 according to the Herschel-Bulkley and Bingham approximation. Similar to the analysis of NaCMC solutions, the smaller the n value (less than 1), the stronger the deviation from the Newtonian behavior. The plastic viscosity of each sample is shown in Table 4.3.1.3.

4.3.1.3) Viscosity curve analysis of samples of 50% kaolin suspensions

In Figure 4.3.1.3, 0.5% lv NaCMC-added 50% kaolin suspension shows the lowest viscosity in the whole investigated shear rate range. The most effective stabilizing agent for 50%

kaolin suspension was 0.5% lv NaCMC. Adding a small amount of mv NaCMC (0.01% or 0.25%) into this sample, the viscosity is higher due to the bridging flocculation effect. The presence of the low viscosity (and low molecular weight) polymer, by the site-blocking mechanism (Aksberg and Ödberg, 1990) [10], enhances the bridge flocculation capability of the medium viscosity (higher molecular weight) polymer. In the meantime, the highest viscosity is found for the sample of (l-m)v NaCMC: 0.1% - 0.002% and 0.5% NaCl added to the kaolin suspension. In this situation, 0.5% NaCl increased the viscosity value at each shear rate investigated. Besides, it is very interesting to note that 1% NaCl decreased the stability of the 50% kaolin suspension, while it increased the stability of the 40% kaolin suspension. The reason for this effect is not yet known. The inorganic electrolyte in this case acts as a “salting-out” agent causing destabilization of the suspension. Therefore, the observed behaviour can be attributed to two opposite effects: screening of the face-edge attraction and salting-out. The salting-out effect can be related to the diminished hydration repulsion (Derjaguin and Churaev, 1989) [51] between the particles. In the work of Ghannam and Esmail, they explained the effect of electrolyte on the flow of coating pigments as follows. They indicated that due to the process of NaCl adsorption from solution onto the surface of the pigment particles, the number of aggregates and floc bulkiness in the suspension increased. This leads to an increase in the volume of immobilized water, and eventually the viscosity increases [52]. In the dense suspension, the addition of NaCl drastically decreased the amount of free water molecules originally at a lower level. Where kaolin solid content is up to 50%, the main role to stabilize the suspensions was the 0.5% low viscosity NaCMC. It correlates well with the result of the sedimentation volume investigations. (also see the result (I) of sedimentation volumes study).

The flow curves of 50% kaolin suspensions are presented in Figure 4.3.1.6. The flow parameters of samples with the 50% kaolin content according to the Herschel-Bulkley and Bingham approximation, and plastic viscosity of samples measured at higher shear rate are given in Tables 4.3.1.4 and 4.3.1.5.

Table 4.3.1.1

Effect of samples of NaCMC aqueous solutions on k and n according to the Ostwald-de-Waele equation.

lv: low viscosity; mv: medium viscosity.

Sample	k [Pa· s]	n
1% mv NaCMC	0.11	0.87
2% mv NaCMC	2.89	0.66
3% mv NaCMC	13.99	0.52
4% mv NaCMC	35	0.45
5% mv NaCMC	134.4	0.33
5% lv NaCMC	0.27	0.86
1% mv NaCMC + 1% NaCl	0.09	0.88

Table 4.3.1.2

Effect of samples of 40% kaolin suspensions on k and n according to the Herschel-Bulkley equation in a steady-state condition.

τ_{HB} : Herschel-Bulkley yield stress; mv: medium viscosity.

Sample	τ_{HB} [Pa]	k [Pa· s]	n
40% K suspension	209.3	29.45	0.5
40% K with 1% mv NaCMC	81.35	16.28	0.5
40% K with 1% NaCl	101.2	13.93	0.5
40% K with 1% NaCl + 1% mv NaCMC	167.2	19.29	0.5

Table 4.3.1.3

Effect of samples of 40% kaolin suspensions on τ_B and η_P according to the Bingham equation.

τ_B : Bingham yield stress; mv: medium viscosity.

Sample	τ_B [Pa]	η_P [Pa· s]
40% K suspension	209.3	2.64
40% K with 1% mv NaCMC	81.35	1.11
40% K with 1% NaCl	101.2	1.25
40% K with 1% NaCl + 1% mv NaCMC	167.2	1.32

Table 4.3.1.4

Effect of samples of 50% kaolin suspensions on k and n according to the Herschel-Bulkley equation in a steady-state condition. τ_{HB} : Herschel-Bulkley yield stress
lv: low viscosity; mv: medium viscosity.

Sample		τ_{HB} [Pa]	k [Pa·s]	n
1	50% kaolin *	221.4	15.02	0.16
2	50% k with 1% NaCl	220.2	25.34	0.01
3	50% K with 0.5% mv NaCMC	80.1	8.17	0.37
4	50% K with 0.25% lv NaCMC and 0.25% mv NaCMC	9.54	2.15	0.67
5	50% K with 0.5% lv NaCMC	2.52	1.24	0.44
6	50% K with 0.1% lv NaCMC	173.6	12.21	0.22
7	50% K with (l-m)v NaCMC: 0.5% - 0.01%	7.92	2.25	0.71
8	50% K with 0.5% lv NaCMC and 1% NaCl	125.4	6.53	0.09
9	50% K with (l-m)v NaCMC: 0.1% - 0.002%	130.1	16.31	0.01
10	50% K with (l-m)v NaCMC: 0.1% - 0.002%, and 0.5% NaCl	303.8	18.39	0.14

* It was not reproducible

Table 4.3.1.5

Effect of samples of 50% kaolin suspensions on τ_B and η_p according to the Bingham equation. τ_B : Bingham yield stress
lv: low viscosity; mv: medium viscosity.

Sample		τ_B [Pa]	η_p [Pa·s]
1	50% kaolin *	221.4	0.55
2	50% k with 1% NaCl	220.2	1.91
3	50% K with 0.5% mv NaCMC	80.1	0.31
4	50% K with 0.25% lv NaCMC and 0.25% mv NaCMC	9.54	0.11
5	50% K with 0.5% lv NaCMC	2.52	0.03
6	50% K with 0.1% lv NaCMC	173.6	0.45
7	50% K with (l-m)v NaCMC: 0.5% - 0.01%	7.92	0.08
8	50% K with 0.5% lv NaCMC and 1% NaCl	125.4	0.24
9	50% K with (l-m)v NaCMC: 0.1% - 0.002%	130.1	0.33
10	50% K with (l-m)v NaCMC : 0.1% - 0.002%, and 0.5% NaCl	303.8	0.67

* It was not reproducible

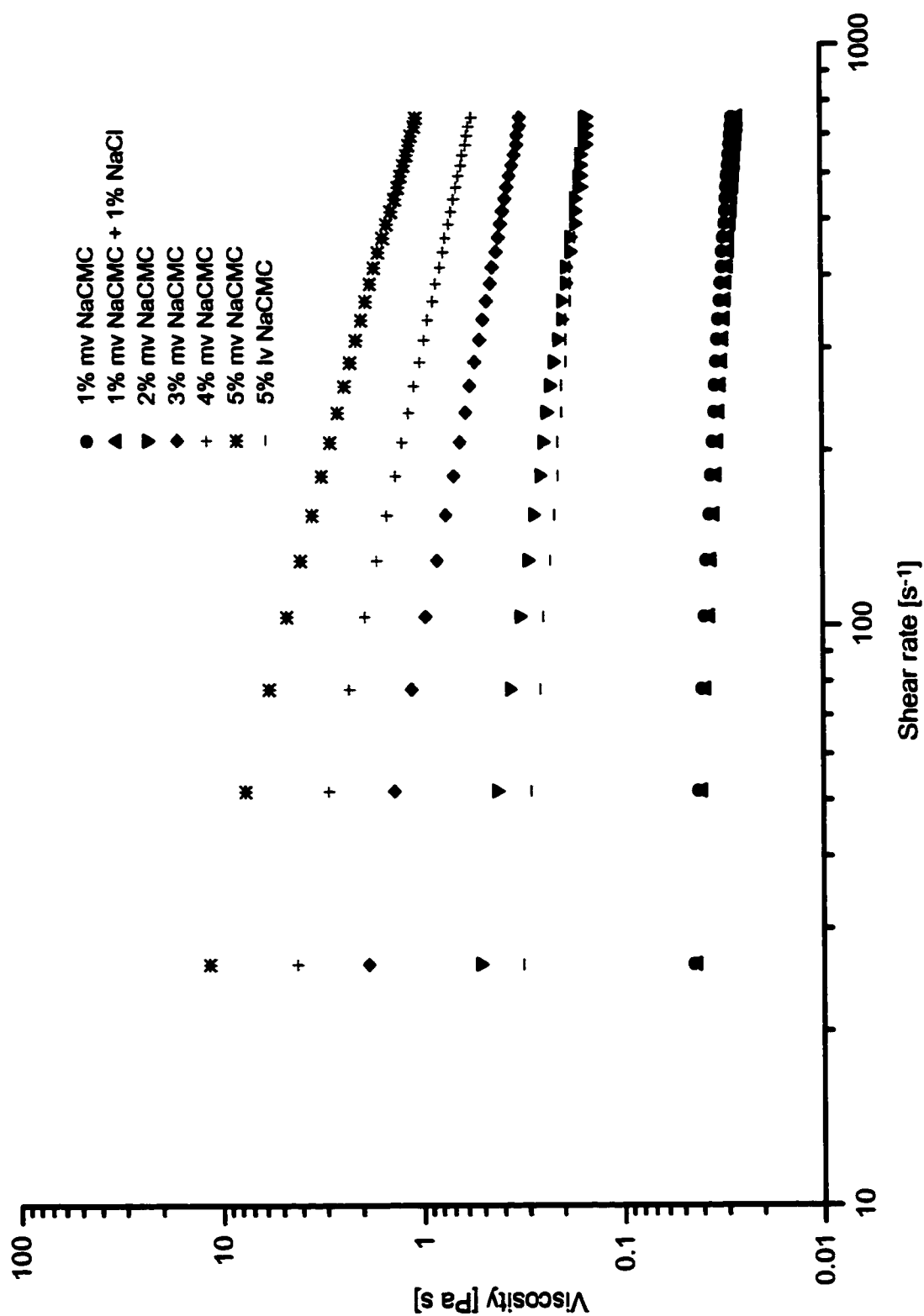


Figure 4.3.1.1. Viscosity curves of aqueous NaCMC solutions. lv: low viscosity; mv: medium viscosity.

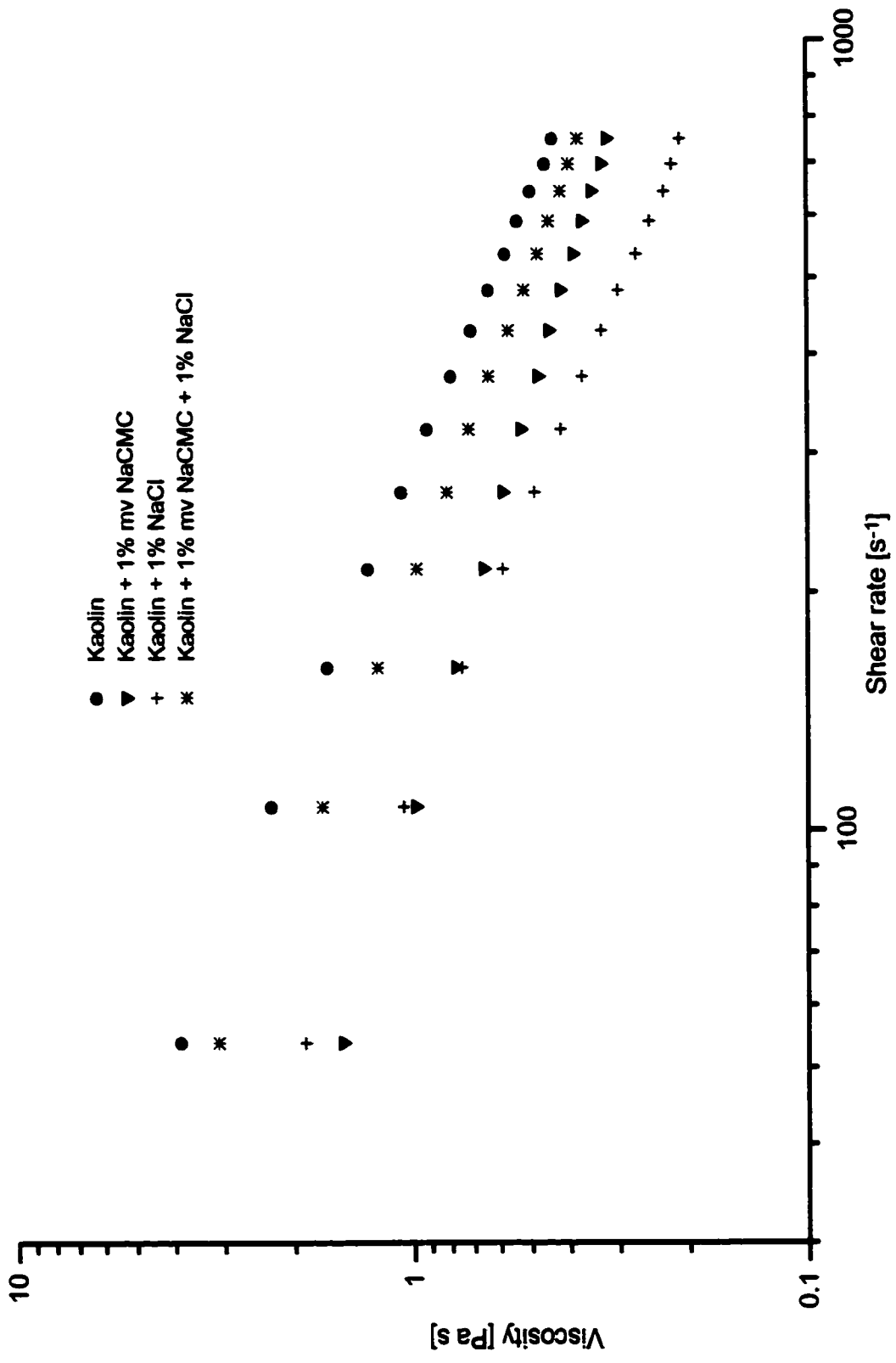


Figure 4.3.1.2. Viscosity curves of 40% kaolin suspensions. mv: medium viscosity.

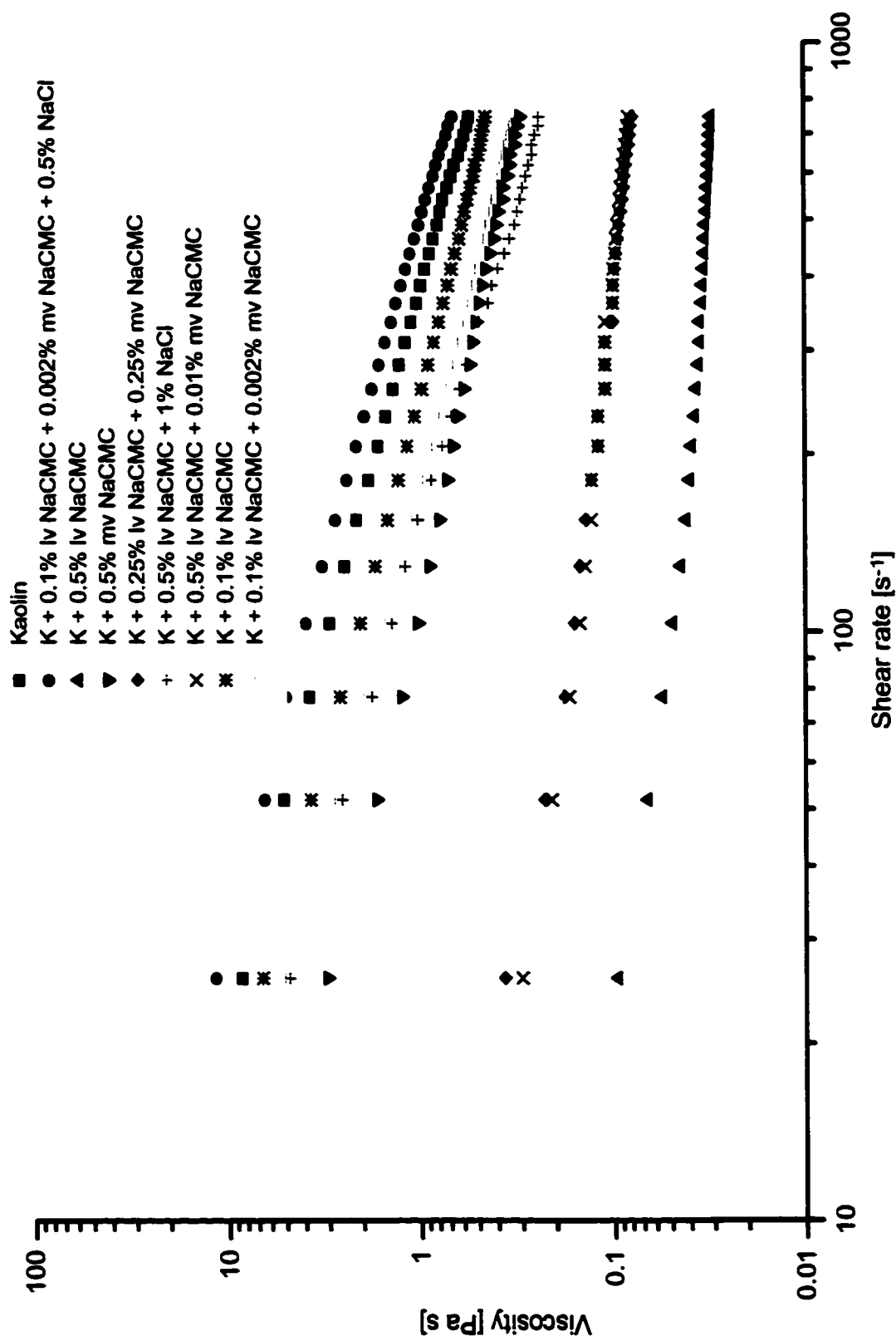


Figure 4.3.1.3. Viscosity curves of 50% kaolin suspensions. lv: low viscosity; mv: medium viscosity.

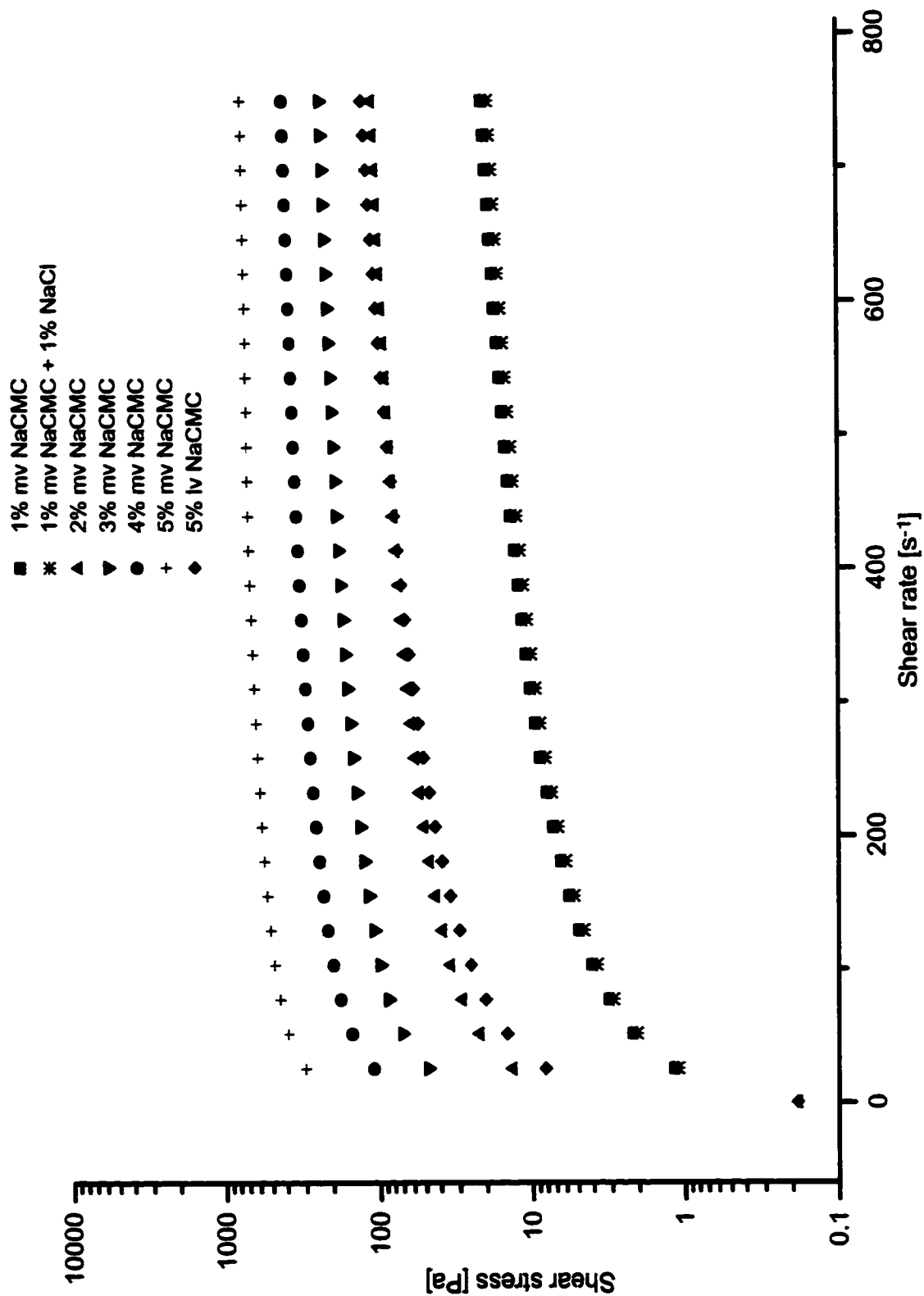


Figure 4.3.1.4. Flow curves of aqueous NaCMC solutions. lv: low viscosity; mv: medium viscosity.

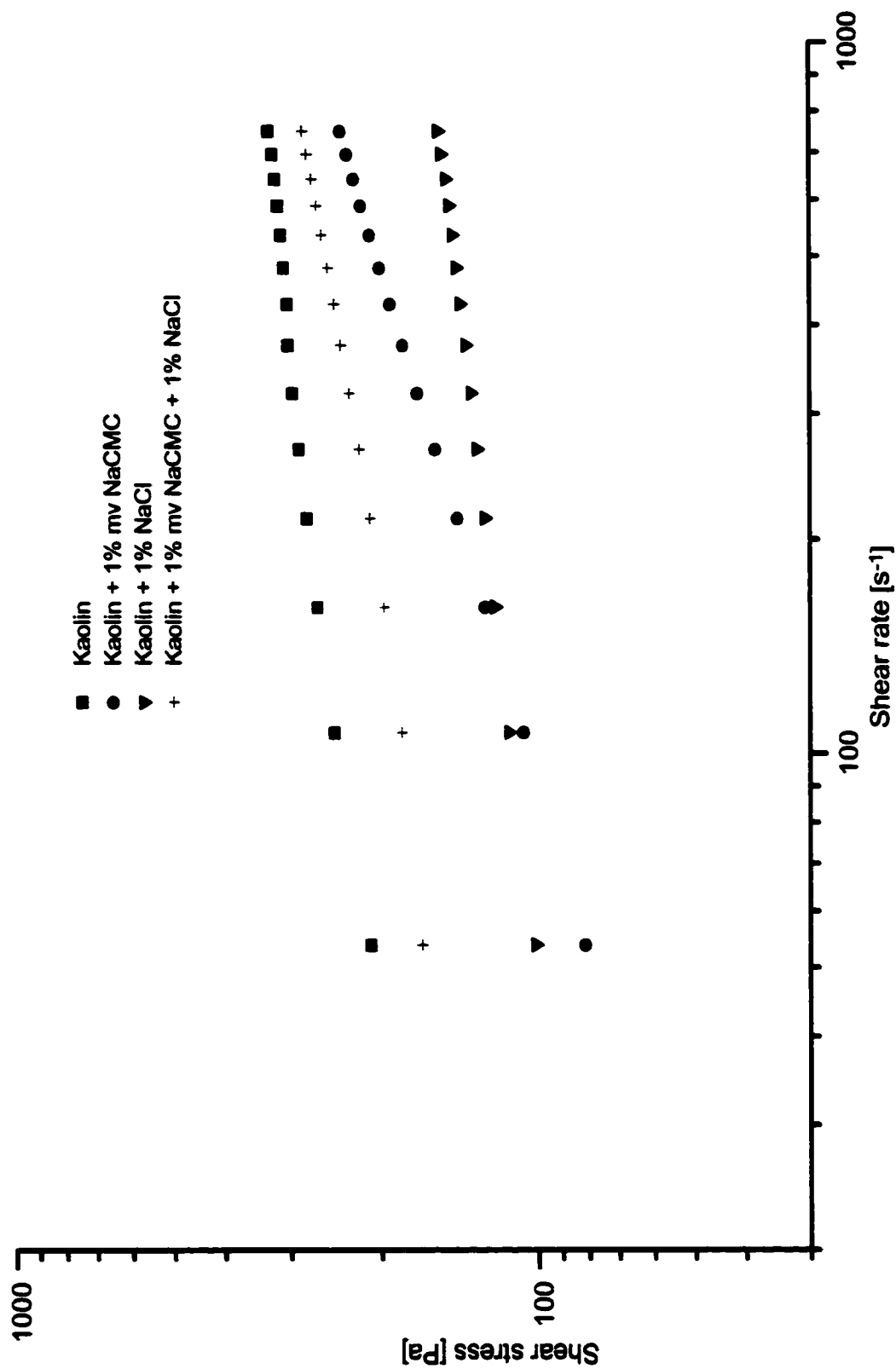


Figure 4.3.1.5. Flow curves of 40% kaolin suspensions. mv: medium viscosity.

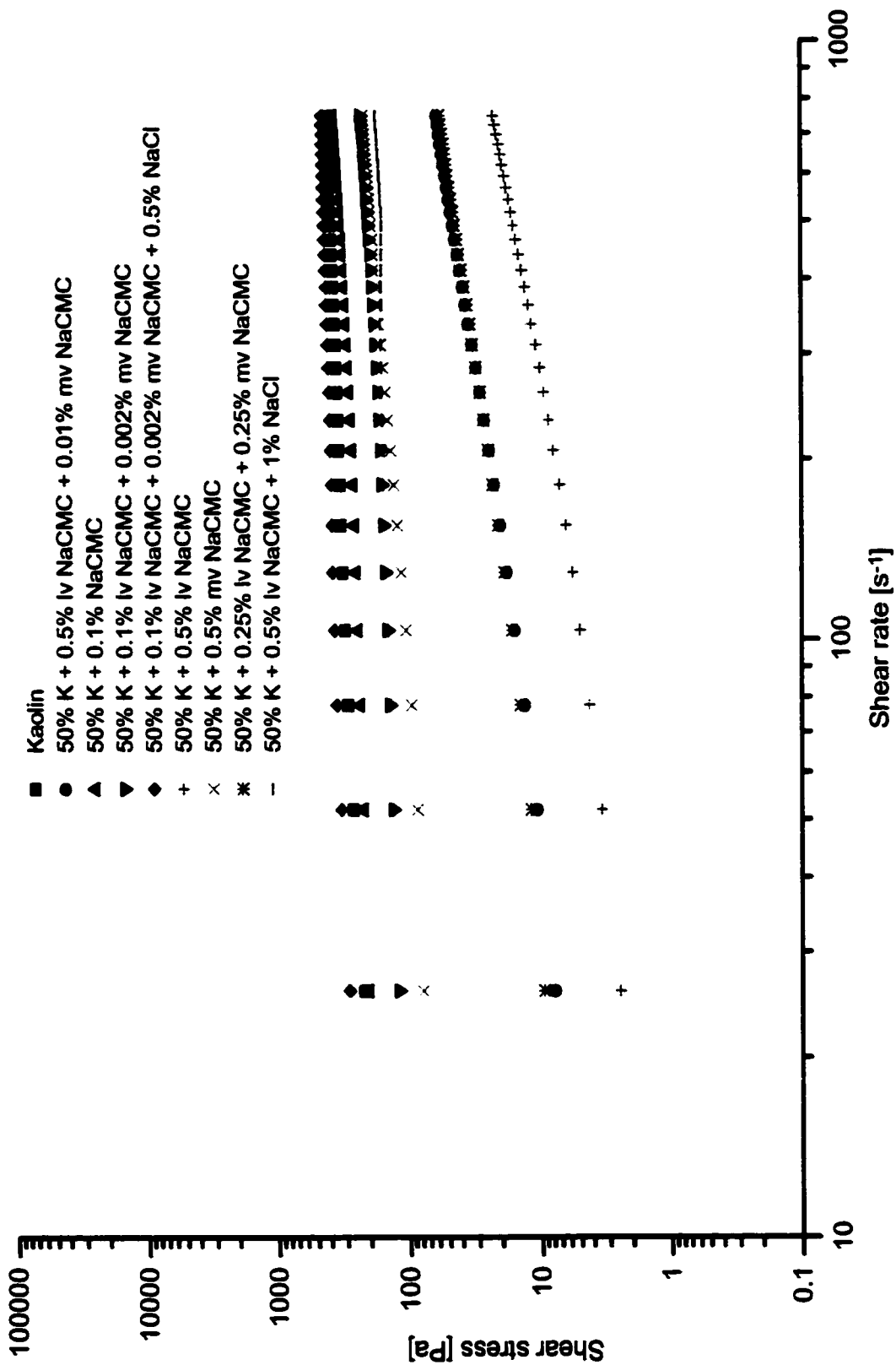


Figure 4.3.1.6. Flow curves of 50% kaolin suspensions. lv: low viscosity; mv: medium viscosity.

4.3.2) Results of yield stress analysis

4.3.2.1) *Yield stress analysis of samples of 40% kaolin suspensions*

As shown in Table 4.3.2.1, 40% kaolin suspension has the largest yield stress (using Herschel-Bulkley & Bingham approximation) among the samples. Adding polymer or inorganic salt, decreased the yield stresses. 1% mv NaCMC-added kaolin suspension has the smallest value among the samples. The kaolin particles aggregate in the suspension, they form the 'card-house' structure, and the suspension is not stable. The negatively charged (CMC) chains of the dissolved NaCMC can adsorb onto the positively charged surface of kaolin particles: the card-house structure breaks down. The steric and electrostatic stabilization of the suspension is formed (viscosity decreases). The yield stress in the stabilized suspension is lower or diminished. Since the viscosity of suspension with the addition of 1% NaCl decreased due to the stabilizing ability of NaCl, the yield stress also becomes lower.

4.3.2.2) *Yield stress analysis of samples of 50% kaolin suspensions*

As can be seen in Table 4.3.2.2, the samples of 50% kaolin suspension with 1% NaCl and 50% kaolin suspension with 0.1% lv as well as 0.002% mv NaCMC as well as with 0.5% NaCl show the largest yield values (using Herschel-Bulkley & Bingham approximation). The addition of inorganic salt resulted in a smaller yield stress compared with that of just 50% kaolin suspension. 0.5% lv NaCMC-added kaolin suspension shows the smallest yield value among these samples, while 0.1% lv NaCMC-added kaolin suspension shows a much larger yield

value than the 0.5% added sample. When 1% NaCl is added to the sample with 0.5% lv NaCMC content, the yield stress caused much higher. In the same time, putting small amount (0.01% or 0.25%) of mv NaCMC into the 0.5% lv NaCMC-added kaolin suspension simultaneously, the yield stress becomes greater. The low viscosity (and low molecular weight) polymer, enhances the bridging flocculation capability of the medium viscosity (higher molecular weight) polymer by a site-blocking mechanism [10].

Table 4.3.2.1

Herschel-Bulkley and Bingham yield stresses of samples of 40% kaolin suspensions in a non steady-state condition. mv: medium viscosity.

τ_{HB} : Herschel-Bulkley yield stress

τ_B : Bingham yield stress

Samples	τ_{HB} (Pa)	τ_B (Pa)
40% Kaolin	60	240
40% K with 1% mv NaCMC	10	110
40% K with 1% NaCl	22	125
40% K with 1% mv NaCMC and 1% NaCl	40	212

Table 4.3.2.2

The Herschel-Bulkley and Bingham yield stresses of samples of 50% kaolin suspensions in a non steady-state condition.

τ_{HB} : Herschel-Bulkley yield stress

τ_B : Bingham yield stress

lv: low viscosity; mv: medium viscosity.

Sample		τ_{HB} (Pa)	τ_B (Pa)
1	50% Kaolin *	-	330
2	50% K with 1% NaCl	305	390
3	50% K with 0.5% mv NaCMC	100	116
4	50% K with 0.25% lv NaCMC and 0.25% mv NaCMC	11	16
5	50% K with 0.5% lv NaCMC	2.2	2.4
6	50% K with 0.1% lv NaCMC	140	225
7	50% K with 0.5% lv NaCMC and 0.01% mv NaCMC	10	15
8	50% K with 0.5% lv NaCMC and 1% NaCl	120	122
9	50% K with 0.1% lv NaCMC and 0.002% mv NaCMC	130	151
10	50% K with 0.1% lv NaCMC and 0.002% mv NaCMC, 0.5% NaCl as well	250	419

* It was unmeasurably high

4.3.3) Results of thixotropy analysis

4.3.3.1) *Thixotropy curve analysis of samples of 40% kaolin suspensions*

The simultaneously added 1% NaCl and 1% mv NaCMC cause the most significant thixotropy (Figure 4.3.3.1). Adding 1% NaCl only, the system does not show significant thixotropy. Thixotropy is a very time-dependent property of samples as the structure changes. 1% mv NaCMC-added sample also shows more significant thixotropy than 40% kaolin suspension. 1% mv NaCMC increases the thixotropy of 40% kaolin suspension. A modest thixotropy was observed for the 40% kaolin suspension indicating the presence of a weakly aggregated structure due to the face-edge attraction of particles (card-house structure). The hysteresis loop area values of the samples are shown in Table 4.3.3.1. As is well known, the condition of thixotropy is a weakly flocculated state of the samples (flocculation to the secondary minimum in the interparticle potential energy curve). The mv NaCMC increases the area of the thixotropy loop that can be interpreted in terms of NaCMC initiated flocculation of macromolecules. It means that small amounts of mv NaCMC polymer takes part in bridge formation. The added NaCl screens the repulsion of the NaCMC-added particles by means of the secondary energy minimum in the pair-potential energy function becoming deeper, manifesting itself in a more significant thixotropy.

4.3.3.2) *Thixotropy curves of samples of 50% kaolin suspensions*

In Figure 4.3.3.2, 0.1% lv NaCMC, 0.002% mv NaCMC and 0.5% NaCl together cause the most significant thixotropic behavior. 0.5% mv NaCMC-added 50% kaolin suspension does not show more thixotropy, compared to 1% mv NaCMC-added 40% kaolin suspension (see the explanation below). In Figure 4.3.3.3, putting a small amount of mv NaCMC (0.01% or 0.25%) into the lv NaCMC-added kaolin suspension results in more important thixotropy due to the bridging flocculation effect. In Figure 4.3.3.4, 0.1% lv NaCMC-added kaolin suspension, and 0.5% lv NaCMC with 1% NaCl simultaneously added kaolin suspension, present not too significant anti-thixotropy behavior, especially at the lower shear rate. The reason for this behavior is not yet known; it maybe due to only a very weak (repulsion) interactions among the particles. The “area” of hysteresis loop was significantly higher for the case of the more concentrated (50%) kaolin suspension compared to the results of the less (40%) concentrated ones. Table 4.3.3.2 presents the hysteresis loop area values for the samples.

There are several possible reasons for samples to show thixotropic property. First, it happens in dense suspensions, composed of anisometrical solid particles; Second, the suspension has to be in a weakly flocculated state (see the definition in the introduction), which can be sheared easily and built up again after removing the applied force. It means that there should be an optimum strength structure in the suspension. The lv NaCMC-added kaolin suspension, does not show thixotropy because the low viscosity polymer stabilizes the suspension; but this is not a gel structure, the particles in this case repulse each other. The mv NaCMC stabilizes (adsorbing on the particles) and destabilizes (forming bridges between

the particles) at the same time which results in significant thixotropy (also see the explanation for the mv NaCMC-added 40% kaolin). The lv NaCMC-added samples in the presence of mv NaCMC show a weakly flocculated suspension. The bridging flocculation occurs by the site-blocking mechanism. The relatively significant thixotropy of 50% kaolin suspension in the presence of 1% NaCl may be attributed to the high kaolin content. The thixotropic behavior becomes more significant for the kaolin suspension after adding the NaCl and CMC simultaneously. The addition of NaCl may cause many different interactions between the kaolin suspension as follows: 1) particle-particle interaction; 2) the hydrodynamic size of macromolecules; 3) the adsorption capability of macromolecules on the same particle; and 4) the bridge forming adsorption.

Table 4.3.3.1**Hysteresis "area" (Pa/s) of samples of 40% kaolin suspensions.****mv: medium viscosity**

Samples	Hysteresis area (Pa/s)
40% Kaolin	1810
40% K with 1% mv NaCMC	3.1e+04
40% K with 1% NaCl	4180
40% K with 1% mv NaCMC + 1% NaCl	4.7e+04

Table 4.3.3.2**Hysteresis "area" (Pa/s) of samples of 50% kaolin suspensions.****lv: low viscosity; mv: medium viscosity**

	Sample	Hysteresis area (Pa/s)
1	50% Kaolin *	4.2e+04
2	50% K with 1% NaCl	3.2e+04
3	50% K with 0.5% mv NaCMC	1.4e+04
4	50% K with 0.25% lv NaCMC and 0.25% mv NaCMC	3040
5	50% K with 0.5% lv NaCMC	750
6	50% K with 0.1% lv NaCMC	-9960
7	50% K with 0.5% lv NaCMC and 0.01% mv NaCMC	2590
8	50% K with 0.5% lv NaCMC and 1% NaCl	3460
9	50% K with 0.1% lv NaCMC and 0.002% mv NaCMC	-4630
10	50% K with 0.1% lv NaCMC and 0.002% mv NaCMC, 0.5% NaCl as well	7.44e+04

* It is not reproducible

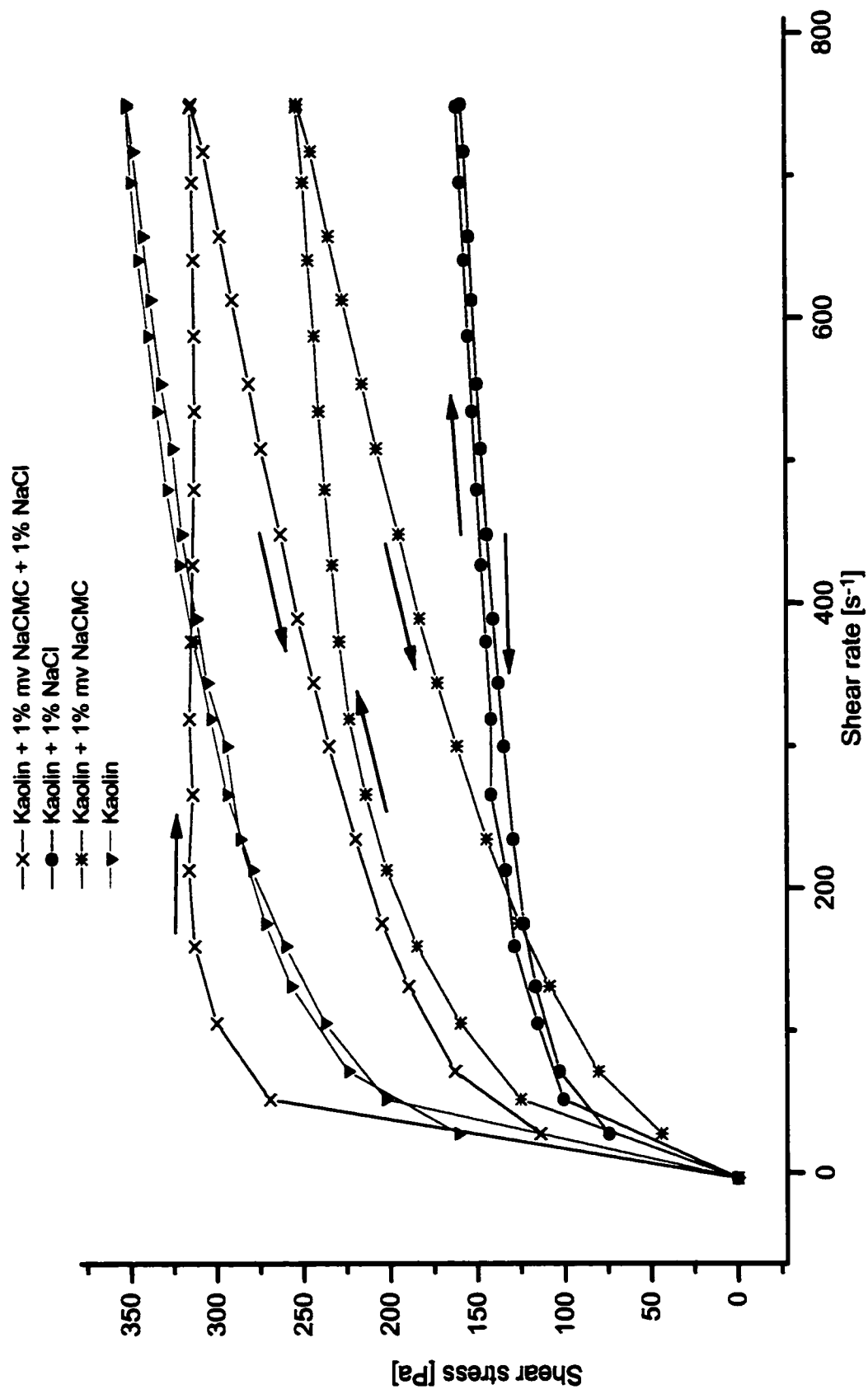


Figure 4.3.3.1. Thixotropy curves of 40% kaolin suspension with additions of NaCMC and NaCl.
mv: medium viscosity.

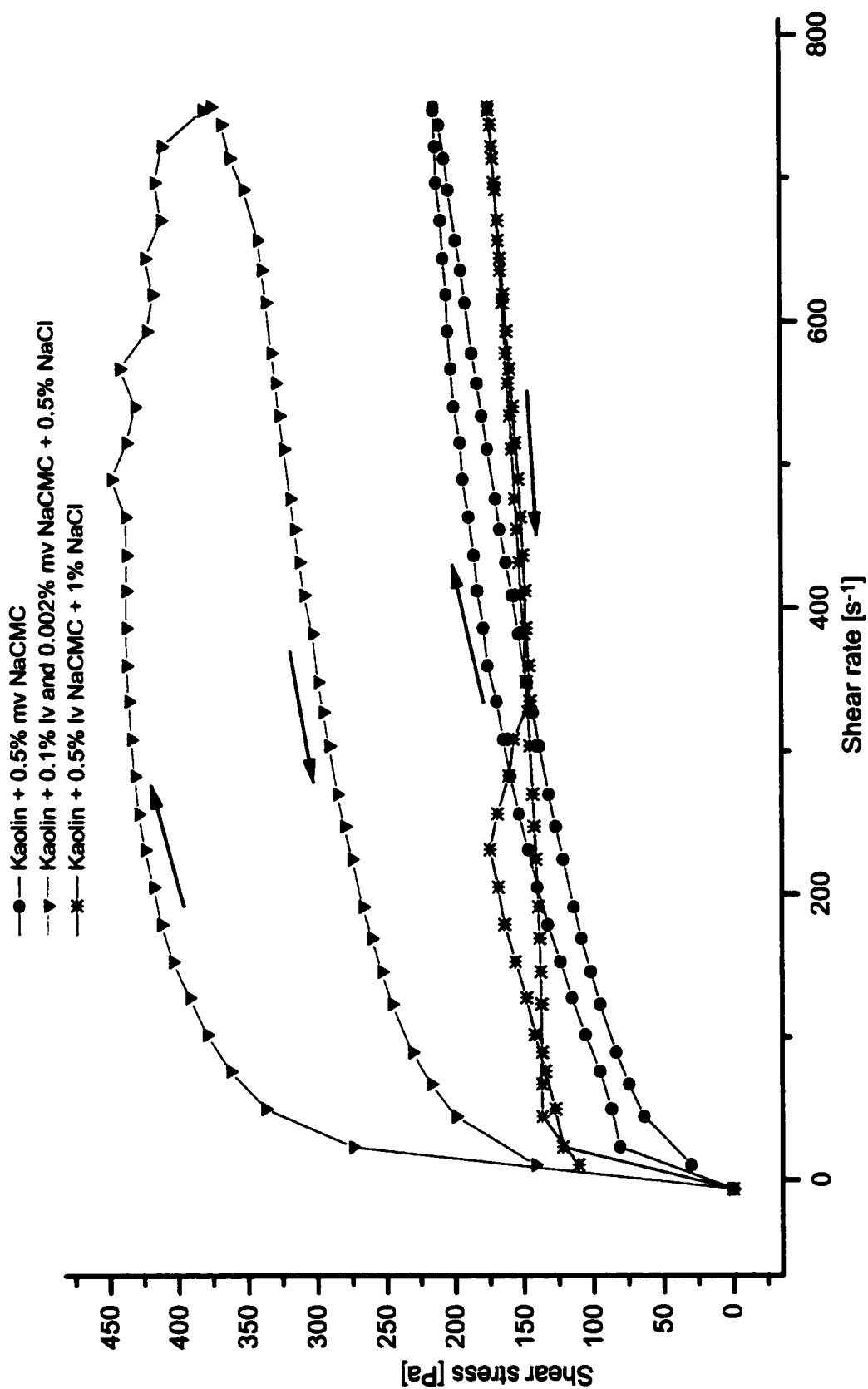


Figure 4.3.3.2. Thixotropy curves of 50% kaolin suspension with additions of NaCMC and NaCl.
lv: medium viscosity; mv: medium viscosity. [1]

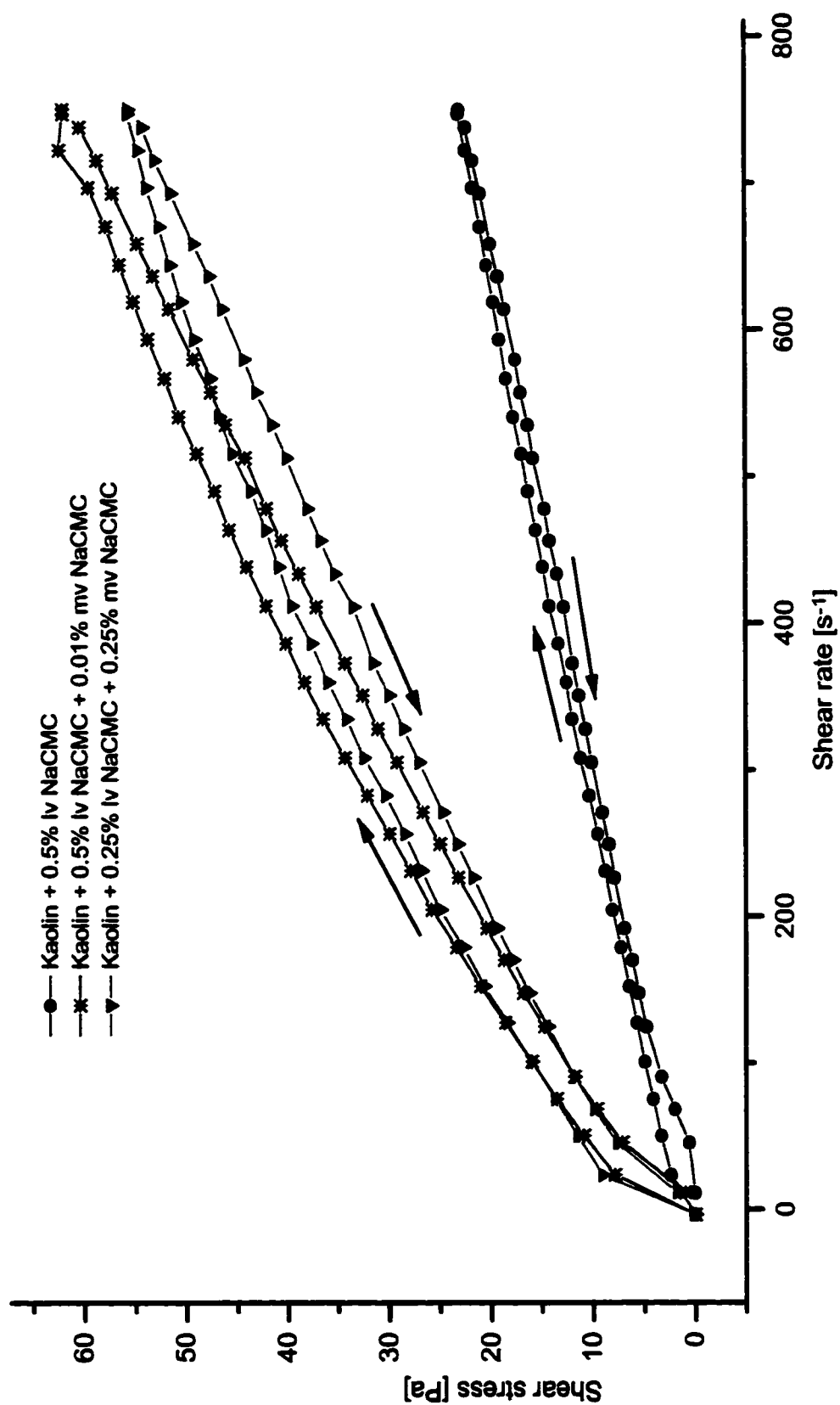


Figure 4.3.3.3. Thixotropy curves of 50% kaolin suspension with additions of NaCMC.
lv: low viscosity; mv: medium viscosity. [2]

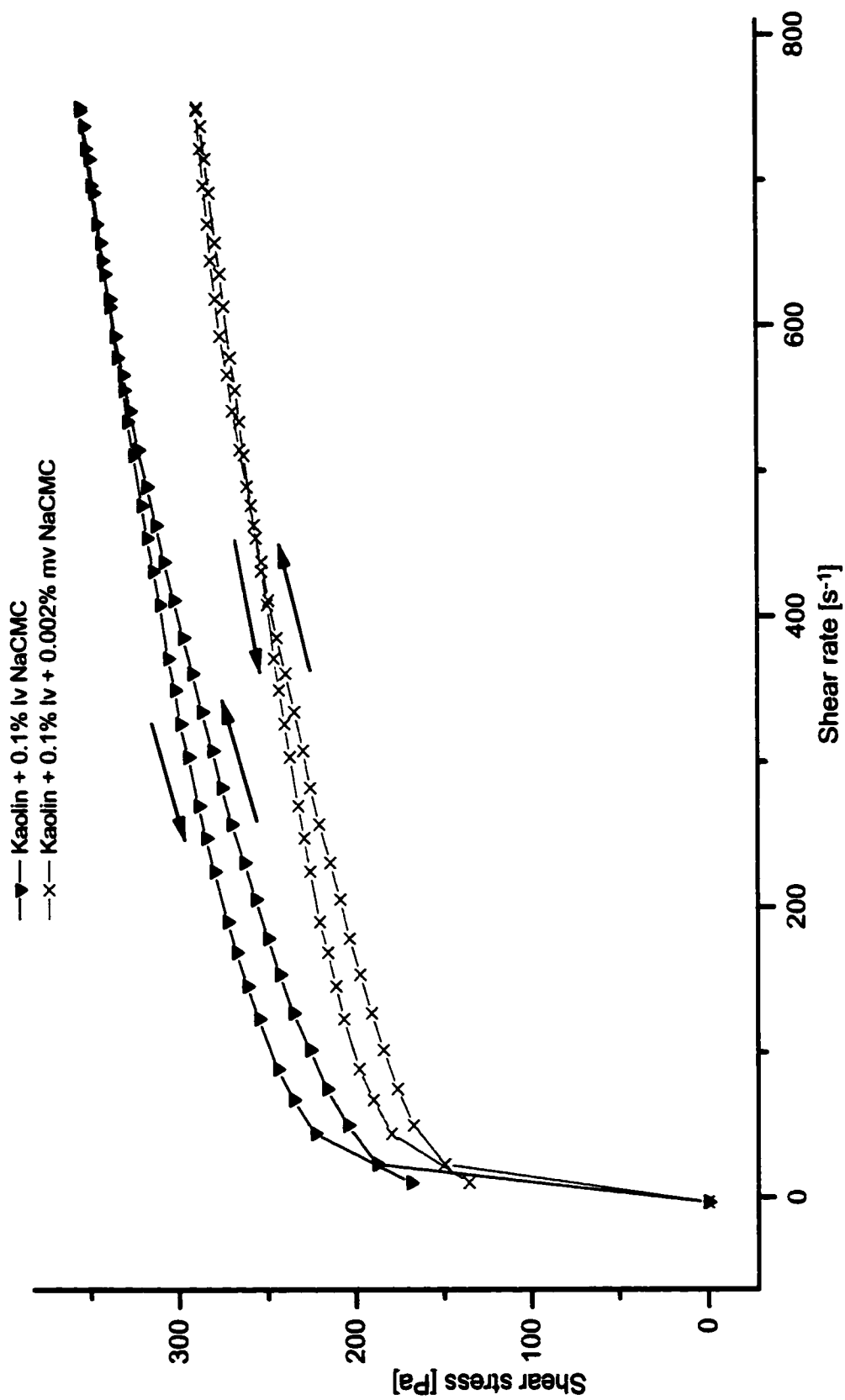


Figure 4.3.3.4. Anti-thixotropy curves of 50% kaolin suspension with additions of NaCMC.
lv: low viscosity; mv: medium viscosity. [3]

4.3.4) Results of creep-recovery analysis

In order to get information about the elasticity of the prepared samples, the creep-recovery behavior was studied using the CS mode of the RS100. In the same period of observation (300 seconds for the creep curve) and (300 seconds for the recovery curve), prepared samples of 40% and 50% kaolin suspensions were investigated. Different shear stresses below the yield stress were applied. At certain stresses, the compliance (J_c) increased with time in a nonlinear manner showing elastic behavior of the samples. At the other stresses, the compliance (J_c) increased with time in a linear manner showing viscous behavior of the samples. For the determination of the samples elasticity, the elasticity ratio (the ratio of the elastic and maximum compliance) for every sample was examined. The elastic compliance was determined from the creep curve fitting a straight line to the near linear (viscous) part of the curve. The intersection of the fitted line and the vertical axis provided the elastic compliance. The maximum compliance was given directly from the creep curve (at the highest value).

4.3.4.1) *Creep-recovery test for the 40% kaolin suspensions*

The creep-recovery functions for 40% kaolin samples were given at the same shear stress ($\tau = 50\text{Pa}$) in Figures 4.3.4.1 ~ 4.3.4.4. In order to characterize the elasticity of the prepared samples, the calculated elasticity ratios are given in Table 4. 1. Despite the high elastic ratio showed in Table 4.1, some systems were not real elastic because there was no entire recovery during the observation time (see Figures 4.3.4.1 and 4.3.4.3). Real elastic behavior was not observed for the kaolin suspensions (Figure 4.3.4.1). The relatively high elasticity ratio (Table

4.1) demonstrates rigidity rather than elasticity. There is no significant recovery after ceasing the stress. For the 1% mv NaCMC-added sample, the curve showed liquid-like behavior at this shear stress (see Figure 4.3.4.2). As can be seen in Figure 4.3.4.4, the 1% mv NaCMC & 1% NaCl together show really elastic behavior.

The mv NaCMC stabilized the 40% kaolin suspension, as the macromolecules adsorbed onto the kaolin particles. Under higher shear stress ($\tau = 50\text{Pa}$), the suspension was very liquid-like, there was no agglomeration which could cause elasticity in it. The particles repelled each other. When 1% NaCl was added into the above sample, some aggregates could form due to the screening effect of (Na^+) manifesting itself in more elastic behavior.

4.3.4.2) *Creep-recovery test for the 50% kaolin suspensions*

The creep-recovery functions for 50% kaolin samples are given at the shear stress ($\tau = 0.5\text{Pa}$ and 5Pa) in Figures 4.3.4.5 ~ 4.3.4.7. In order to characterize the elasticity of the prepared samples, the calculated elasticity ratios ($J_{\text{eq}}/J_{\text{max}}$) are given in Table 4.2. As can be seen in Figure 4.3.4.6, 0.5% mv NaCMC causes the most elastic behavior; the elasticity ratio was 0.92. The 0.25% lv NaCMC and 0.25% mv NaCMC together caused the most viscous behavior at this stress (the elasticity ratio was 0.26). The 0.5% lv NaCMC at even lower ($\tau = 0.5\text{ Pa}$) shear stress showed rather viscous behavior (the elasticity ratio was 0.39). It should be noted that the elasticity measurements were found to be non-reproducible for the denser kaolin suspension. All the data for this section can be seen in Table 4.2.

As can be seen in Table 4.3.4.1 the elasticity ratio for 0.5% mv NaCMC-added kaolin suspension was larger than that for the 0.25% lv NaCMC and 0.25% mv NaCMC simultaneously added sample at the same shear stress ($\tau = 5\text{Pa}$). It showed that 0.5% mv NaCMC individually can cause the more elastic behavior. With increasing shear stress, the ratios for (l-m)v NaCMC-added sample decreased: it showed more and more viscous behavior as expected. The mv NaCMC-added sample, however did not show this result due to more elasticity (rigidity). The higher the shear stress, the lower the elasticity ratio was found due to the structural break-down. Besides, the sample with the 0.5% mv NaCMC showed more elasticity even at higher shear stress ($\tau = 50\text{Pa}$).

According to the data in Table 4.3.4.2, 0.5% lv NaCMC has the most stabilizing ability. It shows viscous properties even at very small shear stresses. Putting a small amount of mv NaCMC (0.01%) into this sample, it shows higher elasticity ratio values; the elasticity itself is significant even at larger shear stresses. The addition of 0.01% mv NaCMC can cause the elastic behavior. As can be seen in Table 4.3.4.3, the elasticity ratio value of 0.5% mv NaCMC-added suspension is larger at high shear stress, comparing with that of 0.5% lv NaCMC-added sample, which lead to more significant elastic property due to the bridging flocculation.

Table 4.3.4.1

Elasticity ratios of two different samples: 50% K + 0.5% mv NaCMC and 50% K + 0.25% lv NaCMC + 0.25% mv NaCMC.

mv: medium viscosity

	Shear stress [Pa]	Elasticity ratio (J_{eo}/J_{max})
50% kaolin suspension with 0.5% mv NaCMC	$\tau = 5$ Pa	0.92
	$\tau = 10$ Pa	0.95
	$\tau = 20$ Pa	0.93
	$\tau = 50$ Pa	0.92
50% kaolin suspension with 0.25% lv NaCMC and 0.25% mv NaCMC	$\tau = 1$ Pa	0.93
	$\tau = 2$ Pa	0.92
	$\tau = 3$ Pa	0.93
	$\tau = 4$ Pa	0.56
	$\tau = 5$ Pa	0.26

Table 4.3.4.2

Elasticity ratios of two different samples: 50% K + 0.5% lv NaCMC and 50% K + 0.5% lv NaCMC + 0.01% mv NaCMC.

lv: low viscosity

	Shear stress [Pa]	Elasticity ratio (J_{eo}/J_{max})
50% kaolin suspension with 0.5% lv NaCMC	$\tau = 0.088$ Pa	0.79
	$\tau = 0.5$ Pa	0.39
50% kaolin suspension with 0.5% lv NaCMC and 0.01% mv NaCMC	$\tau = 1$ Pa	0.90
	$\tau = 2$ Pa	0.93
	$\tau = 3$ Pa	0.95

Table 4.3.4.3

**Elasticity ratios of two different samples: 50% K + 0.5% lv NaCMC
and 50% K + 0.5% mv NaCMC.**

lv: low viscosity; mv: medium viscosity

	Shear stress [Pa]	Elasticity ratio (J_{eo}/J_{max})
50% kaolin suspension with 0.5% lv NaCMC	$\tau = 0.088$ Pa	0.79
	$\tau = 0.5$ Pa	0.39
50% kaolin suspension with 0.5% mv NaCMC	$\tau = 5$ Pa	0.92

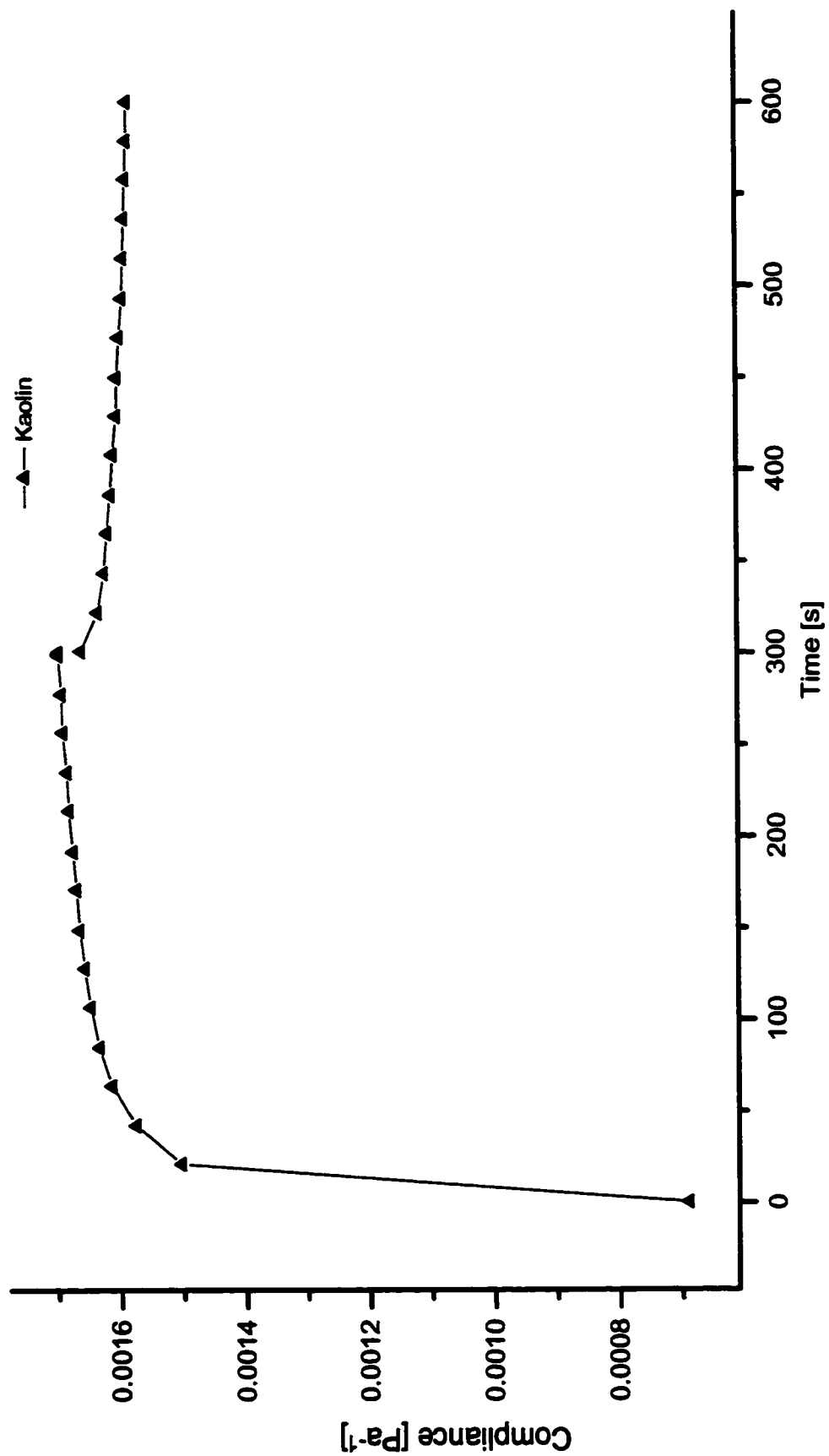


Figure 4.3.4.1. Creep-recovery curve of 40% kaolin suspension ($\tau = 50\text{Pa}$).

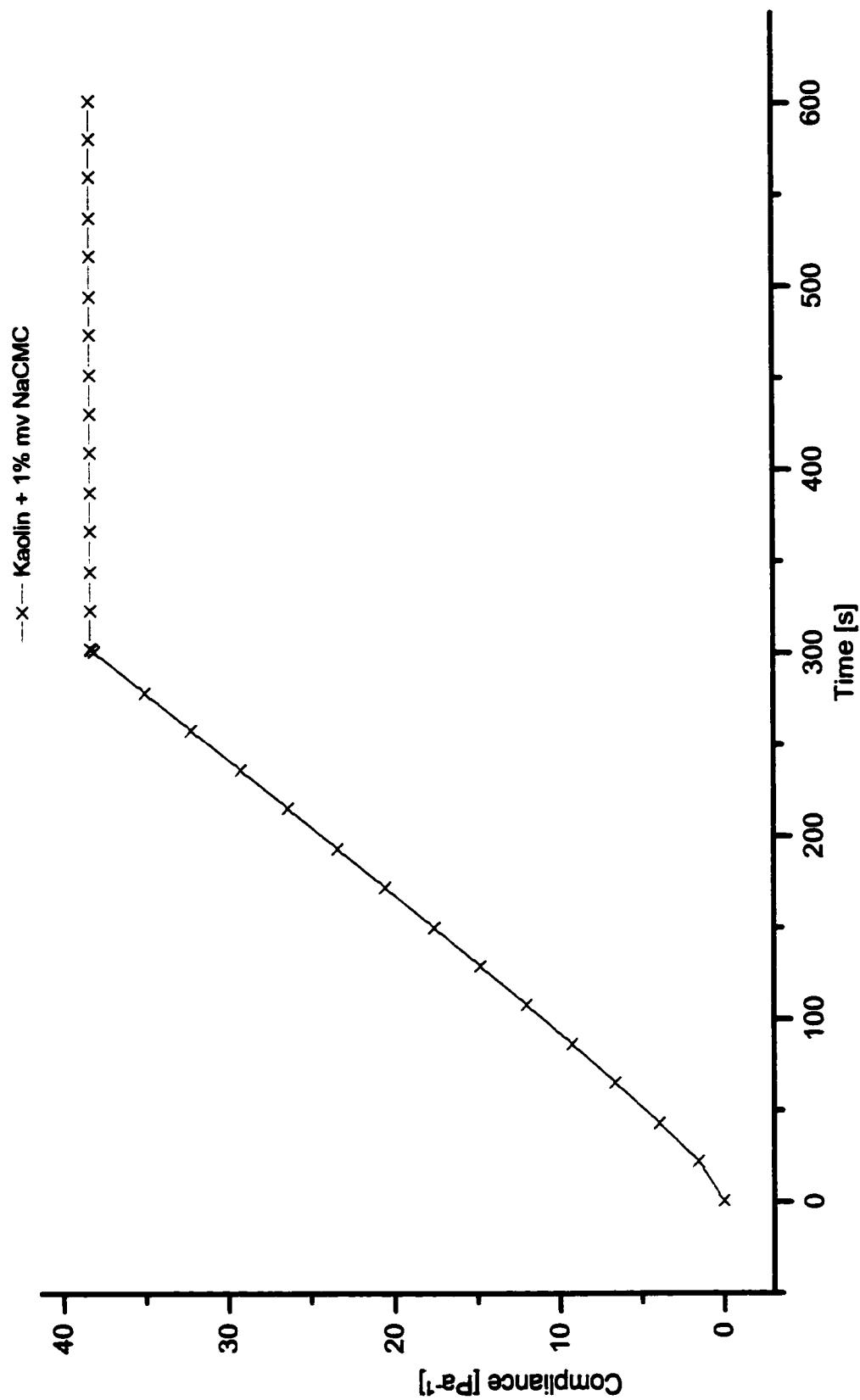


Figure 4.3.4.2. Creep-recovery curve of 40% kaolin suspension with addition of mv NaCMC ($\tau = 50\text{Pa}$). mv: medium viscosity.

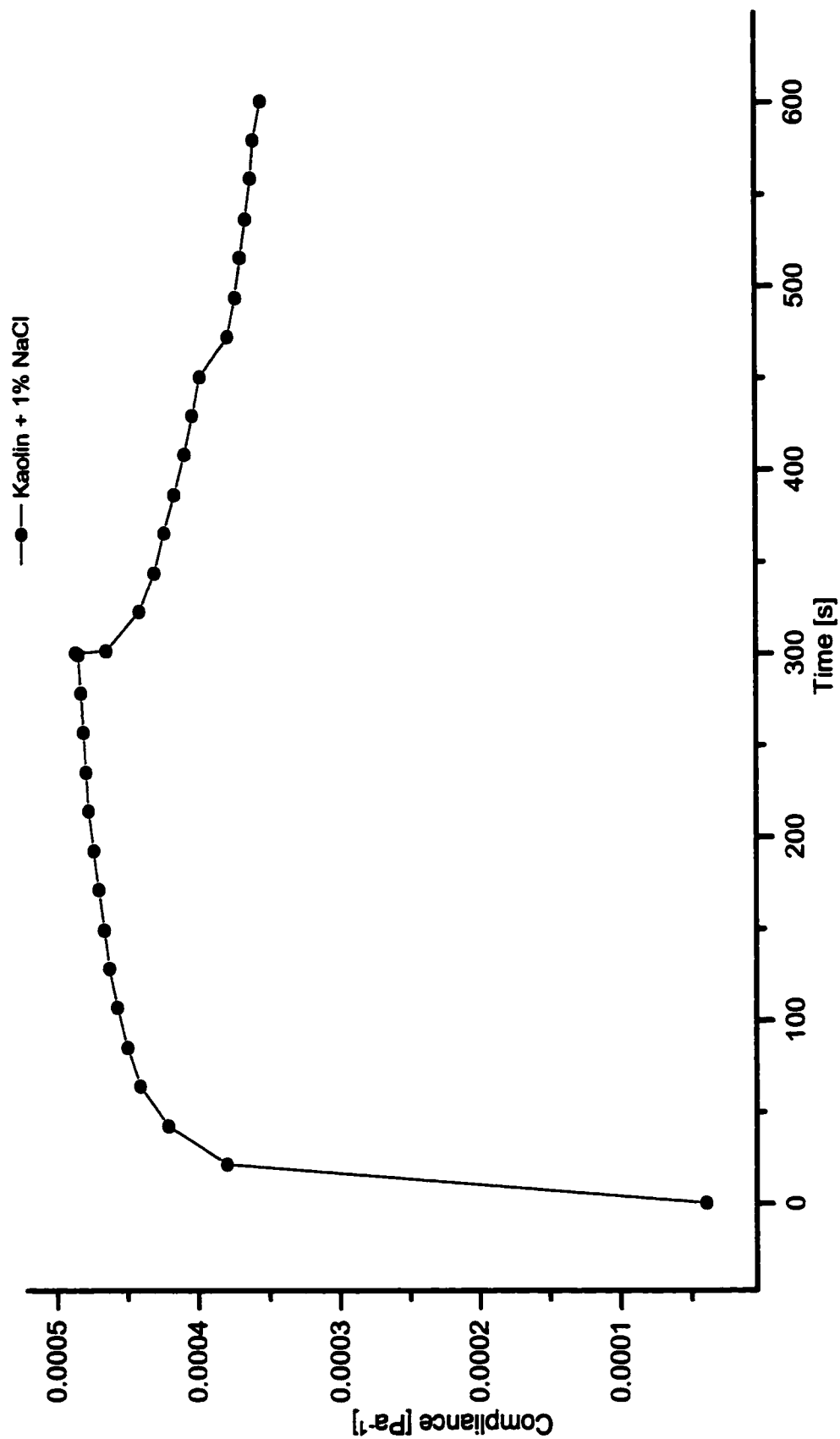


Figure 4.3.4.3. Creep-recovery curve of 40% kaolin suspension with addition of NaCl. ($\tau = 50\text{Pa}$).

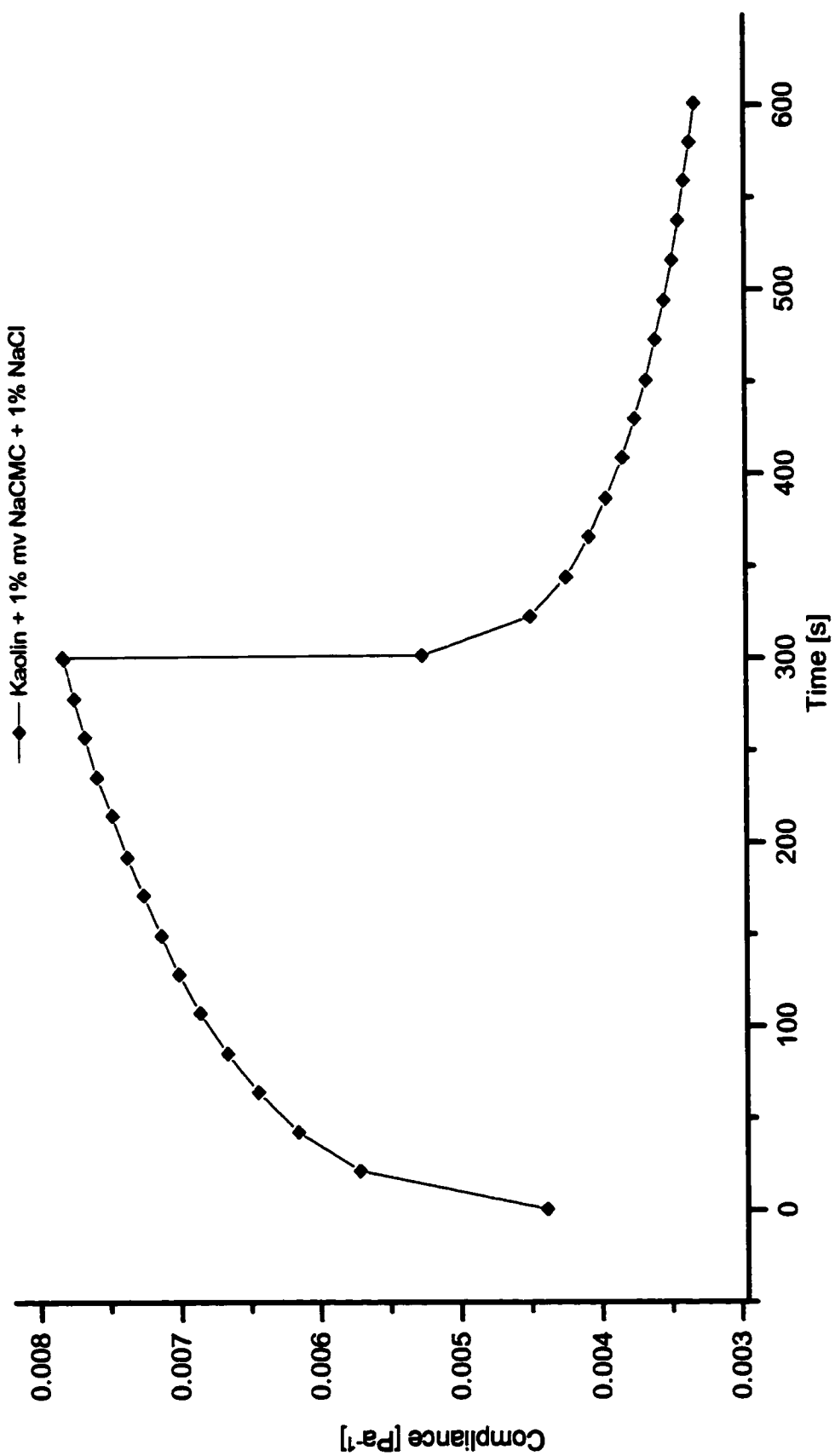


Figure 4.3.4.4. Creep-recovery curve of 40% kaolin suspension with additions of mv NaCMC and NaCl ($\tau = 50\text{Pa}$). mv: medium viscosity.

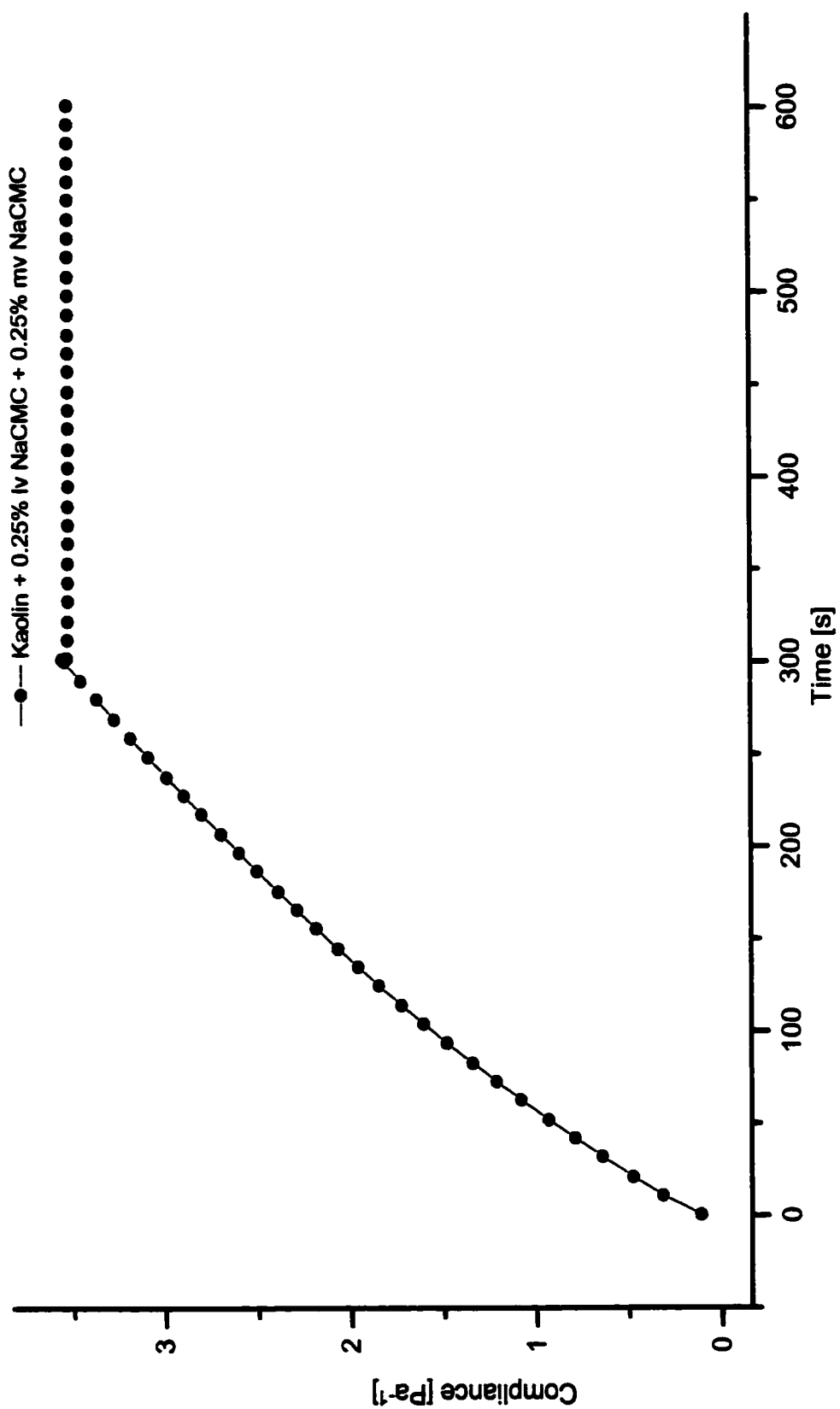


Figure 4.3.4.5. Creep-recovery curve of 50% kaolin suspension with additions of NaCMC.
lv: low viscosity; mv: medium viscosity. ($\tau = 5\text{Pa}$)

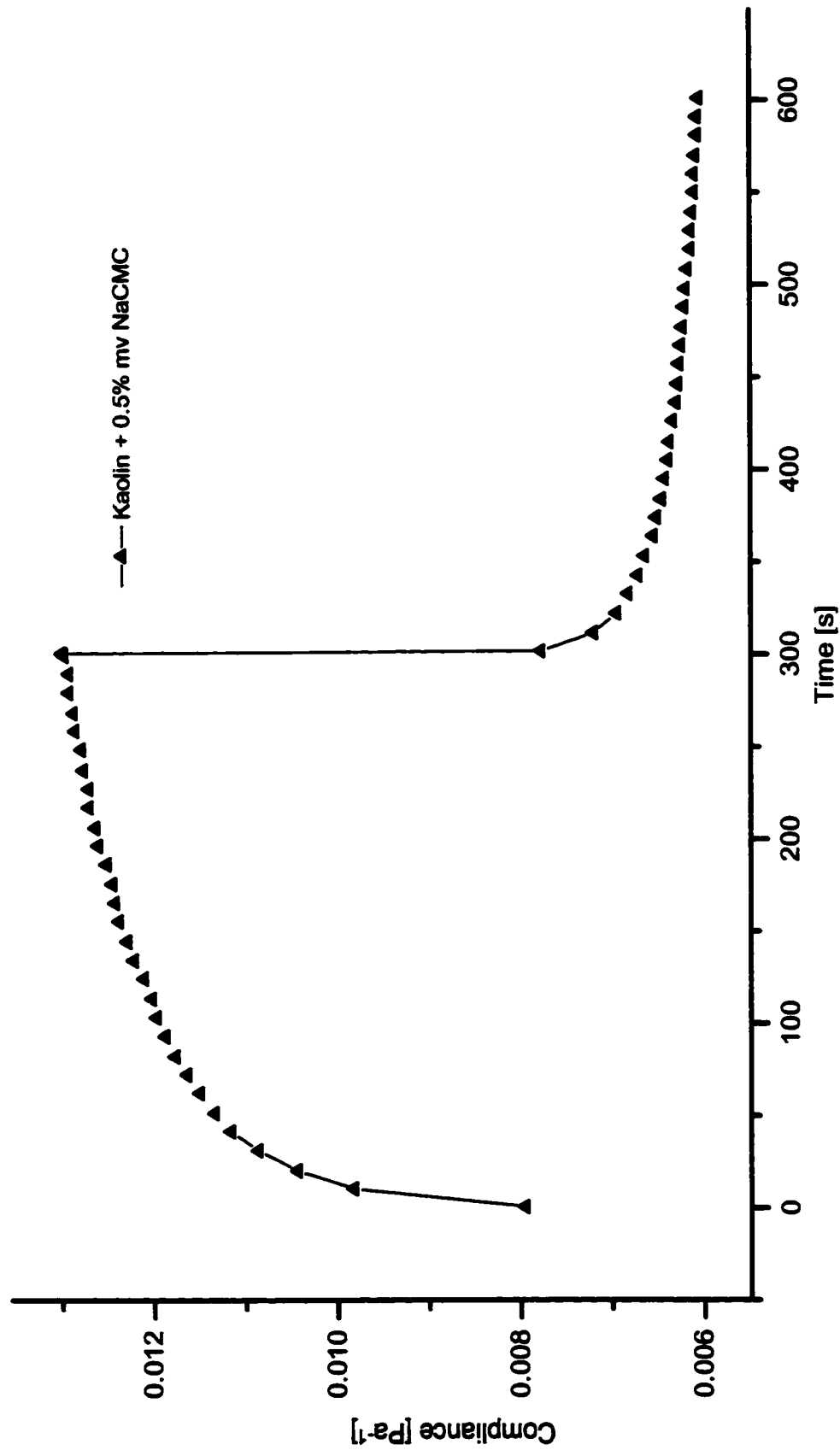


Figure 4.3.4.6. Creep-recovery curve of 50% kaolin suspension with addition of mv NaCMC.
mv: medium viscosity. ($\tau = 5\text{Pa}$)

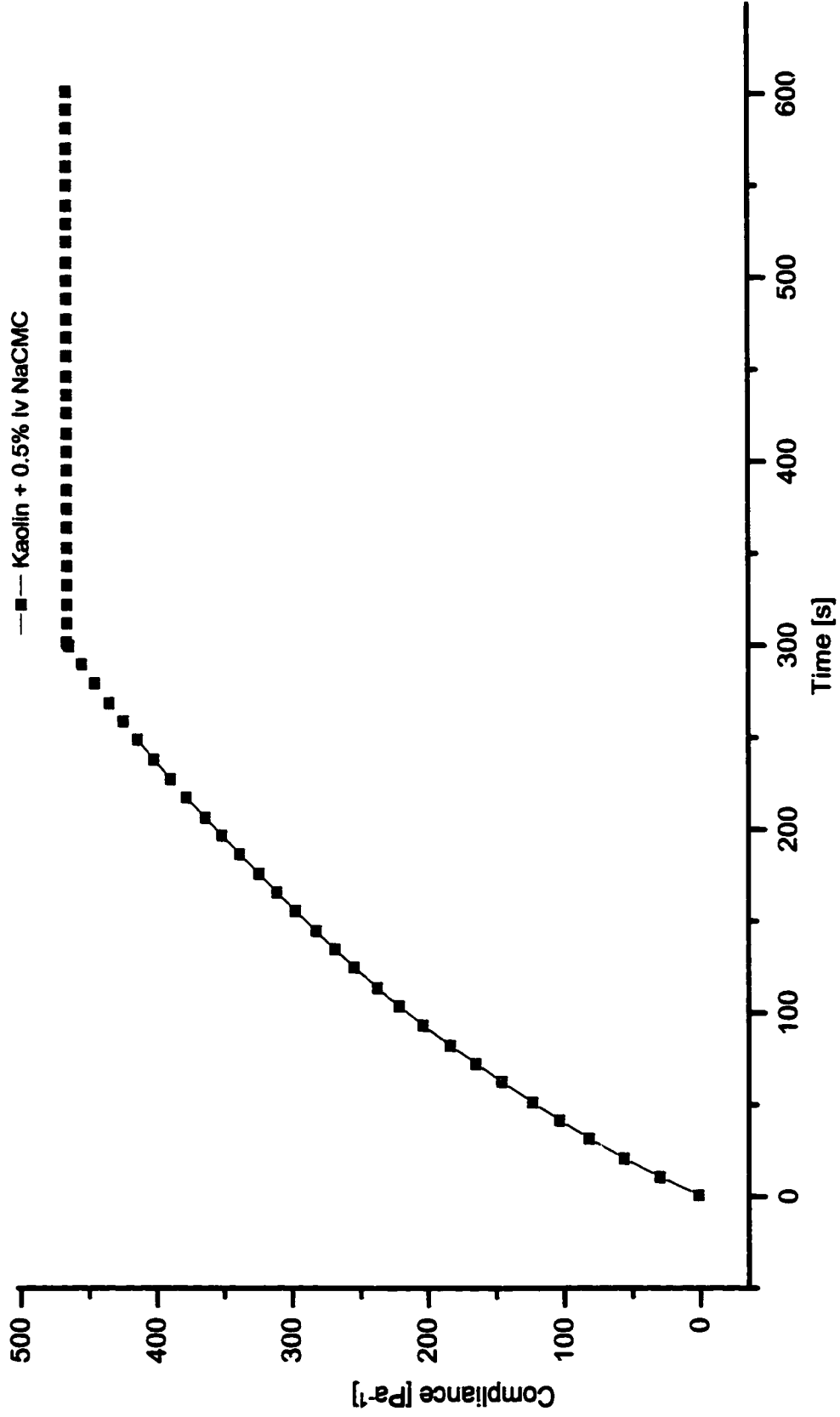


Figure 4.3.4.7. Creep-recovery curve of 50% kaolin suspension with addition of Iv NaCMC.
Iv: low viscosity. ($\tau = 0.5\text{Pa}$)

4.3.5) Summary of rheological investigations of kaolin samples

For comparison, the collected rheological parameters in Table 4.1 (for the 40% kaolin samples) and Table 4.2 (for the 50% kaolin samples) are given here.

Table 4.1

The calculated rheological properties for the 40% kaolin samples. The apparent viscosities are measured at 750s^{-1} and 54s^{-1} , respectively. The standard deviation of averaged values was found to be $\pm 5\%$ in most cases.

mv: medium viscosity

Sample		Elasticity ratio (J_{e0}/J_{max}) [$\tau = 50\text{Pa}$]	Viscosity [Pa·s]		Thixotropy hysteresis "area" (Pa/s)	Yield stress τ [Pa]	
			Apparent viscosity range	Plastic viscosity		Herschel-Bulkley (τ_{HB})	Bingham (τ_B)
1	40% Kaolin	0.81	0.44~3.89	0.12	1810	60	240
		0.43 ($\tau=60\text{Pa}$)					
2	40% K with 1% mv NaCMC	0.09	0.32~1.51	0.12	$3.1\text{e} + 04$	10	150
3	40% K with 1% NaCl	0.96	0.21~1.88	0.05	4180	22	125
4	40% K with 1% mv NaCMC and 1% NaCl	0.89	0.38~3.11	0.06	$4.7\text{e} + 04$	40	212

Table 4.2

The calculated rheological properties for the 50% kaolin samples.

The apparent viscosities are measured at 750s^{-1} and 26s^{-1} , respectively. The standard deviation of averaged values of viscosities and yield stresses was found to be $\pm 10\%$ in most cases. The standard deviation of averaged loop areas was $\pm 15\%$.

lv: low viscosity; mv: medium viscosity.

Sample		Elasticity ratio (J_{e0}/J_{max})		Viscosity [Pa·s]		Thixotropy hysteresis "area" (Pa/s)	Yield stress τ [Pa]	
				Apparent viscosity range	Plastic viscosity		Herschel- Bulkley (τ_{HB})	Bingham (τ_B)
1	50% Kaolin	-*		0.55–8.2	0.10	4.2e+04	-*	330
2	50% K with 1% NaCl	($\tau=150\text{Pa}$)	0.79	0.6–10.6	0.096	3.2e+04	305	390
3	50% K with 0.5% mv NaCMC	($\tau=5\text{Pa}$)	0.92	0.3–3.0	0.16	1.4e+04	100	116
		($\tau=10\text{Pa}$)	0.95					
		($\tau=20\text{Pa}$)	0.93					
		($\tau=50\text{Pa}$)	0.92					
4	50% K with 0.25% lv NaCMC and 0.25% mv NaCMC	($\tau=1\text{Pa}$)	0.93	0.08–0.4	0.06	3040	11	16
		($\tau=2\text{Pa}$)	0.92					
		($\tau=3\text{Pa}$)	0.93					
		($\tau=4\text{Pa}$)	0.56					
		($\tau=5\text{Pa}$)	0.26					
5	50% K with 0.5% lv NaCMC	($\tau=0.08\text{Pa}$)	0.79	0.03–0.09	0.03	750	2.2	2.4
		($\tau=0.5\text{Pa}$)	0.39					
6	50% K with 0.1% lv NaCMC	($\tau=75\text{Pa}$)	0.99	0.47–7.26	0.18	-9960	140	225
7	50% K with 0.5% lv NaCMC and 0.01% mv NaCMC	($\tau=1\text{Pa}$)	0.9	0.08–0.3	0.06	2714	10	15
		($\tau=2\text{Pa}$)	0.93					
		($\tau=3\text{Pa}$)	0.95					
8	50% K with 0.5% lv NaCMC and 1% NaCl	($\tau=100\text{Pa}$)	0.99	0.24–4.82	0.07	3461	120	122
		($\tau=150\text{Pa}$)	≈ 1					
9	50% K with 0.1% lv NaCMC and 0.002% mv NaCMC	($\tau=20\text{Pa}$)	≈ 1	0.32–4.9	0.13	-4630	130	151
		($\tau=30\text{Pa}$)	≈ 1					
		($\tau=50\text{Pa}$)	≈ 1					
10	50% K with 0.1% lv NaCMC, 0.002% mv NaCMC and 0.5% NaCl	($\tau=100\text{Pa}$)	0.87	0.65–11.3	0.11	7.44e+04	250	419
		($\tau=125\text{Pa}$)	0.92					

* It is not very reproducible

CHAPTER 5

SUMMARY

The rheological behaviors of aqueous kaolin suspensions ($\text{pH} = 5\sim 6$) were studied in this work. In order to get a better understanding of the rheological results, the sedimentation volume experiments with samples prepared from 2.5% kaolin suspensions were also performed. The compositions were prepared from NaCl, and NaCMC with different viscosity molecular weights. First, the effect of the preparation technique on the rheological behavior was examined; the suspensions having kaolin contents of 40% and 50% from powders (NaCMC, NaCl, kaolin and distilled water) and from starch solutions (NaCMC, NaCl, as well) were made. Regarding the preparation technique, the rheological properties showed time-dependence for samples prepared from powders. Time-dependence was not observed if the samples were prepared from solutions. The sedimentation volumes however, always showed time-dependence. The sedimentation volume investigations revealed that: at the lowest concentration (0.005% – 0.01%) of mv NaCMC, the polymer initiated bridging flocculation. Using the mixture of lv and mv NaCMC, the bridging flocculation could also take place although the sedimentation volumes showed the significant adsorption of lv NaCMC, which means that the bridging flocculation occurred by a site-blocking mechanism. The NaCl oppositely affected the sedimentation volumes of the different viscosity NaCMCs. The stabilizing capability of the lv polymer was decreased by adding NaCl, while the stabilizing capability of the mv polymer was improved with increasing the concentration of NaCl. These effects can be attributed to the electrostatic screening of NaCl that especially hindered the bridge-forming adsorption of mv NaCMC. The rheological results were in good agreement to the Vs results concerning the stabilizing ability of different viscosity

polymers. The bridging flocculation enhanced by a site-blocking mechanism was also revealed. lv NaCMC was a better stabilizing and thinning agent than mv NaCMC. But the NaCl increased the viscosity of CMC added suspensions. Concerning this effect, there is a good correlation between sedimentation volumes and viscosity for lv NaCMC. But there was a contradiction as mv NaCMC. 0.1% lv NaCMC, 0.002% mv NaCMC and 0.5% NaCl together caused the most significant thixotropy; without of NaCl, it shows anti-thixotropy. According to the results, the effect of NaCl in the 20 – 25 times denser kaolin suspensions is even more complicated. Supposedly, the screening of the interparticle repulsion is of great importance; the particles can form aggregates resulting in a viscosity increase of such suspensions. Real-elasticity due to bridge-forming was only found in the presence of mv NaCMC. The samples, prepared from the mixture of low and medium viscosity CMCs, were found to be the best composition for getting low viscosity, significant thixotropy and elasticity.

CHAPTER 6

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