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Academician Bogdan C. Simionescu (1948–2024)*

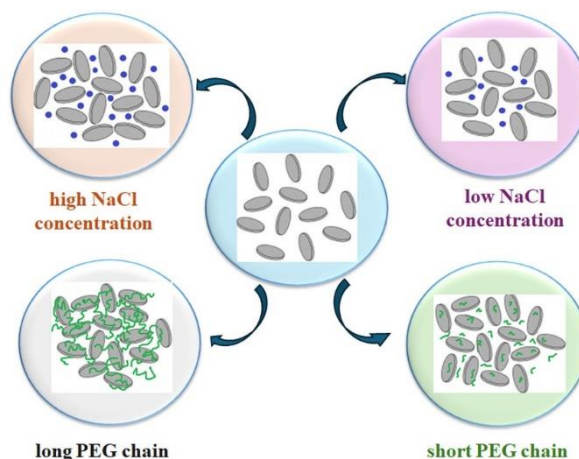
VISCOMETRIC INVESTIGATION OF LAPONITE® RD AQUEOUS DISPERSIONS. EFFECT OF SALT AND POLYMER ADDITION

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This study investigates the impact of salt (NaCl) and a non-ionic polymer (poly(ethylene oxide), PEG) on the flow behavior of Laponite® RD (LRD) aqueous dispersions using viscometric analysis. The results indicate that the electrostatic repulsion interactions between clay particles shielded by the addition of salt cause an increase in the viscosity of the LDR aqueous dispersion from 28.98 (in the absence of salt) to 167.77 (in 0.005M NaCl). For LRD/PEG mixture with weight fraction of polymer (w_{PEG}) of 0.15, the intrinsic viscosity ($[\eta]$) ranges from 21.31 to 29.22 for PEG with a molecular weight of 400 g/mol (PEG400) and 35000 g/mol (PEG35000), respectively. In the system with $w_{PEG} = 0.50$, $[\eta]$ increases significantly, reaching a maximum of 36.25 for PEG35000. At lower PEG concentrations, viscosity deviates from the additive rule more pronounced for high molecular weight PEG. Conversely, at higher PEG concentrations, viscosity approaches the values predicted by the ideal mixture model, indicating stabilization of the system.



INTRODUCTION

Laponite® RD (LRD), with the chemical formula $\text{Na}^{+}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$, is a synthetic smectite clay with a layered structure in which a magnesium octahedral sheet is sandwiched between two silicon tetrahedron sheets. It has a crystal structure having a disc-like shape with a diameter of about 25–30 nm and a thickness of 1 nm.¹ The LRD discs are stacked in a dry state, and they disperse in water, acquiring a negative charge on their surface and a weak positive charge at low pH or a negative

one at high pH on the rim of platelets.² Its ability to form gel-like structures when it is dispersed in water above a concentration of approximately 2% makes it highly useful in various applications such as cosmetics, personal care products, pharmaceuticals, industrial coatings, etc. Additionally, LRD is widely used in formulations requiring controlled release, viscosity enhancement, or suspension stability.

Despite their importance, the viscometric measurements of clay dispersions in water, with or without additives, remain underexplored in the scientific literature, requiring further research to

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enhance the understanding of their flow behavior. Among the first viscometric studies on dispersions of smectite clays (montmorillonite) were reported around the 60s in order to analyze the particle–particle interactions in water and water containing electrolyte or polymer.^{3,4} The investigations on dilute suspensions of montmorillonite at pH = 10 in the presence of NaCl evidenced two distinct domains in the flocculated region: *i*) in the range of 0.06M NaCl – 0.10M NaCl and *ii*) above 0.1M NaCl.⁵ Wierenga *et al.*⁶, for stable gibbsite (hexagonal platelets with the average diameter and thickness of 160 nm and 13 nm, respectively) dispersion, reported a value for the intrinsic viscosity of 23 and a Huggins coefficient (k_H) of 0.4. From viscosity data, van der Kooji and coworkers⁷ calculated the number-average aspect ratio of the gibbsite platelets as 6.5 and 12, respectively, in the investigated suspensions. Bhandari *et al.*⁸ found the value of the intrinsic viscosity of 18.62 and $k_H = 2$ for Laponite[®] JS, which is less sensitive to the presence of ions, maintains suspension stability for a longer period, but does not form as strong a gel network as LRD. The presence of NaCl in LRD dispersion influences the electrostatic interactions between clay platelets, affecting gelation, viscosity, and flow behavior.^{9–11}

The addition of poly(ethylene oxide) (PEO) modifies the dispersion structure as a result of its adsorption onto the LRD platelets surface, impacting the viscosity and stability of the dispersion as well as the network formation.^{12–14} Investigating the effect of NaCl and PEO addition on the structure and properties of LRD aqueous dispersion is essential for applications in pharmaceuticals, cosmetics, and advanced materials, where precise control of clay dispersion flow is critical for performance and processing.

Knowledge of the hydrodynamic properties of the LRD aqueous dispersions is important for various applications like *i*) obtaining of materials for 3D printing, where precise viscosity control after deposition is required; *ii*) cosmetics and personal care products where the addition of polymer and salt can improve the feel upon application and the adjusts the consistency; *iii*) LRD-based controlled release systems where the addition of NaCl or PEO adjusts the release rate by modifying the rheological and colloidal properties; *iv*) thin coatings and smart paints where LRD suspensions with NaCl or polymer are useful in the formulation of self-healing paints or paints that form uniform and durable films; *v*) films and membranes for special applications where

rheological properties are crucial for the manufacturing process.¹¹ Furthermore, the study of LRD dispersions in the presence of salt or polymer is also important from the point of view of fundamental research on colloidal systems. Dilute LRD suspensions serve as models for studying phase transitions, gel behavior, and colloidal stability. In this context, the present work investigates the intrinsic viscosity of aqueous LRD dispersions in the presence of NaCl and low molecular weight PEG, determining additivity relationships and analyzing the interactions between the system components.

RESULTS AND DISCUSSION

The flow behavior of LRD aqueous dispersion was investigated using viscometry and was controlled by changing the solution salinity and some characteristics of the polymer (*i.e.*, the molecular weight and the weight ratio between clay and polymer).

Salinity effect on the viscosity of the LRD aqueous dispersion

The dependence of the relative viscosity, η_r , as a function of the volume fraction of clay, ϕ , for LRD dispersions in water containing different amounts of NaCl is shown in Fig. 1. For the studied dispersions, the evolution of η_r with ϕ reflects the interactions between LRD particles.

In the absence of salt, disk-like LRD particles, with negatively charged faces and slightly positive edges, repel each other. By adding salt, the electrostatic repulsions interactions between particles are screened, allowing them to come closer and form some aggregate. In our study, the significant increase in viscosity observed for LRD dispersion with high salt content (0.005M NaCl) suggests the transition to a more structured system. According to the phase diagram of salt-controlled diluted LRD dispersions proposed by various authors, at very low clay concentrations (below 0.5%) the dispersion exists as a stable liquid phase in which the LRD particles are homogeneously dispersed as individual units stabilized by electrostatic repulsion (Fig. 1).^{15,16} The addition of NaCl up to 10⁻²M facilitates particles to come together and form a stable inhomogeneous phase (sol), where clusters with a finite lifetime are present (Fig. 1). By adding a larger amount of NaCl, more compact structures (aggregates) are formed that

can sediment, leading to a decrease in viscosity. This behavior indicates that salt concentration plays a

crucial role in controlling the flow behavior of LRD dispersions.

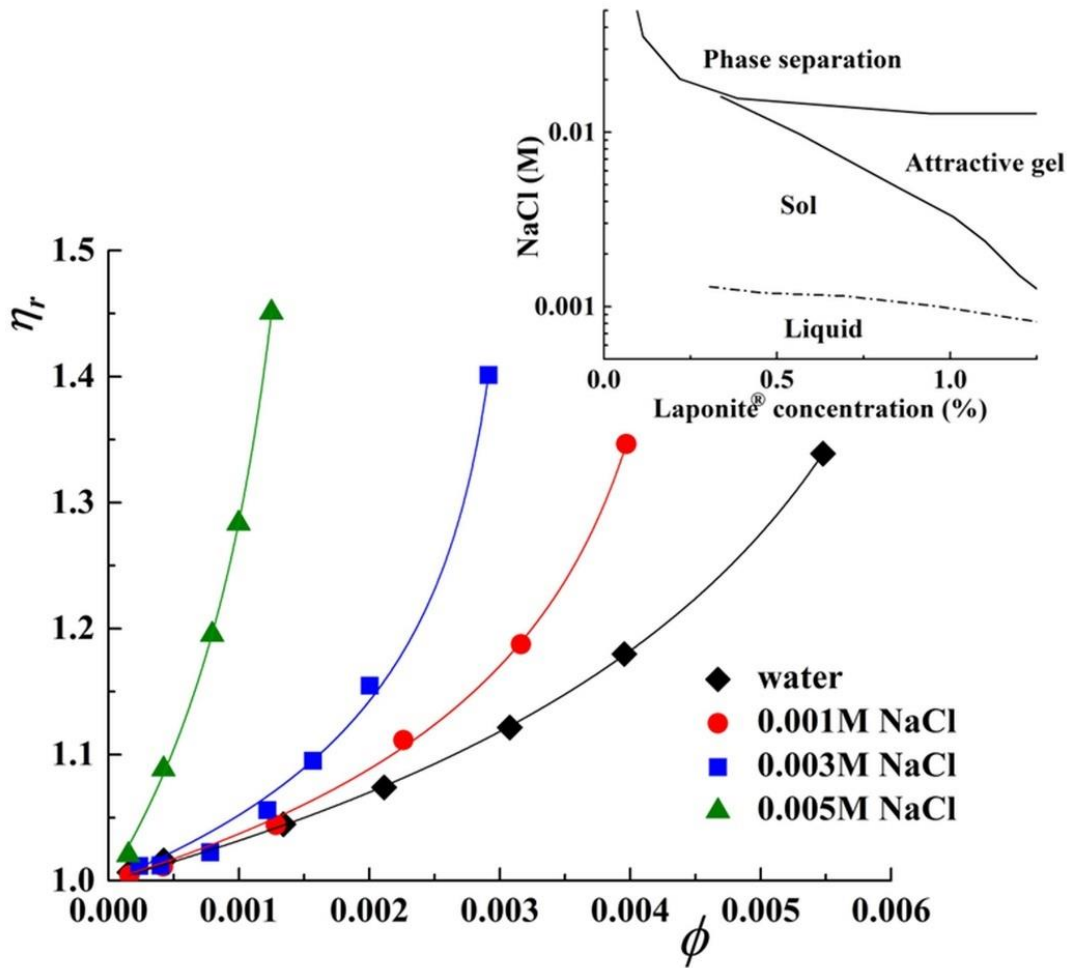


Fig. 1 – Dependence of relative viscosity, η_r , on the volume fraction of LRD, ϕ , for the LRD dispersions in the absence/presence of NaCl. The lines represent the fitting of experimental data with the K–D model (eq.1). The inset figure shows the phase diagram of diluted LRD aqueous dispersion with various ionic strengths.

One of the most widely applied models to determine the intrinsic viscosity of the colloidal systems is the Krieger–Dougherty (K–D) equation:¹⁸

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-[\eta]\phi_{max}} \quad (1)$$

where η_r represents the relative viscosity defined as the ratio between the viscosity of the suspension (η)

and that of the solvent (η_0), ϕ is the volume fraction of the solid in continuous medium, ϕ_{max} is the maximum packing fraction defined as the volume fraction where the viscosity appears infinite, and $[\eta]$ represents the intrinsic viscosity.

The intrinsic viscosity, $[\eta]$, and ϕ_{max} values obtained by fitting the experimental data with the K–D model are shown in Table 1.

Table 1

The viscometric parameters estimated for the LRD dispersion in the absence/presence of NaCl

LRD dispersion in	$[\eta]$	ϕ_{max}	R^2
water	28.98	0.0073	0.9998
0.001M NaCl solution	32.27	0.0046	0.9988
0.003M NaCl solution	42.11	0.0032	0.9944
0.005M NaCl solution	167.77	0.0017	0.9993

Figure 2 illustrates the variation of the two parameters with salt concentration. As NaCl concentration increases, $[\eta]$ initially remains low, and then, due to the shielding of repulsion interactions between particles, the formation of the small aggregates or clusters occurs, increasing the

viscosity of dispersion. On the other hand, the increase of NaCl concentration decreases ϕ_{max} due to the stabilization of particles by salt ions, which prevents their agglomeration, thereby reducing their ability to form dense and blocking structures in the suspension.

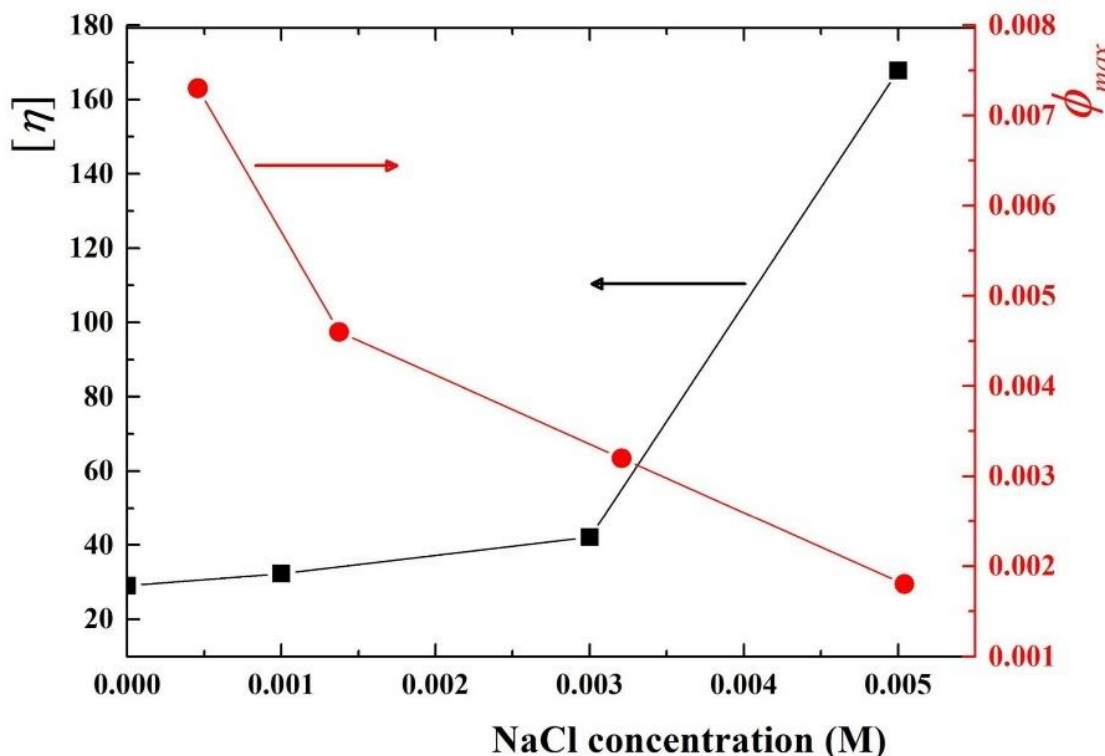


Fig. 2 – Variation of $[\eta]$ and ϕ_{max} with the content of NaCl in the LRD dispersion.

Influence of poly(ethylene glycol) on the viscosity of the LRD aqueous dispersion

As can be seen in Fig. 3, the η_r values rise with increasing of ϕ , regardless of the molecular mass of the added polymer and its weight fraction (w_{PEG}) in the LRD/PEG mixture.

The values of $[\eta]$ and ϕ_{max} , calculated with eq. 1, for LRD/PEG aqueous dispersions are listed in Table 2.

For the system with $w_{PEG} = 0.15$, the intrinsic

viscosity range from 20.94 to 29.22, with the lowest value observed for the PEG400 solution and the highest for the PEG35000 solution. Similarly, ϕ_{max} , varies from 0.0073 to 0.0108, with higher values observed for higher molecular weight PEG.

In the systems with $w_{PEG} = 0.50$, $[\eta]$ values increase significantly with molecular weight, reaching a maximum of 36.25 for PEG35000. ϕ_{max} is also notably higher for PEG10000 and PEG35000 solutions (0.8053 and 0.8038, respectively) compared to lower molecular weight PEG.

Table 2

The viscometric parameters estimated for the LRD dispersion in the absence/presence of PEG

LRD dispersion in	$w_{PEG} = 0.15$			$w_{PEG} = 0.50$		
	$[\eta]$	ϕ_{max}	R^2	$[\eta]$	ϕ_{max}	R^2
water	28.98	0.0073	0.9998	28.98	0.0073	0.9998
PEG400 solution	20.94	0.0100	0.9986	11.74	0.0240	0.9840
PEG10000 solution	24.07	0.0108	0.9967	27.65	0.8053	0.9980
PEG35000 solution	29.22	0.0108	0.9945	36.25	0.8038	0.9992

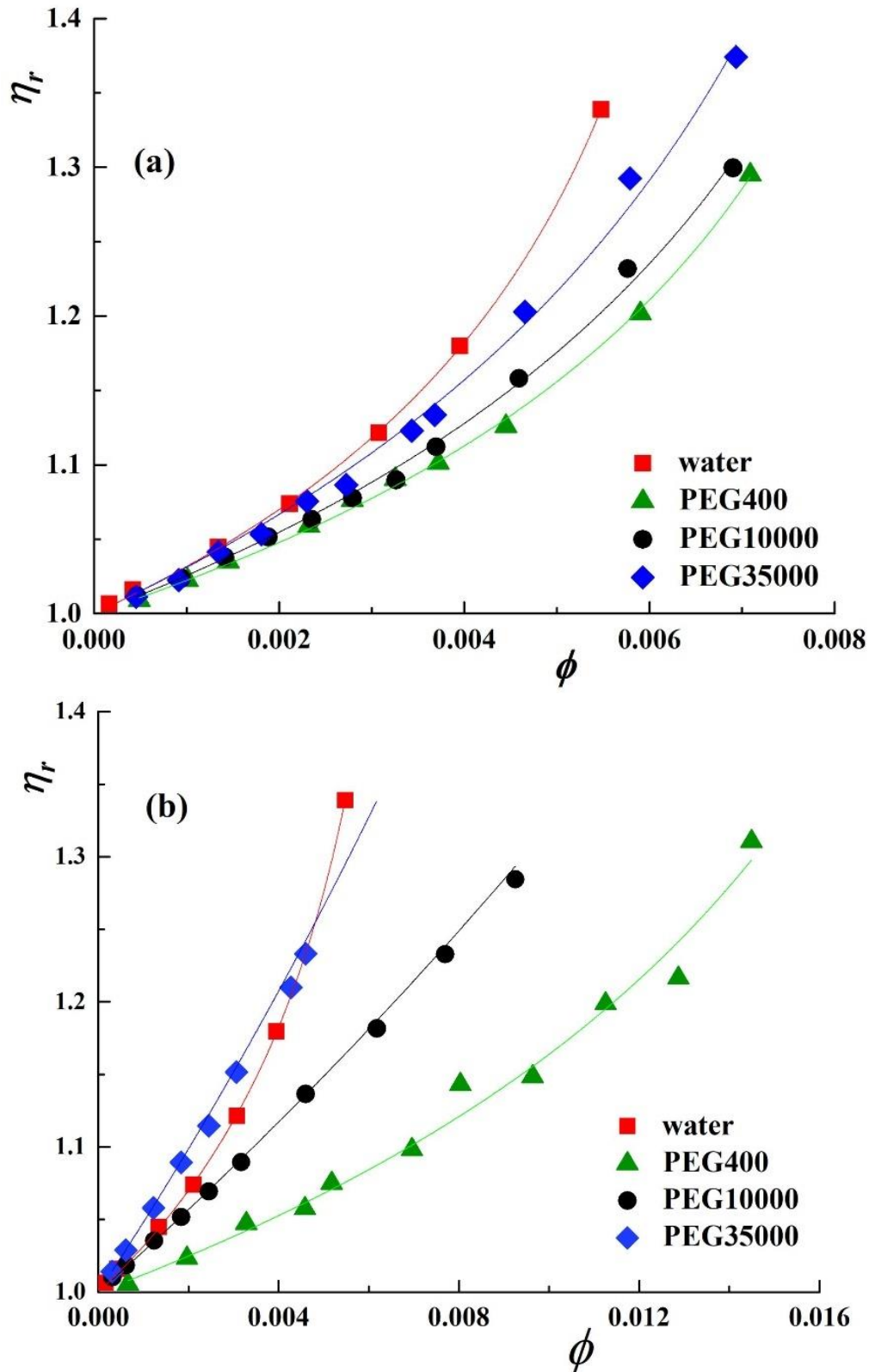


Fig. 3 – Dependence of relative viscosity, η_r , on the volume fraction of LRD, ϕ , for the LRD dispersions in the absence/presence of non-ionic polymer with w_{PEG} of (a) 0.15 and (b) 0.50. The lines represent the fitting of experimental data with the K–D model (eq. 1).

These results indicate that increasing the molecular weight of PEG enhances both intrinsic viscosity and maximum packing fraction, with a

more pronounced effect in the system with w_{PEG} of 0.50 due to the higher polymer content, which likely influences dispersion stability and network

formation. These trends suggest that the molecular weight and solvent interactions play a crucial role in determining viscosity, with higher molecular weight polymers contributing more significantly to the increase due to stronger intermolecular forces.

In Fig. 4 the variation of $[\eta]$ and ϕ_{max} with the molecular weight of added polymer for $w_{PEG} = 0.15$ is shown. Notably, at lower molecular weights, the viscosity decreases before steadily increasing with higher molecular weight. This behavior can be attributed to the fact that $[\eta]$ is closely related to the hydrodynamic volume of polymer chains in solution. At low molecular weights, polymer chains are shorter and less entangled leading to lower resistance to flow and consequently lower viscosity. As molecular weight increases, polymer chains become longer, experience greater entanglements, and occupy a larger hydrodynamic volume,

contributing to a higher $[\eta]$. Moreover, the addition of polymer with low molecular weight determines a depletion attraction between clay particles, reducing the flow parameters. The addition of PEG with higher molecular weight causes the formation of the bridges between two or more clay particles, leading to the increase of $[\eta]$. A similar behavior was previously observed when a low value of the elastic modulus was observed in samples containing low molecular weight polymer. Thus, by adding 2% PEG in a 2.5% LRD dispersion and 2% LRD, a minimum of the elastic modulus was observed for samples with PEG of molecular weight of 10000 g/mol and 49000 g/mol, respectively.^{19,20} The increase in ϕ_{max} with molecular weight suggests that higher molecular weight PEG can form more stable or extended structures in solution, further influencing viscosity.

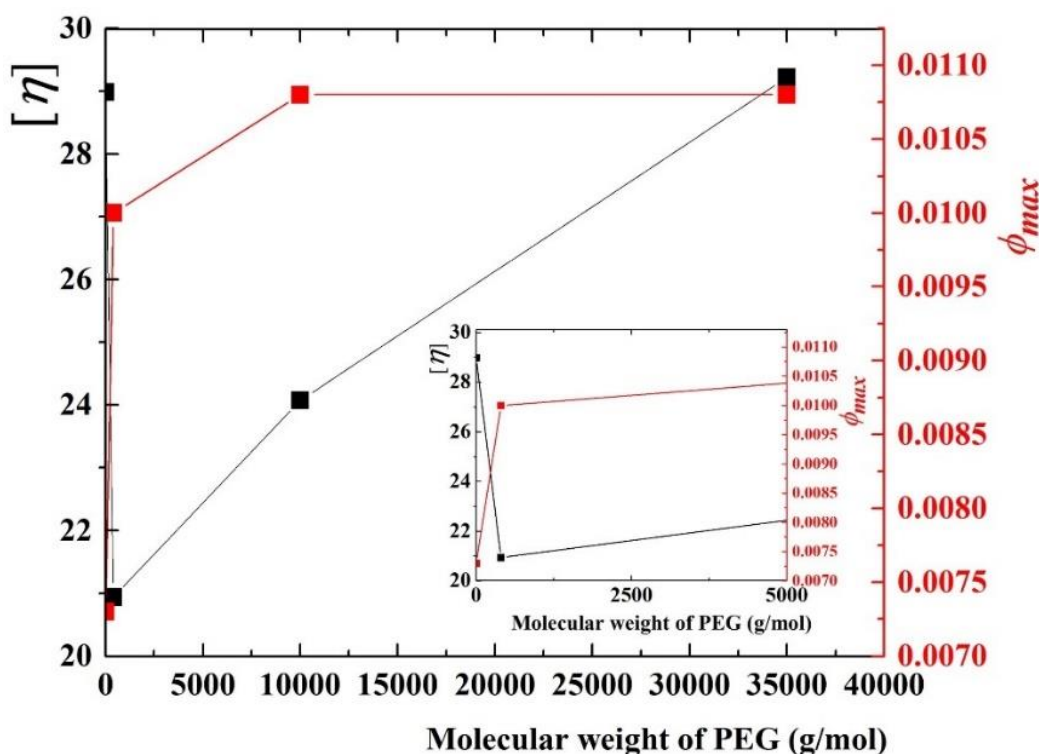


Fig. 4 – Variation of $[\eta]$ and ϕ_{max} with the molecular weight of added PEG for $w_{PEG} = 0.15$.

The w_{PEG} value has an influence on the intrinsic viscosity, as can be seen in Fig. 5. Although the additive viscosity relation was developed for polymer-polymer mixtures,²¹ we applied this relation to the clay/polymer system as a reference model, assuming that LRD behaves similarly to a polyelectrolyte due to the charges on the surface and edges of the disks. The deviations from this model indicate specific interactions between LRD and PEG. Under conditions of infinite dilution, it can be considered that the

components of the mixture coexist in the system without interacting with each other, and the intrinsic viscosity can be written as a function of composition according to the following relationship:

$$[\eta]_m = w_{LRD} \cdot [\eta]_{LRD} + w_{PEG} \cdot [\eta]_{PEG} \quad (2)$$

where w_{LRD} and w_{PEG} represent the weight fractions of clay and polymer, respectively. $[\eta]_{LRD}$ and $[\eta]_{PEG}$ are the intrinsic viscosity of the two components of the mixture.

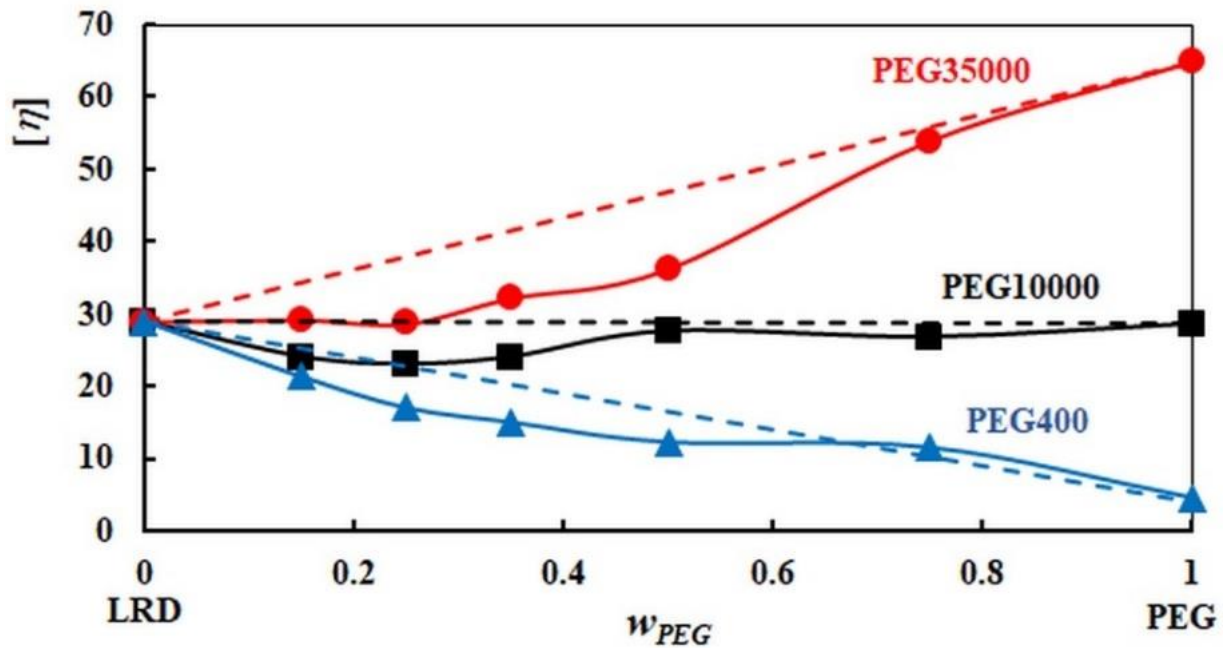


Fig. 5. – The intrinsic viscosity as a function of w_{PEG} . The dashed lines show the viscosity obtained by the additive rule (eq. 2).

The variation of $[\eta]$ compared with the additive rule can provide information concerning the role of PEG in modifying the dispersion microstructure and interactions between LRD particles. At low PEG concentrations, $[\eta]$ deviates from the additivity rule, showing lower values than expected for the mixture. This behavior is attributed to the interaction between PEG and LRD platelets, where PEG molecules adsorb onto the surface of the LRD particles or form steric layers around them. These interactions weaken the particle–particle network and decrease the viscosity of the dispersion. This viscosity reduction is more pronounced for higher molecular weight PEGs, likely due to their larger size, which enhances their ability to disrupt the LRD network. By the addition of PEG with a molecular weight of 400 g/mol and 10000 g/mol up to w_{PEG} of 0.7 and 0.5, respectively, the PEG chains are able to significantly alter the microstructure of the dispersion, leading to lower viscosity values. Above these weight fractions of PEG, $[\eta]$ starts to obey the additive rule with the viscosity approaching the predicted value for an ideal mixture. In the case of PEG with a molecular weight of 35000 g/mol, $[\eta]$ was lower than expected from the additivity rule up to approximately $w_{PEG} = 0.75$. At concentrations lower than 0.75, the higher molecular weight of PEG causes stronger interactions with LRD platelets, further disrupting the network and leading to a more pronounced deviation from additivity. Above w_{PEG} of 0.75, $[\eta]$ approaches the additive value, suggesting that the system has stabilized and

PEG and LRD behave as independent components, contributing additively to the overall viscosity.

EXPERIMENTAL

Laponite® RD (LRD), used in the present study, was acquired from BYK Additives Ltd. (Widnes, U.K.). Poly(ethylene glycol)s (PEG) samples with the molecular weights of 400 g/mol (PEG400), 10000 g/mol (PEG10000), and 35000 g/mol (PEG35000) were purchased from Fluka (Honeywell Research Chemicals, Seelze, Germany). NaCl was supplied by Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and used as received.

Clay dispersions and PEG solutions with concentrations of 2% were prepared in deionized water by moderate stirring for 15 min. NaCl solutions (0.001M, 0.003M, and 0.005M) were also prepared in deionized water. The clay dispersions containing PEG were prepared by mixing different quantities of the initial dispersions and solutions in such proportions as to obtain the set mass fractions. LRD dispersions in the presence of NaCl were prepared by the addition of clay in NaCl solution. The clay concentration in the prepared dispersions did not exceed 0.5% to ensure that they have the Newtonian behavior required for correct viscometric measurements. Stable dispersions in the absence/presence of NaCl or PEG were sonicated for 1 h and prepared one day before the viscometric measurements.

Viscometric measurements were performed with an automatic LAUDA viscothermostat LMV 830 Instrument (Lauda-Königshofen, Germany) at 25 °C, using an Ubbelohde suspended-level viscometer (SCHOTT Geräte) with a 0.63 mm capillary diameter (I type viscometer). Clay dispersions in the presence of salt were diluted with NaCl solution inside the viscometer and kept at rest for approximately 5 min before each measurement. Dilution was performed up to the flow time of samples was very close to NaCl solution used as solvent. For the viscometric measurements of clay dispersions in the presence of PEG, no dilution was performed. Separate samples were prepared for each concentration, ensuring a fixed clay/polymer ratio. The time obtained is the average of five times to obtain the flow time measurements for each measurement with an accuracy of ± 0.05 s.

The intrinsic viscosity of the LRD dispersion in the absence/presence of salt and polymer was calculated with the Krieger–Dougherty (K–D) relationship (eq. 1). For PEG solutions, the Huggins equation was used:

$$\frac{\eta_r - 1}{c} = [\eta] + K_H \cdot [\eta]^2 \cdot c \quad (3)$$

where η_r and $[\eta]$ are the relative viscosity and the intrinsic viscosity, respectively, k_H represents the Huggins constant, and c is the PEG concentration.

The $[\eta]$ values, obtained by the Huggins method in mL/g (4.03 mL/g, 23.89 mL/g, and 53.99 mL/g for PEG400, PEG10000, and PEG35000, respectively), were converted into a dimensionless viscosity by multiplying them with the polymer density. This transformation was performed in order to directly compare these viscosities with the viscosities of the clay dispersion in the absence/presence of PEG, obtained using the K–D relationship (eq. 1). The PEG densities considered in all calculations were 1.128 g/mL for PEG400 and 1.2 g/mL for PEG10000 and PEG35000 (provided by the manufacturer).

Volume fractions of particles, ϕ , were calculated using the following relationship:

$$\phi = \frac{\rho_s \cdot \phi_w}{\phi_w \cdot (\rho_s - \rho_d) + \rho_d} \quad (4)$$

where ρ_s and ρ_d represent the densities of continuous phase (salt solution or water) and dispersed phase (clay or clay/PEG mixture), respectively. ϕ_w is the weight fraction of particles

The densities at 25 °C used in the calculations were as follows: water (0.99704 g/mL), 0.001M NaCl solution (0.99734 g/mL), 0.003M NaCl

solution (0.99742 g/mL), and 0.005M NaCl solution (0.99750 g/mL).²² The densities of the LRD/PEG solid mixture were determined theoretically based on the known densities of the individual components and their weight fractions:

$$\rho_{mix} = \frac{1}{\frac{w_{LRD}}{\rho_{LRD}} + \frac{w_{PEG}}{\rho_{PEG}}} \quad (5)$$

where ρ_{mix} is the density of the final mixture, ρ_{LRD} and ρ_{PEG} are the densities of LRD and PEG, respectively. w_{LRD} and w_{PEG} represent the weight fractions of LRD and PEG, respectively.

CONCLUSIONS

The study investigates the effect of NaCl and PEG on the flow behavior of LRD aqueous dispersions, with a focus on viscometric measurements. The findings reveal that NaCl concentration plays a significant role in organization of clay particles in the dispersion and so, on its viscosity.

Thereby, as NaCl concentration increases, the relative viscosity also increases due to the enhanced clay particle interactions as a result of the reduction of the electrostatic repulsion between particles, facilitating the formation of aggregates.

Furthermore, the effect of PEG, with varying molecular weights, on the viscometric parameters was analyzed. The intrinsic viscosity ($[\eta]$) and maximum packing fraction (ϕ_{max}) increase as the molecular weight of PEG increases, with higher molecular weight PEG having a more pronounced impact.

The addition of PEG with higher molecular weight enhances the dispersion stability and network formation by promoting the formation of bridges between LRD particles. At low molecular weights, however, PEG disrupts the particle–particle network, leading to lower viscosity values due to weaker particle interactions. Viscosity behavior deviates from the additive rule, indicating that PEG molecules influence the structure and interactions of the LRD particles in the dispersion. At low PEG concentrations, $[\eta]$ deviates from the additive rule, indicating that polymer adsorption onto particle surfaces weakens the LRD network, thereby reducing viscosity. This effect is more pronounced with higher molecular weight PEG due to its larger hydrodynamic size, which disrupts particle–particle interactions more effectively, weakening the network. At higher PEG concentrations, the viscosity

approaches the additive value, indicating a stabilized system where PEG and LRD act as independent components, contributing to the overall viscosity in a predictable manner. These insights are important for understanding how the molecular characteristics of additives like NaCl and PEG influence the flow properties and stability of LRD dispersions in industrial and scientific applications involving LRD-based systems. Future studies should focus on a more in-depth investigation of the effects of multivalent salts and other polymers on the rheological properties of aqueous LRD dispersions, particularly in terms of microstructural evolution, viscoelastic behavior, and long-term stability.

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