The Temperature Dependence of the Viscosity of Suspensions of Polystyrene Latices in LiCl Solutions

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The viscosities of suspensions of polystyrene particles in aqueous LiCl solutions (about $3.5 \cdot 10^{-4}$ M) at temperatures from 0 to 60 °C were measured and fitted to relations of the form $\eta = \eta_0(1 + K_1\Phi + K_2\Phi^2)$, where Φ is the volume fraction of the particles.

In contradiction to existing theories the coefficients K_1 and K_2 were found to be temperature dependent.

It is well known that aqueous suspensions of spherical colloidal particles exhibit a pronounced viscosity increase when the electrolyte content in the aqueous phase is reduced. This effect, existing even in extremely diluted suspensions (first electroviscous effect), is due to a distorsion, under a gradient of shear, of the electrical double layer surrounding the dispersed particles. Theoretical treatments of this effect have been proposed by several authors [1], [2], [3], and especially Stone-Masui and Watillon [4] have reported extensive viscosity measurements of polystyrene suspensions at a fixed temperature of 25 °C.

Recently we have observed that the dielectric properties of polystyrene suspensions at microwave frequencies are affected by the ionic species and ionic strength of the continuous medium and show thermal anomalies [5]. As the parameters which influence the dielectric properties are the same as those responsible for the electroviscous effects, in the present study the viscosity of colloidal suspensions of polystyrene particles in LiCl solutions was measured in the temperature range from 0 to 60 °C.

A suspended level Ubbelohde type viscometer with an average shear rate of about 650 sec^{-1} was employed. Five efflux times were measured for each volume concentration and temperature. The mean deviation did not excede 0.02%.

The average particle diameter was 0.091 μm, standard deviation 0.0053 μm. The fractional volumes of the dispersed phase were kept low (from 0.5 to 1.5%) to avoid secondary electroviscous effects. Volume concentrations were determined from dry weights, using a density of 1.052 g/ml for polystyrene.

In order to control the salt contents of the suspensions and to obtain isoionic samples, an ultrafiltration cell Amicon mod. 12 with membrane XM 100 was used. The polystyrene latices were first dialyzed at a temperature of 60 °C against deionized water ($\sigma < 10^{-6}$ Ω^{-1} · cm^{-1}) to remove all free and adsorbed electrolytes, essentially leaving only surface charges. The ionic conductivity was then changed to the desired value ($3.35 10^{-5}$ Ω^{-1} · cm^{-1} at 25 °C) by adding LiCl solution and measured as a function of temperature both before and after each investigation to ensure that contamination did not take place.

The temperature was defined within 0.01 °C.

The surface charge density was calculated from the electrophoretic mobilities at the ionic strengths corresponding to those used in the viscosity measurements. The relation between the charge on the particle and the ζ-potential at the plane of shear, using the simplified method given by Stigter and Mysels [6], yielded a surface charge density of about 750 statcoulomb/cm^2, largely independent of temperature and ionic strength.

Viscosity data are usually analyzed on the basis of equations of the form

$$\eta = \eta_0(1 + K_1\Phi + K_2\Phi^2),$$

where η_0 is the viscosity of the continuous medium and Φ the volume fraction of the particles.

The coefficients K_1 and K_2 (first and second order electroviscous coefficients, respectively) are obtained from the intercept and slope of ($\eta/\eta_0 -$
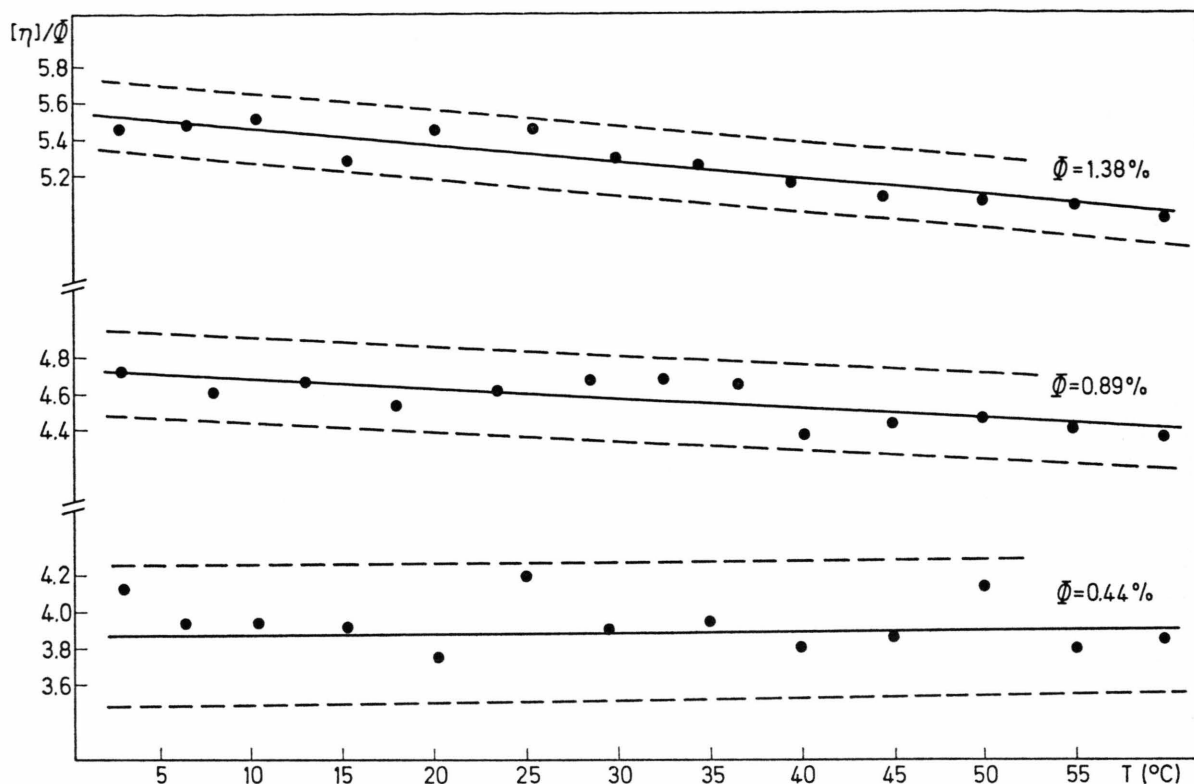
Fig. 1. $[\eta]/\Phi$ vs. temperature for polystyrene particles in LiCl electrolyte solution. $[\eta] = \eta/\eta_0 - 1$, $\Phi = $ fractional volume of dispersed phase. Specific conductivity $\sigma_m = 3.35 \cdot 10^{-5} \, \Omega^{-1} \, cm^{-1}$ at 25 °C. Particle diameter 0.091 μm. The solid lines represent least-squares fits of the data to straight lines and the dashed lines define a confidence level of 95%.

1)$/\Phi$ vs. Φ plots. Figure 1 shows $[\eta]/\Phi = (\eta/\eta_0 - 1)/\Phi$ as a function of temperature for various volume fractions of the particles, and the solid lines represent a least-squares fit of the data to the equation

$$[\eta]/\Phi = \alpha + \beta T . \tag{1}$$

The coefficients K_1 and K_2 for each temperature, were determined by a least-squares fit to the equation $[\eta]/\Phi = K_1 + K_2 \Phi$. This procedure gave the temperature dependence of the electroviscous coefficients with sufficiently small errors, as shown in Figs. 2 and 3 (curves a).

For colloidal suspensions of undeformable spherical charged particles, Booth [2] derived the expression

$$K_1 = 2.5 \left\{ 1 + q^* \left(\frac{Z e^2}{\in a K_B T} \right)^2 F(K_D, a) \right\}, \tag{2}$$

where $\in$ is the static dielectric constant of the continuous medium, a the particle radius, K_B the
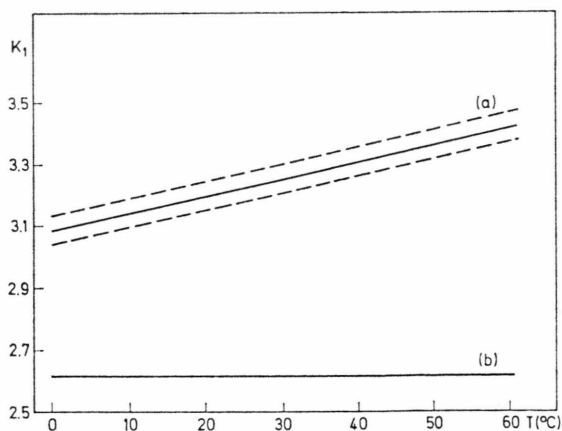

Fig. 2. First-order electroviscous coefficient K_1 vs. temperature.
Curve a) values derived from experimental data with statistical error margins.
Curve b) values calculated from Equation (2).

Boltzmann constant, T the absolute temperature, Ze the charge of the electrokinetic unit, $1/K_D$ the
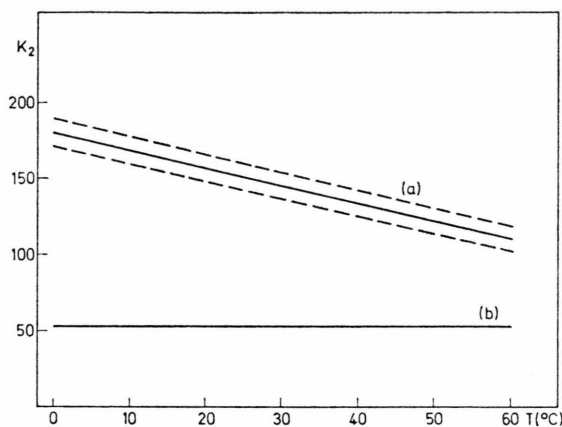
Fig. 3. Second-order electroviscous coefficient K_2 vs. temperature.
Curve a) values derived from experimental data with statistical error margins.
Curve b) values calculated from Equation (3).

Debye-Hückel double layer thickness, $F(K_D a)$ and $q*$ functions given by Booth in [2].

The second order electroviscous coefficient K_2 has been treated by Chan, Blachford, and Goring [3] on the basis of a model taking into account a particular collision process between the charged particles.

In this theory, the coefficient K_2 is given by

$$K_2 = 0.18 [K_0]^2 \left(\frac{a + \delta_c}{a} \right)^5, \qquad (3)$$

where $[K_0]$ is the Einstein coefficient and δ_c is the collision distance evaluated by equilibrating the electrostatic repulsive force and the hydrodynamic compressive force.

The coefficient K_1 calculated from (2) as a function of temperature is shown in Fig. 2 (curve b). As can be seen, the Booth theory predicts values independent of temperature and lower than those derived from the experimental data (curve a).

The coefficient K_2 as a function of temperature, calculated from (3) is shown in Fig. 3 (curve b). Also in this case, the calculated values of K_2 are largely independent of temperature.

The discrepancy between the calculated and measured absolute values of K_1 and K_2 may be meaningless owing to the approximations involved in the determination of the surface charge density from electrophoretic mobilities and the temperature dependence of the ζ-potential from the Debye-Hückel theory. However the temperature dependences of K_1 and K_2 are certainly significant.

In this connection it must be mentioned that in the models the particles are assumed to exhibit no Brownian motion. This assumption seems to be unrealistic for the sample under investigation, and perhaps the effect of temperature on the Brownian motion in shear flow may be the reason for the striking temperature dependence of K_2.

Acknowledgement

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