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Electrokinetics of Polystyrene Latices: The Role of the Hydrophobic Surface

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Experimental data from electrophoretic mobility, conductivity and dielectric response measurements on polystyrene latices and colloidal alkane particles are presented. Interpretation of the data using the exact numerical solution of O'Brien and White (*J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 1607) and De Lacey and White (*J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 2001) does not yield single ζ potentials for the different measurements on the same suspensions. A model is proposed to explain the data in terms of the classical electrokinetic model combined with a spatially varying entropic perturbation in the ion distributions in the interfacial region owing to the presence of destructured water.

Publication of the exact numerical solutions for the mobility/conductivity[1] and the dielectric response[2] problems in colloidal electrokinetics has stimulated much experimental interest.[3–10] Those interested in the physics of electrified interfaces have a readily available interpretation of electrokinetic phenomena based on a continuum model. It is then obvious that a reasonable test of theory is to conduct different electrokinetic measurements on the same suspensions and compare the interpreted ζ potentials.

The fortunate coincidence of the ready availability of the exact numerical solution of the theory with the development of polystyrene latices as model colloids[11,12] has armed the experimentalist with the appropriate tools to test the physical assumptions of the continuum model. Unfortunately, many attempts to vindicate or verify the theory using polystyrene latices have exposed them as being non-ideal electrokinetic systems.[6–8] In fact, agreement has been obtained in isolated cases, but in view of the evidence for artifacts in the experiments, one is forced to question the general validity of such data.[8]

The first significant study was that by Stone-Masui and Watillon who attempted to measure the low-frequency conductivity and mobility.[13] Concordance, or lack thereof, between the ζ potentials from both measurements was used to assess the theory. Unfortunately, their method of controlling the supporting electrolyte concentration in the conductivity measurement does not allow the data to interpreted unambiguously. More recently Zukoski and Saville[4] and Dunstan and White[14,15] have attempted the same experimental test of the theory. In both sets of work it was found that the concentration of ions in the suspension depends on the particle volume fraction. This violates one of the conditions of the theory, namely that the particles are isolated in a sea of infinite electrolyte of known concentration. The conductance increment due to the particles is obscured by the changes in the supporting electrolyte with volume fraction. Hence a straightforward test of theory is not possible from the latex data as the true equilibrium bulk electrolyte concentration is not known. The change in the supporting electrolyte concentration with particle volume fraction has been termed the suspension effect and has been discussed comprehensively by Chernoberzshskii, although no complete physical reason for its presence is presented in this work.[16] Co-ion exclusion from the electrical double layers was postulated elsewhere as the reason for the observed behaviour.[17] The contribution to the conductance increment of the excluded co-ions (and counterions) may be estimated from the mobility measured ζ potential and used to evaluate the co-ion contribution. Strictly, an iterative method should be used as κ, the reciprocal Debye length, is changed by the co-ion exclusion. The idea of co-ion exclusion was vindicated in a study on micelles where the total ion concentrations were known.[18] Convincing evidence that this was the only effect present in the latex suspensions was not obtained, however, as co-ion exclusion alone did not account for the observed conductance increments in prior studies.[14,15] The idea of co-ion exclusion derives from repulsion of the co-ions from the diffuse double layer. In order to obtain charge neutrality outside the double layer, the same number of counterions must also be excluded. The presence of the particles then causes perturbation in the electrolyte beyond its classical double layer. A recent study of the electrophoretic mobility of latices at low electrolyte concentration and volume fractions shows the presence of significant interactions in latex suspensions at interparticle spacings which were previously thought to be non-interacting, *i.e. ca.* $10\kappa^{-1}$.[19] These data indicate that the particles do interact at interparticle spacings which, according to classical ideas, should be non-interacting.

Since the low-frequency conductance data were still not in agreement, work was begun on dielectric response measurements. The advantage of these measurements is obvious in that they are made over a frequency range and should yield information about the spatial distribution of the ions around the particles.[2] Unfortunately, the interpretation of the data requires knowledge of the low-frequency conductance values. The anomalous low-frequency conductances have been, to a certain extent, ignored by workers in this area. Surface conductance was, however, introduced to explain both the anomalous data thus obtained[20] and also observed mobility maxima.[21] While this rationale explains certain aspects of the data it is not a comprehensive description as it fails to account for the volume fraction dependence of the supporting electrolyte concentration,[4,14,15] mass balance measurements reported herein, interaction effects,[19] the alkane mobilities[22] and the dispersion frequencies observed in the dielectric response measurements in this study.

The essential experimental anomalies are as follows: (i) the existence of maxima in the electrophoretic mobility as a function of electrolyte concentration, (ii) the evaluation of the ζ potentials from the various measurements on the same suspensions yield different values for ζ and (iii) perturbations in the electrolyte due to the particles.

In view of the above history, the comprehensive and exacting experimental study reported herein was conducted. Electrophoretic mobilities, low-frequency conductivities, dielectric response and mass balance measurements have been con-

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ducted on a single batch of polystyrene latices. Measurements have been made on both normal (raw) and heat-treated latices.

Consideration of the prior work and the data presented here has enabled a model to be developed which explains all the observed behaviour in terms of the hydrophobic surface playing a crucial role in determining the ion distributions in the interfacial region.

Experimental

Materials and Techniques

Doubly distilled water from a $KMnO_4$–KOH first stage, equilibrated with atmospheric CO_2 in a Pyrex vessel, was used in these experiments (pH = 5.8, conductivity = 0.9 μS cm^{-1}, surface tension = 72.6 mN m^{-1}). Fluka Puriss KCl was used after recrystallization and baking. Latex particles (0.30 μm diameter, 1.2 μC cm^{-2} charge density, sulfate surface groups from Interfacial Dynamics Corporation) were cleaned extensively, by *ca.* 50 centrifugation–redispersions (with sonication) in doubly distilled water using Teflon centrifuge tubes, until the latex exhibited constant conductivity and surface tension (the values of the distilled water). Then two types of sample were prepared. Heat treatment was performed by diluting the suspension to a volume fraction, ϕ, of 0.005 in 10^{-3} mol dm^{-3} KCl and heating to 120° for 12 h. These latices were then allowed to cool and extensively cleaned again.

For samples on which conductance and dielectric spectra were to be measured, the cleaned sample in water was centrifuged in the suspending electrolyte until the supernatant was the same composition as the electrolyte. This usually took another eight centrifugation–redispersion cycles. Using this method, a stock solution of volume fraction of *ca.* 0.05 was prepared. This stock solution was then diluted with the electrolyte to a series of volume fractions, by mass, at which the measurements were made. The volume fraction of the stock was determined by drying to constant mass.

Mass Balance Measurements

A stock solution of the particles in water was prepared as above. Measured aliquots were delivered to a number of centrifuge tubes. Electrolyte at a range of concentrations was then added to the particles to dilute the suspension to a final volume fraction of 0.01 in a volume of 35.0 cm^{-3}. These were then centrifuged and the supernatant conductivity measured. The electrolyte concentration of the supernatant was then calculated from the measured conductivity using an iterative program based on the Fuoss–Onsager equation. The predicted concentration from the dilution of the electrolyte was also calculated. The difference between these values is the excluded electrolyte concentration. This experiment was also conducted at a series of volume fractions up to 0.05 in 1.0×10^{-3} mol dm^{-3} KCl. Linearity in the excluded electrolyte concentration was observed in this experiment.

Mobility Measurements

Mobilities were measured in a Coulter Delsa 440 laser–Doppler electrophoresis apparatus by measurement of the mobility at both stationary layers. Agreement between the values obtained at both stationary layers was to within ± 0.2 μm cm s^{-1} V.

Mobility *vs.* electrolyte concentration measurements were performed by taking a dilute stock solution in water and adding small aliquots of concentrated electrolyte to increase the electrolyte concentration. In this manner, the same particles and approximate volume fraction were measured over the range of electrolyte concentrations. Each solution was equilibrated for 10 min at the new concentration before the mobility measurement was conducted.

Dielectric Response Measurements

Dielectric response measurements were conducted using a four-electrode system which has been described previously.[6] The reported spectra are normalized by the volume fractions at which the measurements were made. The data are plotted as $(\varepsilon' - \varepsilon_r)/\phi$ and ε''/ϕ for the real and imaginary components of the dielectric response, respectively. Here ε' is the real part of the dielectric response, ε_r the reference value at 500 Hz and ε'' the dielectric loss with ϕ the volume fraction. Conductivity measurements were made using the dielectric cell source electrodes joined to an Altex conductivity bridge at 1 kHz, 25.0°, cell constant, $C_c = 0.309$ cm.

The experimental difficulties in obtaining the data should not be underestimated. One of the main concerns when conducting the dielectric response measurements is electrode polarization. The magnitude of the capacitances resulting from this effect are orders of magnitude greater than the signals due to the suspensions, hence the use of the four-electrode design.[6,23] However, the four-electrode assembly does not eliminate electrode polarization effects completely as a finite current passes through the suspension. Measurements on the electrolyte solutions show that in order to obtain 78.5 for the relative permittivity of water, the balance correction must be nominally 5.0 pF over the measured frequency range. Measurements not reported here at the same electrolyte concentration, and therefore the same electrode polarization impedances, show the relaxation frequency to decrease with decreasing particle size. In view of this, the trends in relaxation frequency with electrolyte concentration can be considered not to be due to electrode effects. If an electrode polarization contribution to the measured signals existed it would tend to reduce the relaxation frequency of the lower electrolyte concentrations more than those at higher concentration. Its presence is therefore inconsistent with the observed trend in the relaxation frequencies (see Results and Discussion).

Results and Discussion

Fig. 1 shows the measured electrophoretic mobility values for the raw (not heat-treated), thoroughly cleaned sulfate latices, the heat-treated sulfate latices and the docosane particles as a function of KCl electrolyte concentration. Two significant features are apparent, the mobility maxima are present both

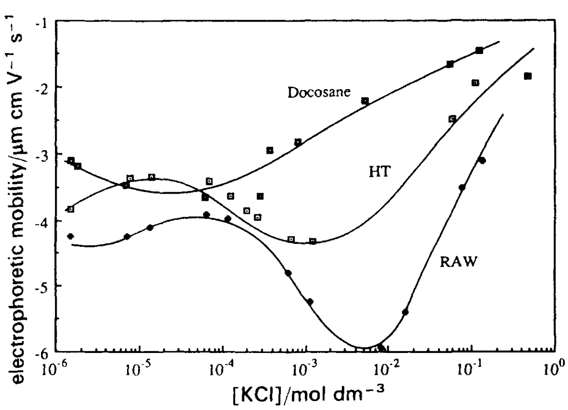

Fig. 1 Electrophoretic mobility of 0.30 μm diameter sulfate latices *vs.* KCl concentration. The two data sets are for the heat-treated (□) and raw (◆) latices. Also shown are the data for 1.0 μm diameter docosane particles (■). Measurements were performed at 25 °C at an ambient pH of 5.8

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before and after heat treatment and the colloidal alkane particles show mobility maxima. While the mobilities of the latices are reduced by the heat treatment, a maximum is still observed, indicating that the particles are still not ideal after heat treatment. The data presented for the docosane particles also show a maximum with KCl concentration. It is readily concluded from this that the electrophoretic mobility maxima are not due to surface hairiness as has been postulated previously.[9,10,24,25] The docosane particles do not have polymeric hairs protruding into solution. The reduced mobility for the heat-treated particles compared with the raw particles arises from hydrolysis of some of the sulfate groups on the surfaces of the latices. The greater absolute mobilities for the latex particles compared with those of the docosane particles derives from the presence of the fixed charge on the latex surface. Given the magnitude of the mobilities for the docosane particles relative to that of the latices ($\sigma = 1.2$ μC cm^{-2}), the effect of the charge on the particles on the mobility is relatively small.

Fig. 2 shows the concentration of excluded electrolyte as a function of the electrolyte concentration to which the particles were exposed. The data are for volume fractions of 0.01 at final dilution for the raw sulfate latices. The same experiment conducted at 10^{-3} mol dm^{-3} KCl showed linearity over a range of volume fractions from 0.01 to 0.05. The presence of the particles causes a significant perturbation in the supporting electrolyte concentration. Initially, it was thought that ions would be 'adsorbed' onto the surface of the particles and thus the ion exclusion values would be negative. The presence of surface conductance due to ions adsorbed on the particle surface was the rationale for the expected adsorption. These data show that no specific co-ion adsorption occurs on the surface of the particles. That ions are, on the whole, excluded from around the particles is consistent with surface tension data which require that the ions are depleted from the interfacial region.[26] The hydrophobic surface causes exclusion of ions near it, which in turn gives rise to the volume fraction dependence of the supporting electrolyte concentration.

The low-frequency conductance increments and mobilities for the latices are reported in Table 1. The conductance values determined from the measured mobilities using the theory of O'Brien and White[1] are also shown. In all cases, the measured conductance increments are larger than those predicted from the measured mobilities. This is consistent with the observed ion exclusion data. Note that the sample preparation procedure for the conductance measurements requires that any ions excluded from around the particles will contribute to the 'bulk' electrolyte concentration and thus the measured conductance increment.

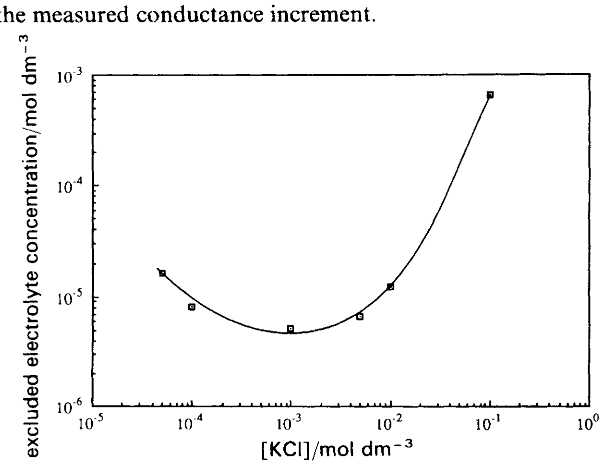

Fig. 2 Concentration of excluded electrolyte as a function of electrolyte concentration for the raw latices; see Experimental for details

Table 1 Conductance increments, mobilities and ζ potentials for the raw latices in the different electrolytes measured

electrolyte concentration /mol dm^{-3}	mobility/ μm cm V^{-1} s^{-1}	ζ potential /mV	ΔK_{meas}	ΔK_{ζ}
KCl 10^{-4}	−3.7	−80	+4.44	0.18
KCl 10^{-3}	−5.0	−100	—[a]	−0.38
HCl 10^{-4}	−3.7	−73	+4.6	+1.22
HCl 10^{-3}	−5.0	−90	+0.42	+0.00

[a] The conductance–volume fraction behaviour was not linear.

A discussion of the theory is worthwhile at this point. The theoretical interpretations of both the mobility and conductance/dielectric response measurements are based on the same physical assumptions. There is a temptation to assume that the experimental conditions necessary for correct theoretical interpretation are fulfilled by the mobility measurements which are conducted at infinitely dilute particle volume fraction ($\phi \approx 0.0005$) and that it is the conductance measurement that is erroneous because it measures a volume fraction dependent contribution to the bulk electrolyte concentration. This obscures the true isolated-particle contribution. However, the mobility maxima are observed at very low volume fractions which indicates that the particles are not ideal electrophoretic entities. A phenomenon which gives rise to the volume fraction dependence of the bulk electrolyte concentration may also give rise to the observed mobility behaviour. The concentration of excluded electrolyte varies with electrolyte concentration. The maxima in the mobility curves occur at approximately the same concentration as the minimum in the excluded electrolyte concentration curve. Interestingly, the magnitudes of the measured mobilities for the intrinsically uncharged docosane particles and the latices ($\sigma = 1.2$ μC cm^{-2}) are very similar at 10^{-4} mol dm^{-3} KCl (see Fig. 1). Obviously, an effect other than surface hairiness or surface conductance may give rise to the observed electrophoretic mobilities.

Dielectric response data for the raw and heat-treated latices in 10^{-3} mol dm^{-3} KCl are presented in Fig. 3 and 4. Given the difference in the ζ potentials interpreted from the mobilities, the differences between the spectra are not large. The measured values in both cases are much larger than the theory of De Lacey and White would predict.[2] The frequencies at which the dielectric loss spectra, ε'', show maxima are lower than the theoretically predicted values. The heat treatment process has not made the particles ideal. Other workers have reported that heat treatment of polystyrene latices produces ideal particles.[7,9,10] While small differences due to hydrolysis of the SO_4^{2-} groups on the surface in the heat treatment process may occur, the same relaxation frequency and magnitude of the dielectric response measurements are observed as for the untreated particles. Only small differences in the measured electrophoretic mobilities are observed at the measured electrolyte concentrations. The lack of a significant change in the relaxation frequency indicates that the surface is altered little by the heat treatment process. For latex suspensions which are not stringently cleaned the heat treatment may result only in the removal of polymeric material still present.

Data for the dielectric response for the raw latices in different electrolytes are shown in Fig. 5–8. The essential features of these data are as follows. The signals are all larger than theoretically predicted for the ζ potential interpreted from the measured mobilities. The theoretical curves for the mobility-interpreted ζ potentials are shown in Fig. 5–8. The frequencies of the maxima in the dielectric loss are in all cases

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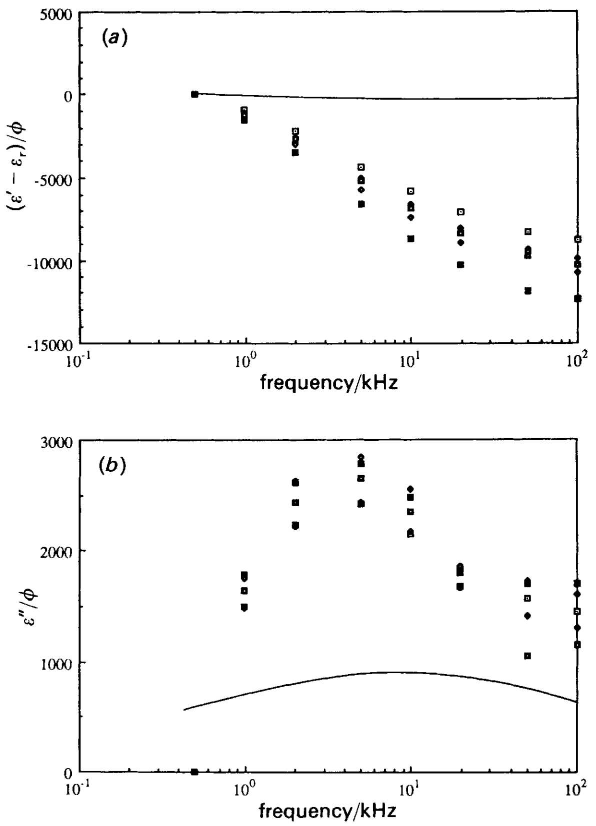

Fig. 3 Dielectric response data for the raw latices in 10^{-3} mol dm^{-3} KCl at different volume fractions. (*a*) Dielectric response *vs.* frequency; (*b*) dielectric loss *vs.* frequency. The solid curves are for the theory using a ζ potential of -100 mV

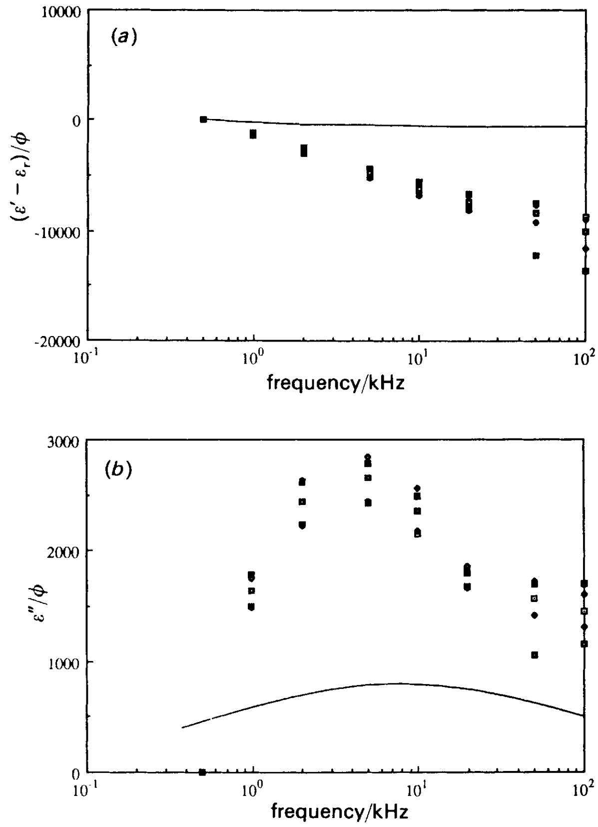

Fig. 4 Dielectric response data for the heat-treated latices in 10^{-3} mol dm^{-3} KCl. (*a*) Dielectric response *vs.* frequency; (*b*) dielectric loss *vs.* frequency. The solid curves are for the theory using a ζ potential of -100 mV

lower than predicted from the theory at the given electrolyte concentration and particle size. The measured frequencies at the maxima, the dispersion frequencies, are lower for the 10^{-3} mol dm^{-3} concentrations than for the 10^{-4} mol dm^{-3} concentrations in both HCl and KCl electrolytes. The maxima also occur at approximately the same frequency for both electrolytes at a given concentration. This is surprising given the higher limiting conductance for the H^+ ion, *ca.* five times that of the K^+ ion (*ca.* 349.8 cm^2 int S equiv.$^{-1}$ for H^+, compared with 73.50 cm^2 int S equiv.$^{-1}$ for K^+). The trend of lower measured dispersion frequencies at higher electrolyte concentration is difficult to understand. Surface hairiness is a possible explanation in that compression of the polymer hairs with increasing electrolyte concentration increases the ionic drag in the interfacial region. The observed trend in mobility with electrolyte concentration is consistent with this, where the retardation of the particles is less at higher electrolyte concentrations. However, the similar relaxation frequencies observed for the HCl and KCl electrolytes at the same concentrations require that the H^+ mobility is reduced much more than the K^+ mobility in the hairy interfacial region. A mechanism which reduces the H^+ mobility more than the K^+ mobility in the interfacial region may derive from structural effects in the water which interrupt the proton-jump mechanism.

In all cases measured, the dielectric spectra do not normalize with volume fraction but show a volume fraction dependence in the measured signals. The signal intensity decreases with decreasing volume fraction. The observed behaviour is not inconsistent with the ion exclusion measurements which indicate that the suspending electrolyte concentration changes with volume fraction. Given that interpretation of the dielectric response spectra relies on the low-frequency conductance increment, the data are not surprising.

The magnitude of the dielectric response signals suggests that either the material in the double layers is much more effectively conducting than is accounted for by theory, or the effective surface charge is spatially distributed further from the particle surface than predicted by the theory. The measured dispersion frequencies require that the ions are either reduced in their mobilities or spatially distributed further away from the particles than Poisson–Boltzmann electrostatics would indicate. The possibilities of co-ion adsorption and surface hairiness are not supported by the ion exclusion data and docosane mobilities, however. Furthermore, the lower frequencies and high magnitudes of the dielectric response suggest that a great deal of conducting material of reduced mobility was present in the interfacial region consistent with surface conductance. However, surface conductance is not required to explain the conductivity and mobility data obtained for micellar systems where the degree of ion binding is of the order of 0.8.[17] The micellar surface is highly hydrophilic in nature. The measured electrophoretic mobilities for the intrinsically uncharged hydrocarbons also show that large electrophoretic mobilities may be measured without any inherent charge present. Note that the very large dielectric response signals should give rise to very large retardation effects in the particle mobilities. Despite the larger dielectric response signals at higher electrolyte concentrations, and therefore retardation, the measured mobilities are higher than the mobility maximum. In some cases, mobilities that are higher than theoretically possible have been measured.[19]

The suggestion that the hydrophobic surface perturbs the water structure thus causing preferential solvation of the ions

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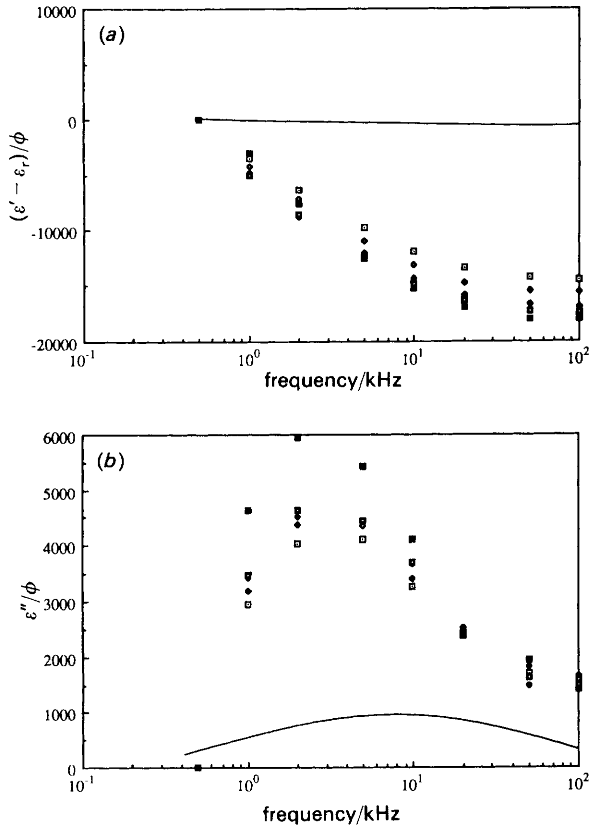

Fig. 5 Dielectric spectra for the raw latices in 10^{-3} mol dm^{-3} KCl. (*a*) and (*b*) show the real and imaginary components of the spectra. Comparison with Fig. 3 enables the reproducibility of the measurements from one suspension preparation to the next to be determined. The solid curves are for the theory using a ζ potential of -100 mV

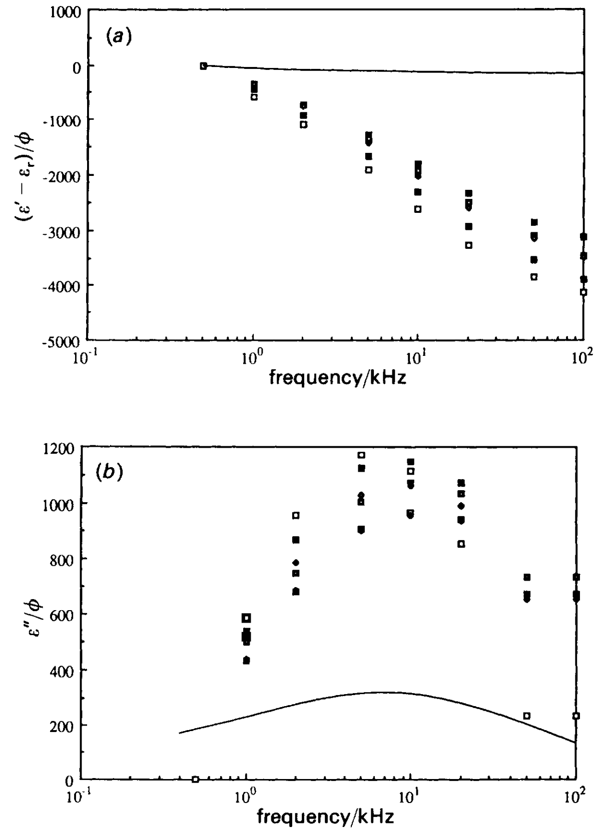

Fig. 6 Dielectric spectra for the raw latices in 10^{-4} mol dm^{-3} KCl. (*a*) and (*b*) are for the real and imaginary components of the spectra. The solid curves are for the theory using a ζ potential of -80 mV

of one charge in the interfacial region, combined with overall exclusion of those ions from the interfacial region, is consistent with the data presented. Surface force measurements indicate the range of the hydrophobic interaction to be of the order of 100 nm in water and to vary with electrolyte concentration.[27,28] These measurements are direct evidence that no co-ion adsorption on hydrocarbon surfaces occurs. No screened Coulombic forces are observed in the SFA measurements. In turn, the electrolyte concentration in the interfacial region will vary with the bulk concentration. While the ions will be excluded overall, a preferential solubility gives rise to the observed mobilities and dielectric response signals. The effective electrokinetic charge will then be very mobile and far from the particle, hence the lower than expected relaxation frequencies and the very large dielectric response signals *vis-a-vis* the large dipole moments set up by the larger 'effective Debye length' and highly mobile effective surface charge. The larger than theoretically predicted mobilities measured indicate that the charge which gives rise to the large polarization effects does not increase the retardation to the same degree as expected from classical theory. The idea of preferential solubility also accounts for the similarities between the H^+ and K^+ ions where the preferential solubilities of the Cl^- ions in the interfacial region explain most of the observed electrokinetic behaviour and destructuring of the interfacial water reduces the proton mobility *via* the jump mechanism.

Conclusions

Interpretation of the electrokinetic data obtained from the different measurements does not yield single values for the ζ

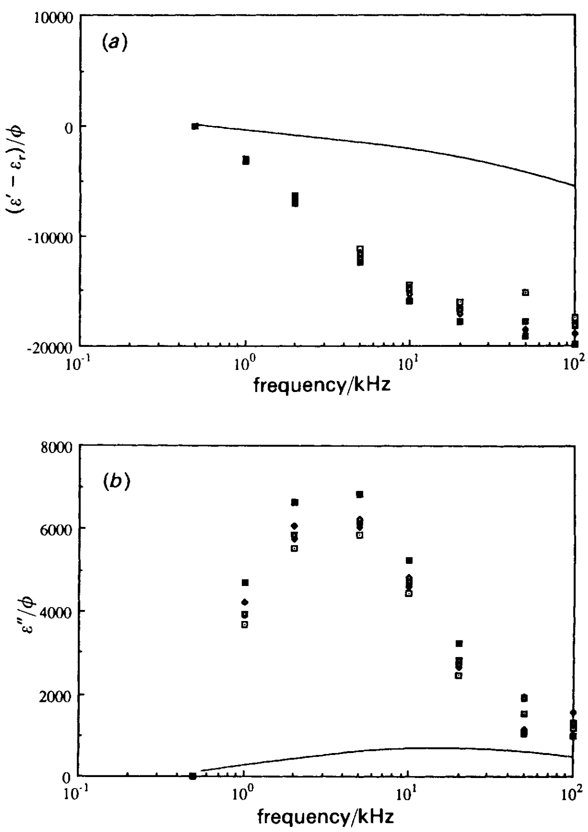

Fig. 7 Dielectric spectra for the raw latices in 10^{-3} mol dm^{-3} HCl. (*a*) and (*b*) are for the real and imaginary components of the spectra. The solid curves are for the theory using a ζ potential of -90 mV

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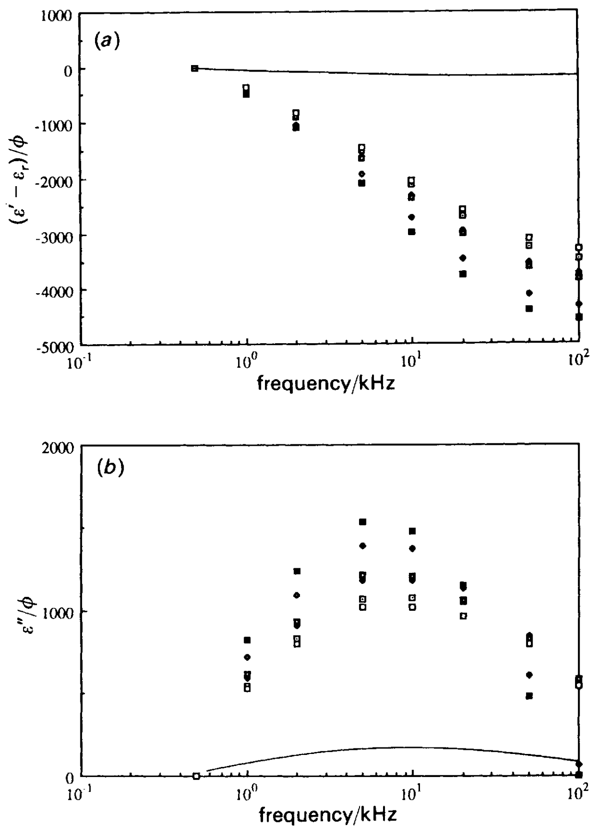

Fig. 8 Dielectric spectra for the raw latices in 10^{-4} mol dm^{-3} HCl. (*a*) and (*b*) are for the real and imaginary components of the spectra. The solid curves are for the theory using a ζ potential of -73 mV

potentials of the same suspension. The perturbation in the ion distributions due to the hydrophobic surface of the latices is postulated as the reason for the inadequacy of the theory. As such, polystyrene latices are not ideal classical electrokinetic model colloids. To describe these systems electrokinetically, a spatially varying electrostatic and chemical potential should be used in the Poisson–Boltzmann description of the interface. The spatially varying chemical potential term arises from the fact that the interfacial water is entropically different from the bulk water. In other words, the chemical potential of the solvent, water, is not constant throughout the suspension and gives rise to the preferential solvation of one ion in the interfacial region.

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