Electrokinetic studies of colloidal silica particles dispersed in non-aqueous media in the presence of a nonionic surfactant, dodecylhexaethylene glycol monoether ($C_{12}E_6$)

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ABSTRACT

The change in charge on the addition of $C_{12}E_6$, acid (terephthalic acid) and salt (KCl) was studied using measurements of electrophoretic mobility and electrokinetic sonic amplitude (ESA). Electrophoretic mobilities were measured using conventional electrophoresis from a Penkem 3000 system. ESA measurements were made using a Matec, an electro acoustic technique. Zeta potentials of the order of -30 to -50 mV were obtained. This implies that the electrostatic contribution to stability cannot be neglected for non-aqueous systems of intermediate polarity. The surfactant showed very insignificant electrostatic stabilisation. $C_{12}E_6$ slightly increased the zeta potential at low levels. This is due to ionization of the silica particles on adsorption of the polar head group of the surfactant molecule. The surfactant, $C_{12}E_6$, reduced the zeta potential at high levels (above saturation of the silica surface) probably due to the shift in the shear (Stern) plane. Stabilisation of the particles is therefore by both electrostatic means and steric means (in the presence of surfactant). The thickness of the adsorbed layer was estimated to 8 nm indicative of globular aggregation. Water addition showed a constant zeta potential at low levels (<2%, v/v) and an increase at higher levels (>2%, v/v). The acid gave an isoelectric point of about pH $\sim$4 and KCl additions gave a critical coagulation concentration of about 0.02 mol/dm^3 ($\zeta \sim 30$ mV). Dodecane displayed a positive charge for the particles at low added concentrations of water (<0.1%) and reversed their charge at higher levels. Charging of silica particles in aprotic organic media of low donicity is explained in terms of electron and proton transfer between the liquid media and silica particles.

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1. Introduction

Charging of surfaces in non-aqueous media is a common phenomenon and insufficient charging is not the general reason for the usually small electrostatic repulsion in media with low dielectric constant, ε. In fact, because of the low double layer capacitance, only a few charges are needed to obtain surface potentials that, in aqueous media, are high enough to ensure electrostatic stabilisation of pairs of particles [1–2]. Such high potentials are well documented [2–5]. Values between 50–100 mV are common and rarely values >150 mV are reported [6–11]. In media of low dielectric constant the differences between surface potential, ψ^o and zeta potentials, ζ, are, contrary to those in aqueous systems, small and $\psi^o \approx \zeta$. To obtain an electrostatic repulsive force which is sufficiently strong in media with low values of ε, it is not sufficient to have a high ψ^o. In addition, a large gradient of potential $-d\psi/dx$ is required, where 'x' is the distance from the surface. If this condition is not met, the repulsive force between interacting particles is too low [1].

There are many dispersions of industrial importance (ranging from inks, paints, electrorheological fluids, and precursors to fire retardancy products and ceramics) consisting of inorganic particles dispersed in media of polarity lying between that of water and that of pure hydrocarbon that have been widely studied. Some of these systems have been shown to reverse the sign of their charge with addition of water and, in general, the charging mechanism is the result of specific chemical interactions between solution species and those attached to the surface. The acid/base character of the underlying surface, adsorbed species and the species in solution all play a part in determining the sign and the magnitude of the surface charge and hence the dispersion stability and subsequent handling properties.

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In this study silica particles were investigated. Silica particles were prepared in monodisperse form using the Stober technique and some were supplied as commercial products. The media that was investigated is monoethylene glycol (MEG). Glycols have always been of great industrial importance, especially in the polymer industry. For example, the production of polyethylene terephthalate, PET, uses MEG. The choice of glycols offers great latitude in the design of polymer backbones. They offer varied structural properties to polymers such as crystallinity, chemical resistance, surface cure, fire retardancy, low viscosity, heat stability and so on. The addition of fillers to these polymer melts has also been widely used to improve the functionality of a variety of polymer products. Polyester production is, however, accompanied by side products such as water, methanol and acids which can lead to polymer degradation and filler aggregation. The stability of these systems has not been widely studied. Hence the above particles and liquid media were chosen as a model non-aqueous colloidal system for this work.

A variety of stabilisers are used to maintain the stability of inorganic suspensions in these intermediate polarity media. They range from inorganic materials such as potassium tripolyphosphate, through polyelectrolytes such as sodium polyacrylate to nonionic glycol surfactants typified by dodecyl hexaethylene glycol monoether, $C_{12}E_6$. The latter material and its effect on the electrical double layer has been investigated in other interfaces, i.e. at the mercury/solution interface by Watanabe [10], at the polystyrene/solution interface by Partridge [11] and the AgI/solution interface by Ottewill and Walker [12]. $C_{12}E_6$ has not so far been investigated at the silica/glycol interface.

The experimental programme was based on studying the charge behaviour and adsorption isotherms on the additions of small quantities of soluble species of varying acid/base behaviour such as water and terephthalic acid. A combination of conventional electrophoresis and acoustic methods enabled the study of these effects in highly viscous glycol systems. The study also includes dispersions of silica in other organic media with donicities ranging from 0 to 30 (0–30 kJ mol^{-1}).

1.1. Microelectrophoresis

Microelectrophoresis was used to determine the electrophoretic mobility required to calculate the zeta potential, ζ, for the silica particles in various non-aqueous media reported in this work. The measurements were made in a glass cylindrical cell (3 cm long, 1 mm wide) with palladium electrodes using a Laser Model 3000 Penkem System. This instrument utilizes a Doppler-shift type technique and analyses the motion of many particles simultaneously by a Fourier transform of the multiple sensings. It also uses a helium-neon laser which illuminates only particles at the focal plane of a computer-controlled microscope system. This mobility was then correlated to zeta potential using the theory of O'Brien and White; and from that of Henry [1]. In the Henry's treatment the mobility is given by Eq. (1):

$$\mu_E = \frac{2\varepsilon_r\varepsilon_o\zeta}{3\eta}f(\kappa a) \tag{1}$$

where η the solvent viscosity and the correction for retardation effects is given by Eq. (2):

$$f(\kappa a) = \frac{3}{2} - \frac{9}{2\kappa a} + \frac{75}{2\kappa^2 a^2} - \frac{330}{\kappa^2 a^2} \tag{2}$$

1.2. Electroacoustics

Classical DC microelectrophoresis is not effective for examining high volume fraction dispersions with high conductivities and vis-

cosities as some of those investigated here. The Matec apparatus provides two ways of obtaining mobilities from which zeta potentials can be calculated. These are: the electrokinetic sonic amplitude (ESA), and the ultrasonic vibration potential (UVP). When an alternating field is applied to a colloidal dispersion the particles will move in the electric field due to their net zeta potential. If there is no density difference between the particles and the continuous liquid phase, the particles will follow the oscillatory motion of the liquid due to its compression. No difference in the velocity magnitude or in the phase angle will appear. If there is a density difference between the particles and the medium, this oscillatory motion will result in momentum transfer from the particles to the liquid and a development of an electro acoustic wave (sound wave). This is known as the ESA in units of Pa per volt per meter. This wave creates pressure at the buffer rod. The piezo electric crystal in the buffer than generates an electric current (the signal) (see Fig. 5), this effect was first suggested by Pohl and was proven by Oja, Peterson and Cannon [13–19]. Taking Onsanger type linear expressions for the particle velocity and average current in an alternating field as functions of the pressure gradient and field strength, O'Brien [17–23] found the following expression for the acoustic pressure magnitude, P_o:

$$P_o = \phi\Delta\rho c E_o\mu(\omega) \tag{3}$$

where ϕ is the volume fraction of the particles, E_o is the static electric field, c is the concentration of the particles, $\mu(\omega)$ is the dynamic electrophoretic mobility and $\Delta\rho$ is the density difference between the disperse and the continuous media.

The conversion of ESA to zeta potential is done through the empirical relationship in the limit of low volume fraction:

$$ESA = c\,\rho\,\phi\,\mu(\omega)\,G(\omega,\phi) = S\gamma \tag{4}$$

where c is the speed of sound in the liquid, $\mu(\omega)$ is the dynamic mobility, γ is the instrumental constant determined by calibration, S is the observed signal and $G(\omega,\phi)$ is the geometric coupling constant. The geometric coupling constant is sometimes referred to as the acoustic resonance gain factor which describes the coupling between the suspension and the piezoelectric transducer. It depends on the elasticity of the buffer and can be evaluated theoretically. The factor, $ESA/G(\omega,\phi)$, is independent of the sensor geometry, but depends on properties of the colloid in the limit of ϕ due to variation of acoustic properties with ϕ. ESA measurements were therefore made inside the linear region. The ratio $|\mu(\omega)/\mu(0)|$ is calculated from the theories of Babchin et al. (BCS), [17] the theory of O'Brien (OB) [19], and the theory of Sawatzky et al. (SB) [17]. The electrophoretic mobility is represented by $\mu(0)$.

The O'Brien result, valid for $\kappa a > 1$ may be written [18]

$$\left|\frac{\mu(\omega)}{\mu(0)}\right| = \left|\left[\frac{1 - (i/9)\alpha(3 + 2\Delta\rho/\rho)^{1/2^{-1}}}{(1 + (1+i)(\alpha/2))}\right]\right| \tag{5}$$

where $\alpha = \omega a^2/\upsilon$, a is the particle radius, and υ is the kinematic viscosity (η/ρ, where η and ρ are the viscosity and density, respectively, of the continuous phase). The corresponding result of Babchin et al. (BCS) [17] is written

$$\left|\frac{\mu(\omega)}{\mu(0)}\right| = \frac{6\pi\eta}{\sqrt{\left(6\pi\eta\overline{R}\right)^2 + \left(4/3\pi\omega\rho_{eff}R^2\right)^2}} \tag{6}$$

where $\overline{R} = 1 + \frac{\alpha}{\delta}$, $\delta = (2\upsilon/\omega)^{1/2}$,

$$\rho_{eff} = \rho_o + \frac{9}{R\sqrt{\eta\rho/8\omega}} + \frac{\rho}{2} \tag{7}$$

and ρ_o is the particle density. A more recent theory, due to Sawatzky et al. (SB), develops a frequency dependent Henry function which