

CHARACTERIZATION OF THE LINEAR VISCOELASTIC REGION IN SUSPENSIONS OF ZIRCONIUM OXIDE: COHESIVE ENERGY OBTAINED FROM THE CRITICAL PARAMETERS

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Received: 22.10.2003, Final version: 26.2.2004

ABSTRACT:

The linear viscoelastic regions (L.V.R.) of suspensions of zirconium oxide particles were determined and characterized through the so-called "critical parameters". These are the values of shear-stress and strain at the crossover between the linear and the non-linear viscoelastic responses. From these magnitudes, the cohesive energy between the particles is calculated as a function of volume fraction of solids and at different electrolyte concentrations. The oscillatory measurements were carried out using a constant-stress rheometer at a fixed frequency of 1 Hz and increasing shear-stress. The suspensions cover a volume fraction range between 3% - 25% with electrolyte (sodium chloride) concentrations of 10^{-1} M, 10^{-2} M, 10^{-3} M and 10^{-5} M. Two different kinds of ZrO_2 particles were used: commercially obtained -with no defined geometry- and spheres synthesized by us following the method described by Aiken, Hsu and Matijevic [1].

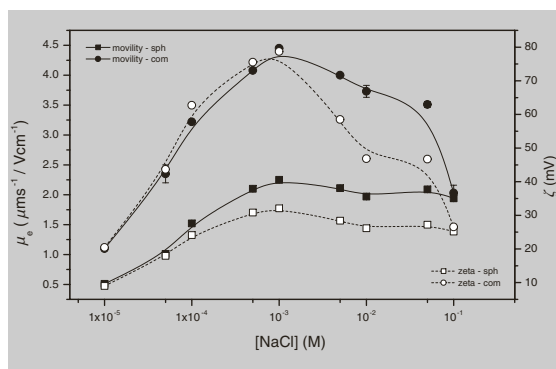
ZUSAMMENFASSUNG:

Der linear viskoelastische Bereich von Zirkondioxid Suspensionen wurde mittels einiger sogenannter "kritischen Parameter" bestimmt und charakterisiert. Dies sind die Werte der Scherrate und Deformation beim Übergang von den linearen zu den nicht-linear viskoelastischen Antwortfunktionen. Aus diesen Größen wird die Kohäsionsenergie zwischen den Teilchen als Funktion des Volumenanteils an Feststoff und bei verschiedenen Elektrolytkonzentration berechnet. Die Oszillationsmessungen wurden mit Hilfe eines schubspannungsgesteuerten Rheometers durchgeführt wobei eine feste Frequenz von 1 Hz und eine ansteigende Schubspannung gewählt wurden. Die Suspensionen umfassen einen Feststoffanteil zwischen 3 und 25% mit Elektrolytkonzentrationen (Natriumchlorid) von 10^{-1} , 10^{-2} , 10^{-3} und 10^{-5} M. Zwei Arten von Zirkondioxidteilchen wurden benutzt: kommerziell verfügbare Teilchen mit undefinierter Geometrie und Kugeln, welche von uns nach der Methode von Aiken, Hsu und Matijevic synthetisiert wurden.

RÉSUMÉ:

Les régimes viscoélastiques linéaires (L.V.R.) de suspensions de particules d'oxyde de zirconium ont été déterminés et caractérisés à travers les dénommés "paramètres critiques". Ceux-ci sont les valeurs des contrainte et déformation de cisaillement à l'intersection entre les réponses viscoélastiques linéaires et non linéaires. A partir de ces grandeurs, l'énergie cohésive entre les particules est calculée en fonction de la fraction volumique des solides et à différentes concentrations en électrolytes. Les mesures oscillatoires ont été entreprises à l'aide d'un rhéomètre à contrainte constante à une fréquence fixe de 1 Hz et en accroissant la contrainte de cisaillement. Les suspensions couvrent une gamme de fractions volumiques entre 3 et 25% avec des concentrations en électrolytes (chlorure de sodium) de 10^{-1} , 10^{-2} , 10^{-3} et 10^{-5} M. Deux types différents de particules de ZrO_2 ont été utilisés: de source commerciale, ne possédant pas de géométrie définie, et des sphères synthétisées par nos soins en suivant la méthode décrite par Aiken, Hsu et Matijevic [1].

KEY WORDS: zirconia, viscoelasticity, critical parameters



es until it reaches a maximum at $[\text{NaCl}] = 10^{-3} \text{ M}$; after this point, ζ decreases. This behavior is, as expected, the same for both kinds of Zr_2O (the spheres are bigger than the commercial particles and so, they move slower under the application of the electric field, leading to smaller values of ζ). The electrokinetic potential governs the electrical interaction between the particles and so, its dependence on the ionic strength (Fig. 7) implies that the electrostatic repulsion between the particles should follow the same trend, having a maximum at $[\text{NaCl}] = 10^{-3} \text{ M}$.

The cohesive energy has a behavior respect to the electrolyte concentration in agreement with the behavior of the electrokinetic potential: as the surface charge on the particles increases, the electrostatic repulsion between the particles increases, and consequently, the energy necessary for keeping them linked in the flocculated state is higher (Fig. 6).

In the other hand, the decreasing value of ζ for ionic strengths higher than 1 mM in NaCl leads to a monotonic decrease of E_{coh} -at each volume fraction of solid- which values follows the sequence $10^{-3} \text{ M} > 10^{-2} \text{ M} > 10^{-1} \text{ M}$. In this case, the reduction of the repulsive interaction between particles demands less energy for aggregate them, as observed in Fig. 6.

CONCLUSION

The shear-stress regions of linear viscoelasticity of suspensions of zirconium oxide were determined and characterized as a function of volume fraction of solid in the suspensions as well as the presence of sodium chloride as electrolyte. These linear viscoelastic regions (L.V.R.) have been characterized throughout the mean value of the plateau of elastic modulus, and the so-called "critical parameters" which are the limiting values of shear-stress and strain between the linear and non-linear behavior.

It was observed that the structure in the suspensions depends mainly on the amount of solid content, being more and more compact as the volume fraction increases. This packing effect has been quantitatively characterized through a power law scaling of the elastic mod-

ulus, which in addition let us to classify our suspensions as flocculated systems. The electrolyte concentration has a significant impact on the developing of the three dimensional structuring of the particles.

From the knowledge of the critical parameters it was possible to determine the cohesive energy necessary for aggregating the particles in their packed structure. Experiments showed a linear relationship between the cohesive energy and the volume fraction of solids. The dependence of the cohesive energy on the ionic strength was correlated to the electrical interaction between the particles, which is governed by the electrokinetic potential. It was found that the trend followed by the ζ potential is coupled by the corresponding behavior of the cohesive energy at each volume fraction: increasing energy for maintain the flocculation up to $[\text{NaCl}] = 10^{-3} \text{ M}$ and a decreasing for the higher ionic strengths.

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Figure 7: Electrophoretic mobility (solid symbols) and zeta potential (open symbols) -calculated using the model of O'Brien and White- of commercial and synthesized zirconia particles as a function of $[\text{NaCl}]$.

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