

Dispersion of Aqueous Al_2O_3 Suspensions with Electrolytes; Influence of the Counter Ion

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The electrolyte, $(\text{HO})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2\cdot\text{H}_2\text{O}$ (Tiron), disperses efficiently alumina powder in aqueous media and stable suspensions with 60 vol% solid loading can be prepared. The strong adsorption of this additive is mainly due to the ability of the molecule to form chelate rings with the particle surface but electrostatic interactions between the surface charge and the anionic dispersant strongly influence the amount of Tiron adsorbed. By using a cationic exchange route to substitute the counter ion which neutralizes the sulfonate groups, new molecules of dispersant have been prepared, either with mineral cations as Li^+ , Na^+ , NH_4^+ , or with organic cations as $\text{N}(\text{CH}_2(\text{CH}_2)_n)^+$ with $n=0, 1, 2, 3$. Adsorption and electrokinetic properties are not affected by the nature of the counter ion but organic counter ions lead to less viscous suspensions than Na^+ in particular when the number of carbon atoms of the aliphatic chain increases from 1 to 3.

Key words: Alumina suspension, Dispersion, Counter-ion

I. Introduction

To lead for a dense ceramic green body with good mechanical properties, processes such as tape casting or DCC (Direct Coagulation Casting) require dispersed colloidal suspensions with a high solid loading and a low viscosity. In particular, the quality of the ceramic products obtained by D.C.C. depends on the amplitude of the shrinkage which should be as low as possible when the suspension coagulates into the mold, and which depends directly on the concentration of solids in the starting suspension. In aqueous media, colloidal processing of ceramic powders is controlled by interparticle forces. In particular high repulsive potential produced at the particles surface improves the stability of colloidal suspensions. Organic additives, like dispersants, either synthetic polymers or electrolytes, can create these repulsive forces between particles. Several studies¹⁻²⁾ have shown that adsorbed polyelectrolyte develops charge onto the surface of particles, but the relatively thick layer of polymer around the particles prevents from obtaining very high concentrated slurries.³⁾ On the other hand, to carry out the DCC process, Graule and all.⁴⁾ dispersed the alumina powder in water by varying the pH of the suspension or by adding a citrate ion as dispersant. It was shown⁵⁻⁷⁾ that a small organic molecule used as dispersant is more efficient to prepare suspensions with high solid loadings in aqueous media. The aim of this work is to determine the main parameters which drive the stability of aqueous alumina suspensions when such small organic molecules are used.

The chemical structure of a dispersant should include functional groups which permit the chemisorption of the

molecule onto the particule surface. For alumina, this mechanism should be similar to that which governs the complexation of the aluminium ion in aqueous media. For example, an alcohol group in ortho position of a phenol or of benzoic acid is very efficient to complex metallic ions such as aluminium and should lead to a strong adsorption of the molecule onto the alumina surface.⁸⁻⁹⁾ Secondly, ionisable groups as carboxylates or sulfonates should complete this structure to develop surface charges. The structure of the 4,5 dihydroxy 1,3 benzene disulfonic acid, disodium salt monohydrate, $(\text{HO})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2\cdot\text{H}_2\text{O}$ (Tiron) fulfills the conditions to be an efficient dispersant of alumina and preliminary studies show its potentialities.¹⁰⁾ But a few studies concerning the nature of the counter ion which neutralizes the ionisable groups have been carried out. Nevertheless its size which depends on its chemical structure could influence the stability of colloidal suspensions. In this work, molecules of 4,5 dihydroxy 1,3 benzene disulfonic acid with either mineral cations as Li^+ , Na^+ and NH_4^+ or organic cations containing nitrogen as $\text{N}(\text{CH}_2(\text{CH}_2)_n)^+$ with $n=0, 1, 2, 3$ have been prepared by using a cationic exchange route. After chemical characterization, the influence of the nature of the counter ion has been examined on the adsorption, electrophoretic mobility and rheological behaviour of the suspensions.

II. Experimental Procedure

1. Starting materials

The powder used in this study was the AKP30 alumina (Sumitomo, Japan) with an average particle size of $0.40 \mu\text{m}$ (Sedigraph 5100, Micromeritics, U.S.A.) and a specific sur-

face area of 10 m².g⁻¹ once degassed at 300°C during 2h (N₂ BET, Micromeritics, U.S.A.). The cationic exchange resin (DOWEX 50WX2) and the chemical reagents used in this study are supplied by Aldrich.

2. Preparation and characterization of the molecules of dispersant

The molecules studied with a chemical structure based on the 4,5 dihydroxy 1,3 benzene disulfonic acid (HO)₂C₆H₂(SO₃H)₂ differ by the nature of the counter ion. They were prepared by a cationic exchange route. The following flow chart (Fig. 1) summarizes the different steps of the preparation. After each exchange between sodium and hydronium ions, the sodium content of the solution was measured by chemical analysis to ensure that complete exchange was performed. The resin was regenerated with a HCl solution after each use.

3. Adsorption

Slurries were prepared with 3 vol% solid loading, the solvent being an aqueous solution of NaCl (10⁻² mol.l⁻¹) used to fix the ionic strength. If necessary the pH was adjusted by using NaOH or HCl solutions. After 16 hours of slow agitation to reach chemical equilibrium, high speed centrifugation (25000 g) allowed to separate a supernatant in view of analysis. The quantity of the dispersant, the structure of which includes a benzene ring, contained in the supernatant was determined by using U.V. spectroscopy (λ= 290.6 nm).

4. Zeta potential experiments

Zeta potential values of the alumina particles in the slurries were measured using an Electrokinetic Sonic Ampli-

tude (ESA) measurement apparatus (Model ESA8000 Matec, Northborough, MA, USA). This technique and its operating principle have been described previously.¹¹ Measurements were carried out with slurries containing a 3.5 vol% solid loading. The ionic strength was fixed at 10⁻² mol.l⁻¹ with NaCl; this concentration of the background electrolyte implies a very low ESA signal. The data recorded with the acoustosizer correspond to the ultrasonic signal converted to a voltage (ESA). The ESA data being directly proportional to the electrophoretic mobility of the particles, the variation of the electrokinetic properties versus pH will be presented with ESA values as the Y axis.

5. Rheological measurements

A controlled stress rheometer (Carri-med CSL 100, England) with a cone/plate configuration was used for viscosity measurements in the flow mode. The curves corresponding to the decrease of the shear stress were modelled according to the Herschel-Bulkley's equation¹²:

$$\Gamma = \Gamma_0 + K(D)^n \quad (1)$$

where Γ is the applied stress (N.m⁻²), Γ_0 the yield stress (N.m⁻²), D the shear rate (s⁻¹), K a viscosity coefficient (Pa.s) and n the shear rate exponent.

III. Results and Discussion

1. Characterization of the dispersants

The results of chemical analysis carried out on the salt of tetrapropylammonium (TPA) and tetrabutylammonium (TBA) reported in the table 1 confirm that the process of synthesis used is adapted to change the counter ion of the

Table 1. Chemical Analysis of Salts of Tetrapropylammonium and of Tetrabutylammonium

Dispersant	Experimental values wt%(±0.4)			Theoretical values wt%		
	C	H	S	C	H	S
Salt of TPA	54.6	9.1	9.4	56.2	9.3	10.0
Salt of TBA	59.6	10.1	7.6	60.6	9.0	8.5

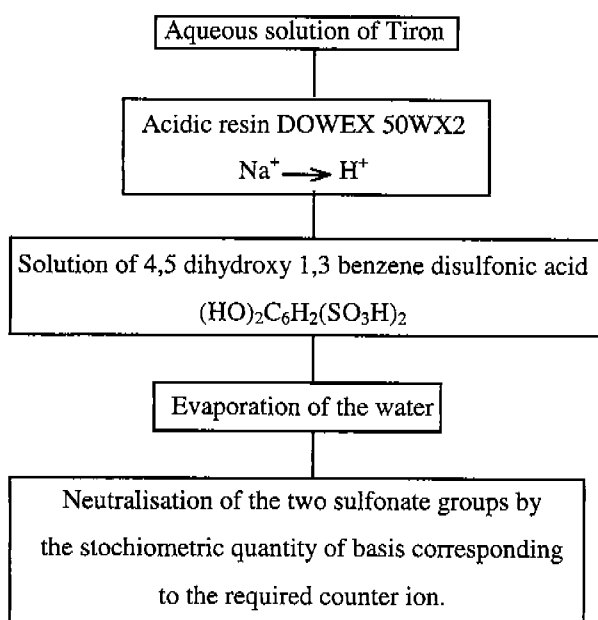


Fig. 1. Preparation of the molecules of dispersant.

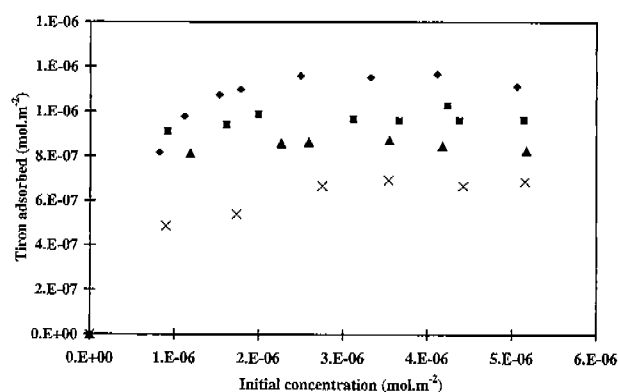


Fig. 2. Adsorption isotherms of Tiron at pH (◆) 5, (■) 7, (▲) 9, (×) 11.

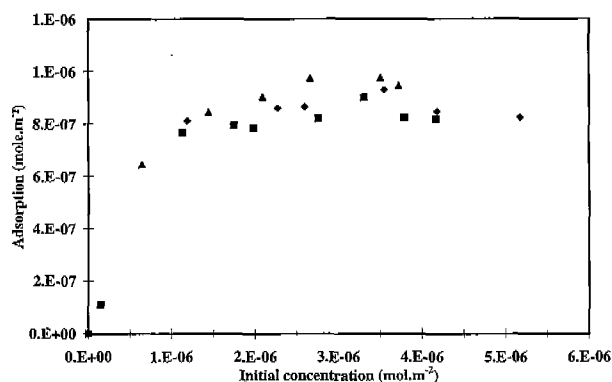


Fig. 3. Adsorption isotherms of (◆) tiron, (■) salt of tetraethylammonium, (▲) salt of tetrabutylammonium at pH 9.

anionic molecule. The salts of ammonium and tetramethylammonium contain one mole of water as does the sodium salt, while in other salts, no water was detected. The wavelength corresponding to the maximum of adsorption for the Tiron in the U.V. spectrum, $\lambda=290.6$ nm, does not vary when the counter ion is exchanged.

2. Adsorption

Adsorption isotherms relative to the Tiron established at pH 5, 7, 9 and 11 at 20°C are presented on Fig. 2. Tiron is strongly adsorbed onto the particles surface at neutral and acidic pH, but the value observed on the plateau at high value of added Tiron depends on the acidity of the suspensions. This maximum adsorbed amount of Tiron increases when the pH becomes more acidic (i.e. a maximum of 6.410^{-7} mol.m⁻² and of 11.210^{-7} mol.m⁻² is measured at pH 11 and at pH 5 respectively). This suggests that a basic medium does not appear favourable for Tiron adsorption onto alumina surface.

Fig. 3 represents the adsorption of the tetraethyl and tetrabutylammonium salts at pH 9 versus amount added. The results relative to the Tiron are plotted for comparison. A strong adsorption, similar to that of the sodium salt, occurs when the structure of the counter ion is based on an aliphatic carbon chain. The nature and the size of the counter ion do not influence the maximum value adsorbed on the plateau (i.e. 8.410^{-7} mol.m⁻²). Furthermore, adsorption experiments of the tetraethylammonium salt, carried out versus pH for a fixed quantity of dispersant of 1.310^{-6} mol.m⁻², indicate that this compound has a higher affinity for alumina surface at acidic pH (i.e. 9.710^{-7} mol.m⁻² at pH 4 and 5.810^{-7} mol.m⁻² at pH 10).

3. Electrophoretic mobility

Figs 4 and 5 depict the variation of ESA data (mPa.m.V⁻¹) versus pH for an alumina suspension prepared with (4b) and without (4a) Tiron and with the tested molecules of dispersant (5). Curve 4a shows that the ZPC of alumina is reached at pH 9. The ionisation of the hydroxyl surface groups respectively positively for pH<9 and negatively for

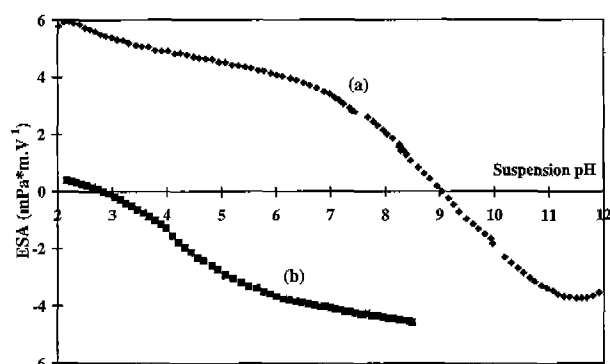


Fig. 4. ESA data of alumina suspensions with (◆, a) no addition of dispersant, with (■, b) 1.10^{-6} mol.m⁻² of Tiron.

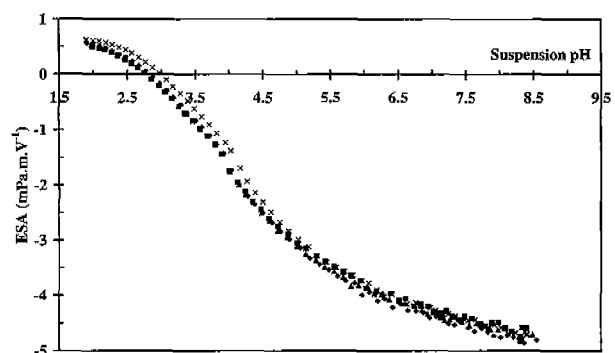


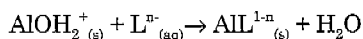
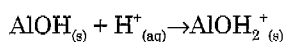
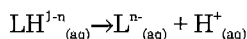
Fig. 5. ESA data of alumina suspensions with 1.10^{-6} mol.m⁻² of (■) Tiron, (◆) salt of lithium, (▲) salt of ammonium, (×) salt of tetraethylammonium.

pH>9 leads to a high surface charge. By creating a repulsive potential between the particles, the powder is deflocculated; but at pH 3 or pH 11.5, some solubility of the powder is expected and such suspensions become not stable with time.

Curve b was obtained after an addition of 1.10^{-6} mol.m⁻² of Tiron. As Tiron is a weak acid, the natural pH of an alumina suspension (3.5 vol%) shifts from 9 to 8.5. At this pH, the Tiron adsorbed onto the particle surface produces a highly negative surface charge which confers to this molecule the ability to disperse alumina powders without a great shift of the pH. As the pH becomes acidic, this negative charge decreases slowly in a first time to pH 5 and more rapidly from pH 5 to 3 which corresponds to an isoelectric point charge (IEP).

To be more comprehensive in Fig. 5, only the curves relative to the counter ions Na⁺, Li⁺, NH₄⁺ and N(C₂H₅)₄⁺ have been reported. The curves relative to the other counter ions studied are similar and superimposed. The nature of the counter ion of the dispersant does not influence the electrokinetic properties of the alumina suspensions. Curves are nearly identical, the negative charge developed by the dispersant has the same amplitude whatever the counter ion at the starting pH and the decrease of this charge varies in the same way as for Tiron leading to an IEP in the range of pH 2.5-3.

The adsorption of Tiron onto alumina particles can be explained by considering the ligand (L)-exchange model, a process involving the following multi-step reaction sequence.¹³⁾



By considering the chemical structure of Tiron, the sulfonate groups ionised in a very large range of pH provide a negative charge to the molecule. The affinity of Tiron for the oxide particles versus pH can be explained by the electrostatic interaction between the dispersant and the surface. When the surface charge of the oxide becomes positive (pH<9), the molecule of dispersant is electrostatically attracted and the affinity of Tiron for the surface increases with the density of positive surface charge. Besides, as the oxide surface becomes negative (pH>9) electrostatic repulsions occur and lead to a decreasing adsorption as pH increases. The ability of the molecule to form one or more chelate rings with the particle surface is favourable for the adsorption, but when ionised anionic groups complete the chemical structure, the electrostatic interactions between the dispersant and the surface control the affinity of the molecule for the oxide surface which depends on the value of the ZPC of the oxide.

As far as the nature of the counter ion is concerned, the electrokinetic properties of a dispersed alumina suspension are not affected by the chemical structure of the counter ion. ESA data (Fig. 5) confirm that whatever the cation the same molar concentration of the anion was chemisorbed onto the surface of alumina particles at a given pH. But by considering the curve relative to an alumina suspension stabilized with the dispersant, it is not consistent that in spite of a larger quantity of anion adsorbed at acidic pH's, the negative surface charge decreases. At pH 9, the surface of alumina particles is not saturated by the Tiron molecule, then exchange between the hydroxyl surface groups and the anion (cf ligand exchange model) are able to occur because hydroxyl groups remain free onto the surface. For example, for a density of 5 sites.nm⁻² of hydroxyl surface groups, at pH 9 the quantity of Tiron adsorbed, 8.410⁻⁷ mol.m⁻², represents only 10% of the available sites and the free groups should be considered in the variation of the surface charge versus pH. Then the total surface charge measured is the sum of a negative contribution due to the adsorbed Tiron and a positive contribution due to the protonation of the free hydroxyl groups. The positive contribution is equal to zero at pH 9 and increases as the pH becomes acidic (curve 4a) compensating the negative at the IEP.

4. Rheological behaviour

4a. Dispersant concentration

In order to determine the amount of dispersant leading to the best state of dispersion, suspensions containing 53.4

Table 2. Herschel-Bulkley's Parameters: Viscosity Coefficient K (Pa.s) and Shear Rate Exponent n, for Alumina Suspensions (53.4 vol%) Prepared with Different Amounts of Tiron

Tiron concentration (mol.m ⁻²)	K (Pa.s)(±0.02)	n(±0.02)
4.310 ⁻⁷	4.50	0.50
8.610 ⁻⁷	0.65	0.70
12.910 ⁻⁷	0.37	0.77
17.210 ⁻⁷	0.40	0.78
21.510 ⁻⁷	0.75	0.70
28.810 ⁻⁷	2.00	0.58

vol% alumina were prepared with different amounts of dispersant for each counter ion tested. The Table 2 summarizes the calculated parameters of the Herschel-Bulkley's equation (eqn 1) relative to the suspensions prepared with the Tiron. The solid concentration of 53.4 vol% imparts a shear thinning flow behaviour with a shear rate exponent lower than 1.

These results confirm that the molar concentration of Tiron used as dispersant strongly influences the rheological behaviour of the suspensions.¹¹⁾ The suspension prepared with an amount of 4.310⁻⁷ mol.m⁻² of Tiron exhibits the largest viscosity coefficient K. Further additions of Tiron up to 12.910⁻⁷ mol.m⁻² result in a large decrease of the viscosity coefficient to reach a minimum value corresponding to the largest value of the shear rate exponent n. According to adsorption isotherms (Fig. 1), for an added amount of 4.310⁻⁷ mol.m⁻² the surface should be not saturated by the dispersant. For a initial Tiron quantity of 12.910⁻⁷ mol.m⁻², which corresponds to the beginning of the plateau obtained at pH 9, and of 17.210⁻⁷ mol.m⁻² the rheological behaviour of the suspensions are similar (very close values of n and K). The quantity of Tiron which remains in the solvent is not large enough to increase the ionic strength significantly and to compress the diffuse electrical double layer. Nevertheless

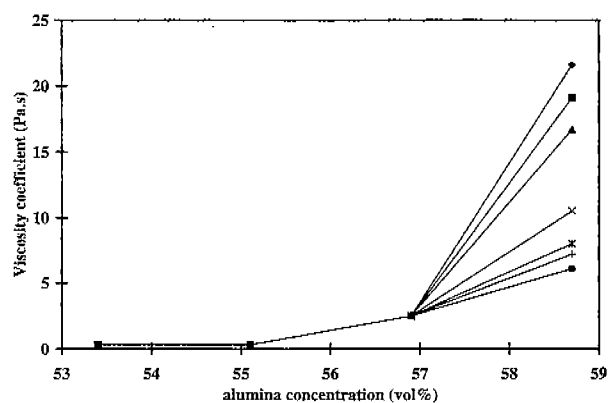


Fig. 6. Viscosity coefficient K (Pa.s) versus concentration of solid for alumina suspensions prepared with (◆) 1.610⁻⁶ mol.m⁻² of salt of Li⁺, with 1.2910⁻⁶ mol.m⁻² of salt of (■) NH₄⁺, (▲) Na⁺, (×) tetramethylammonium, (*) tetraethylammonium, (●) tetrapropylammonium, (+) tetrabutylammonium.

this phenomena occurs for larger additions of Tiron and leads to more viscous suspensions. For the following studies, the optimum amount of added Tiron was fixed at 12.910^{-7} mol·m⁻² corresponding to the minimum of viscosity. For the other counter ions tested, the minimum of viscosity was obtained for the same concentration of added electrolyte except for the lithium salt. For this cation, the best state of dispersion of the alumina suspension was reached for a greater quantity of 1610^{-7} mol·m⁻².

4b. Alumina concentration

Fig. 6 reports the evolution of the viscosity coefficient versus solid concentration for each counter ion. The Herschel-Bulkley's parameters are given in Table 3 for a 58.7 vol% alumina suspension prepared with the different molecules. The viscosity coefficients remain constant whatever the counter ion up to an alumina concentration of 55.1 vol% (Fig. 6). Considering the shear rate exponent obtained from the Herschel-Bulkley model, a solid concentration larger than 56.9 vol% imparts a high shear thinning flow behaviour of suspensions prepared with the molecules (for example with Tiron 56.9 vol% $n=0.63$, 58.7 vol% $n=0.47$). The influence of the chemical structure of the counter ion onto the rheological behaviour was observed for a solid loading larger than 56.9 vol%. The order of the cations which leads to decreasing viscosity coefficient is the following: $\text{Li}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{TMA}^+ < \text{TEA}^+$, $\text{TBA}^+ < \text{TPA}^+$. The lithium ion leads to a very viscous suspension and the counter ions whose structure is based on a nitrogen atom with aliphatic carbon chains improve the stability of the suspensions, in particular when the number of carbon increases from 1 to 3.

The stability of these alumina suspensions is mainly due to the high repulsive potential created by the adsorption of the anion. The adsorption measurements and the electrokinetic properties showed that as the anion is adsorbed in the same quantity, the repulsive potential, for all the molecules whatever the counter ion, is the same. The optimum quantity of dispersant leading to the best state of dispersion, which does not vary with the chemical structure of the counter ion, apart for the lithium, and which was determined for a higher concentration of alumina confirms that the nature of the counter ion does not influence the amount of anion adsorbed onto the alumina particles. A noticeable

influence of the nature of the counter ion on the rheological behaviour was observed for a very high concentration of particles (>56.9 vol%) when the separation distance between the particles becomes very small. The space between two particles is then occupied by the adsorbed anion with respective counter ion and structured water molecules. The ability of the counter ion to structure water molecules can interpret the rheological properties observed. Among the cations studied, Li^+ , Na^+ and NH_4^+ are considered as "structure maker" while these with an aliphatic carbon chain as "structure breaker." The viscosity of the thin film of water between the particles should be influenced by the chemical structure of the counter ion and then the viscosity of the suspension too.

The salt of tetrapropylammonium permits to prepare an aqueous alumina suspension with 59.7 vol% solid loading which possesses similar flow properties than one at 58.7 vol% prepared with Tiron.

IV. Conclusion

The electrokinetic properties of aqueous alumina suspension prepared with the molecule of Tiron as a dispersant, in which the sulfonate groups was neutralized with different counter ions and the adsorption of these dispersants are not affected by the nature of the cation. The influence of the counter ion onto the rheological properties becomes significant at high concentrations of solid (i.e. >56.9 vol%). Cations as TEA^+ or TPA^+ lead to less viscous suspensions than Na^+ or Li^+ . The use of organic cations instead of mineral ones could be better in the development of ceramic processes because the additive would be totally degraded and would not leave impurities in the final product after the debinding and sintering stages.,"

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Table 3. Herschel-Bulkley's Parameters: Viscosity Coefficient K (Pa.s) and Shear Rate Exponent n, for Alumina Suspensions (58.7 vol%) Prepared with the Optimum Amount of Dispersant for Each Counter ion

Counterion	K(Pa.s)(±0.2)	n(±0.02)
Li^+	21.6	0.35
NH_4^+	19.1	0.37
Na^+	16.7	0.41
TMA^+	10.5	0.47
TEA^+	8.0	0.52
TPA^+	6.1	0.55
TBA^+	7.2	0.53

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