Rheological properties of purified illite clays in glycerol/water suspensions

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Abstract. There are many studies about rheological properties of clay-water suspensions, but no published investigations about clay-glycerol suspensions. In this work apparent viscosity of previously purified illite containing clay fraction < 2 μm and glycerol/water suspensions were investigated. Carbonates were removed by dissolution in hydrochloric and citric acids and other non-clay minerals were almost totally removed by centrifugation. All obtained suspensions behaved as shear-thinning fluids with multiple times higher viscosity than pure glycerol/water solutions. Reduction of clay fraction concentration by 5% decreased the apparent viscosity of 50% glycerol/water suspensions approximately 5 times. There was basically no difference in apparent viscosity between all four 50% glycerol/water suspensions, but in 90% glycerol/water suspensions samples from Iecava deposit showed slightly higher apparent viscosity, which could be affected by the particle size distribution.

1. Introduction

Clays and clay minerals are widely used in cosmetics, health care and therapeutic products as excipients and active ingredients. The most important properties for these applications are high specific area and adsorptive capacity, chemical inertness and rheological properties. Most cosmetic and health care products are designed for topical application, which require appropriate rheological properties. These products must flow easily when deformed and retain their shape in repose. The addition of clay minerals improves the rheological properties of suspensions and emulsions, therefore they are used as excipients and thickening agents in many semi-solid preparations [1-4].

An important factor for application of clay minerals in cosmetics and health care is the purity. Most naturally occurring clays typically are mixtures of clay and non-clay minerals [5]. The value and application of certain clays depends on the required purification, which accordingly depends on the type and amount of non-clay minerals. In Latvia the most abundant clay mineral is illite, but it can also contain kaolinite and mixture of non-clay minerals, such as quartz, feldspar, calcite, dolomite, metal oxides and hydroxides and muscovite. Latvia has large clay reserves, but they are traditionally used in building materials and pottery. To use Latvian clays as excipients in cosmetic and therapeutic products, it is necessary to perform simple, but effective purification process and to investigate the rheological properties of purified illite. In this study the rheological properties of illite and glycerol/water suspensions were investigated, because glycerol is often used in semi-solid cosmetic and health care products due to its moisturizing, soothing and healing properties [6].

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2. Materials and methods

2.1. Materials
Clay samples were obtained from two deposits in Latvia – Laza and Iecava. They were matured in distilled water for 1 month and fractionated by wet sieving method through 230 mesh (63 μm) sieve. Both samples have different colour (Figure 1) and mineralogical composition (Table 1).

![Figure 1. Powders of clay samples a) Laza, b) Iecava.](image)

Table 1. Mineralogical composition of clays (wt%) with standard deviation 2-4 %

| Deposit | Illite | Kaolinite | Chlorite | Quartz | Feldspar | Calcite | Dolomite | Muscovite |
|---------|--------|-----------|----------|--------|----------|---------|----------|-----------|
| Iecava  | 51     | -         | -        | 11     | 26       | -       | 4        | 8         |
| Laza    | 34     | 10        | 8        | 13     | 16       | 8       | 5        | 6         |

2.2. Dissolution of carbonates
Calcite and dolomite were removed by dissolution in 1M hydrochloric and citric acid solutions. 50g of clay samples was mixed with 200mL distilled water and stirred. The acid was added stepwise, keeping the pH above 4.5, in order to avoid damaging the structure of clay minerals [7]. All carbonates were dissolved in 2-4 days (depending on the sample and acid), when the pH was constant at values 5-6. Afterwards the clay suspensions were washed with distilled water until the electrical conductivity was under 10 μS/cm.

2.3. Preparation of clay and glycerol/water suspensions
After removal of carbonates clay fraction < 2 μm was obtained by centrifugation of the suspensions at 1100 rpm for 3 minutes, then dried in 105°C and crushed into powder. For the preparation of suspensions, a chosen amount of clay powder was mixed with certain amount of distilled water until the obtained paste was homogenous. Then a pure glycerol was added to obtain 50% or 90% (w/w) glycerol/water concentration. The suspensions of 90% glycerol were homogenized and matured for 1 week, but 50% - for 2 weeks. The chosen concentrations of clay samples were obtained by diluting suspension with the highest concentration.

2.4. Characterization of the samples
X-ray powder diffraction (PANalytical X’Pert PRO diffractometer with spinning sample holder) was used to identify the mineralogical composition of clay samples before and after removal of carbonates (sample fraction < 63 μm) and the purity of obtained clay fraction < 2 μm.

The measurements were taken with rotational viscometer (Fungilab, Expert series) at room temperature 20±1°C and shear rates 1, 5, 10, 20, 50 and 100 rpm. At each shear rate the viscosity data were recorded every 3 seconds for totally 60 seconds (except for 1 rpm where it was 180 seconds),
before changing to higher shear rate. At each shear rate from all recorded viscosity values the average value was used in further research.

The particle size distribution in the suspensions was determined by laser particle size analyser Analysette 22, with measuring range 0.01-53 µm and laser wavelength 650 nm.

3. Results and Discussion

The mineralogical composition of clay samples after the purification process is shown in Table 2. All carbonates are completely dissolved by both acids. Small amounts of quartz and feldspar are still present in clay samples from Laza deposit, but samples from Iecava deposit contain basically pure illite.

Table 2. Mineralogical composition of obtained clay fraction (wt%) with standard deviation 2-4 %

| Deposit | Used acid | Sample  | Illite | Kaolinite | Quartz | Feldspar |
|---------|-----------|---------|--------|-----------|--------|----------|
| HCl     | Ie_HCl    | 97      | -      | 2         | 1      |
| Citric acid | Ie_C  | 96      | -      | 2         | 2      |
| L_HCl   | L_C       | 64      | 20     | 8         | 8      |
| Laza HCl | L_C       | 66      | 18     | 9         | 7      |

Pure 50% and 90% glycerol/water solutions are Newtonian fluids with viscosity 0.006 and 0.219 Pa*s at 20°C, respectively. The results in Figure 3 show that the addition of clay fraction increase the apparent viscosity multiple times and the obtained suspensions behave as Non-Newtonian fluids, where the apparent viscosity decreases by increasing the shear rate. The magnitude of increase depends on the clay sample concentration and shear rate. In 50% glycerol/water suspensions samples

![Figure 2](image)
from both deposits show almost identical viscosity values, only with small differences at the lowest shear rates in suspensions containing 20 and 15 wt% of clay fraction. Reduction of clay fraction concentration by 5% the apparent viscosity decreases approximately 5 times. From all 90% glycerol/water suspensions, clay samples from Iecava deposit shows the highest apparent viscosity (Figure 2 (4)). This could be connected with the particle size distribution (Figure 3), where Ie_HCl and L_C containing suspensions show finer particles than L_HCl and L_C containing suspensions. At the same time the difference between the particle size distribution in 50% glycerol/water suspensions is approximately 2 times smaller, which obviously does not affect the apparent viscosity (Figure 2 (1-3)). The differences in particle size distribution between suspensions containing clay samples from Iecava and Laza deposits could be connected to the fact, that samples from Laza contain quartz and feldspar particles, which act as cementing agents [7].

To describe the rheological behavior of suspensions, Herschel-Bulkley (H-B) model was used:

\[ \tau = \tau_0 + m\gamma^n \]  

where \( \tau \) is the shear stress, \( \tau_0 \) is the yield stress, \( \gamma \) is the shear rate, \( m \) is the consistency coefficient and \( n \) is the flow behavior index. The H-B model can be used for shear-thinning and shear-thickening fluids [8]. The H-B model fits well the \( \tau \) versus \( \gamma \) data, giving correlation coefficients between 0,960 and 0,999. The obtained H-B model parameters are reported in Table 3. As all flow behaviour indices \( n \) are less then 1 (n < 1), all suspensions behave as shear-thinning fluids. All suspensions also exhibit yield stress, where a significant increase is observed at clay concentration 20 wt% in 50% glycerol solution.

| Clay fraction concentration, wt% | Ie_HCl | L_HCl | Ie_C | L_C |
|----------------------------------|-------|------|------|-----|
| 50% glycerol                    |       |      |      |     |
| 90% glycerol                    |       |      |      |     |
| 5%                              | 0,25  | 0,23 | 0,37 | 0,32|
| 10%                             | 0,78  | 0,80 | 0,56 | 0,70|
| 15%                             | 1,88  | 0,87 | 0,64 | 0,68|
| 20%                             | 21,10 | 18,80| 21,90| 19,10|
| Flow behavior index (n)         |       |      |      |     |
| 5%                              | 0,71  | 0,82 | 0,72 | 0,84|
| 10%                             | 0,48  | 0,5  | 0,34 | 0,52|
| 15%                             | 0,35  | 0,23 | 0,24 | 0,21|
| 20%                             | 0,18  | 0,20 | 0,19 | 0,20|
| Flow consistency coefficient (m), Pa*s\(^n\) |       |      |      |     |
| 5%                              | 2,11  | 1,11 | 1,86 | 1,01|
| 10%                             | 0,35  | 0,43 | 0,59 | 0,44|
| 15%                             | 3,90  | 5,80 | 7,26 | 8,52|
| 20%                             | 38,08 | 34,87| 39,5 | 35,64|
4. Conclusions
The addition of clay fraction < 2 μm to glycerol/water solutions increases the viscosity multiple times and the obtained suspensions behave as shear-thinning fluids. The magnitude of increase in 50% glycerol/water suspensions is influenced by the added clay fraction concentration. Based on the obtained results, purified illite containing clay fraction can be used as excipients and thickeners in glycerol containing semi-solid production.

Acknowledgements
This work has been supported by the National Research Program of Latvia 2010-2013 “Sustainable use of local resources (underground resources, wood, food and transport) – new products and technologies (NatRes)” within the project V7904.

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Corrigendum: Rheological properties of purified illite clays in glycerol/water suspensions

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CORRIGENDUM TO: 2015 J. Phys. Conf. Ser. 602 012003

The authors regret that the apparent viscosity values reported in the above paper were incorrect because of some technical problems with the rotational viscometer. The apparent viscosity measurements were retaken with rheometer Rheolab QC (Anton Paar) at shear rates 2, 5, 10, 20, 50 and 100 rpm. The correct data (Figure 2 and Table 3) appears below.

Figure 2. Apparent viscosity of 50% (1-3) and 90% (4) glycerol/water suspensions with 20, 15, 10 and 5 wt% of clay fraction
| Clay fraction concentration, wt% | Ie_HCl | L_HCl | Ie_C | L_C |
|--------------------------------|--------|-------|------|-----|
| 50% glycerol                  |        |       |      |     |
| 90% glycerol                  |        |       |      |     |
| 5%                            | 0      | 0     | 0    | 0   |
| 10%                           | 0      | 0     | 0    | 0   |
| 15%                           | 1.40   | 1.00  | 1.35 | 0.95|
| 20%                           | 21.60  | 9.70  | 21.50| 9.90|
| Yield stress ($\tau_0$), Pa   |        |       |      |     |
| 5%                            | 0.71   | 0.92  | 0.72 | 0.94|
| 10%                           | 0.48   | 0.50  | 0.46 | 0.48|
| 15%                           | 0.35   | 0.39  | 0.35 | 0.37|
| 20%                           | 0.31   | 0.29  | 0.29 | 0.31|
| Flow behavior index (n)       |        |       |      |     |
| 5%                            | 1.23   | 0.36  | 1.21 | 0.35|
| 10%                           | 1.26   | 0.25  | 1.25 | 0.23|
| 15%                           | 3.90   | 1.33  | 3.93 | 1.36|
| 20%                           | 6.82   | 4.16  | 6.88 | 4.19|
| Flow consistency coefficient (m), Pa·s^n |      |       |      |     |
| 5%                            |        |       |      |     |
| 10%                           |        |       |      |     |
| 15%                           |        |       |      |     |
| 20%                           |        |       |      |     |

Due to the corrected values three sentences should be replaced:
1. The last sentence in the abstract should be replaced by:
   From all glycerol/water suspensions samples with clays from Iecava deposit showed slightly higher apparent viscosity, that could be affected by the particle size distribution and mineralogical composition.
2. The sentence that starts in page 3 and ends in page 4 should be replaced by:
   In 50% glycerol/water suspensions samples Ie_HCl and Ie_C show higher viscosity than samples L_HCl and L_C due to higher content of clay minerals.
3. The last sentence in page 4 should be replaced by:
   Only 15 and 20 wt% suspensions exhibit yield stress, where a significant increase is observed at clay concentration 20 wt% in 50% glycerol solution.