Colloid Polym Sci 274:1061–1071 (1996)
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ORIGINAL CONTRIBUTION

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The effect of an anionic surfactant on the rheology and stability of high volume fraction O/W emulsion stabilized by PVA

Received: 26 March 1996
Accepted 28 April 1996

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Abstract The effect of the addition of an anionic surfactant (sodium dodecyl benzene sulphonate) on the rheology and storage stability of concentrated O/W emulsions stabilized by poly (vinyl alcohol) is reported. It was found that the surfactant markedly reduced the magnitudes of the storage modulii of the emulsions. This could be attributed to a reduction in the interfacial tension resulting from the formation of polyelectrolyte type complexes between the PVA and NaDBS at the O/W interface. The results were compared to the equation (given by Princen) relating concentrated emulsion rheology to the interfacial tension and droplet size. Reasonable agreement was found, though there was a small difference in the constants in the equation given by Princen and those found here. The agreement suggested that the emulsions were deforming above a critical volume fraction and that the rheological properties were dominated by the dilation of the interface during shear. Microelectrophoresis measurements showed that the addition of the surfactant conferred a charge onto the PVA stabilized droplets as a result of the formation of the polyelectrolyte complex. The NaDBS was found to reduce the long-term stability of the emulsions compared to emulsions containing PVA alone.

Key words Poly(vinyl) alcohol – surfactants – oil/water emulsions – rheology – polymer–surfactant complexes

Introduction

Highly concentrated emulsions are used to a great extent in the pharmaceutical and cosmetic industries as carriers for active ingredients. It is often desirable to maximize the loading of these formulations to achieve the maximum effect from the active ingredient. However, high loadings are often prohibited due to the very high viscoelastic effects caused by the strong interdroplet forces involved at such high volume fractions. These effects lead to difficulties in their preparation. It is clear that the viscoelastic properties of the emulsions have to be controlled in some manner. The rheology of colloidal suspensions are governed by three main factors, these being [1, 2, 3]: a) Particle volume fraction (ϕ), b) Interparticle interactions, c) Particle size.

As the volume fraction of the dispersion approaches its maximum packing limit the rheological properties increase very rapidly as the interparticle forces become ever greater. The maximum packing fraction for solid in liquid dispersions is of the order of 0.64 under low shear [4], close to the maximum packing fraction of random close packing (this value may be slightly increased in polydisperse systems). The interparticle interaction also affects the volume fraction in that the thickness of the stabilizing barrier (whether electrostatic or steric) must be included as part of the particle and so increases the effective volume fraction [4]. Attractive interactions greatly increase the rheological properties in that the formation of flocs entraps a certain amount of dispersion medium again increasing the effective volume fraction of the particles [3]. Reduction in particle size also tends to increase the modulii of suspensions [1].

Below volume fractions of around 0.64–0.7 these considerations also apply to emulsions; however, as a result of their deformable nature it is possible to make emulsions with volume fractions of up to around 0.98–0.99 [5, 6]. In such systems the droplets are no longer present as spheres but are distorted into polyhedra. The rheological properties of high volume volume fraction emulsions has been dealt with in some detail by Princen et al. [7–9]. The elasticity of the emulsion is determined by the stretching of the interface under shear. They found that the static shear modulus, G_0, of these systems is given by the following equation [7, 8]:

$$G_0 = \frac{\gamma\phi^{1/3}}{\bar{r}_{32}} E(\phi) = \frac{A\gamma\phi^{1/3}}{\bar{r}_{32}} (\phi - \phi_0) \quad (1)$$

where $\bar{r}_{32}$ is the surface (Sauter) mean radius, A is a constant (equal to 1.769) and ϕ_0 is the critical volume fraction at which the undeformed droplets reach close packing and begin to deform [8]. An analogous equation was obtained for the yield stress. From this equation it is apparent that the rheological properties of the emulsions may be controlled through the droplet size or through the interfacial tension. In recent years there have been a number of investigations into the rheological properties of highly concentrated emulsions. Pons et al. [10, 11] have studied the rheological properties of the so-called 'gel-emulsions', highly concentrated W/O emulsions, and have found that their behaviour can be explained in terms of a single Maxwell element in which the elastic component relates to the elastically deformable emulsion droplets and the viscous component is due to the dispersion medium. More recently, Pons et al. [12] have reported the rheological properties of concentrated O/W emulsions stabilized by poly(ethylene oxide)- poly(propylene oxide)- poly(ethylene oxide) (Synperonic PE L62 and L94). They used the limiting high frequency storage modulus rather than the static shear modulus in Princen's equation. The constant A in Eq. (1) was found to be much higher than in both Princen's original work and that found in gel emulsions. This was attributed to these copolymers showing a much higher effective interfacial tension than that obtained in an equilibrium measurement. Otsubo and Prud'homme [13] have recently published data on O/W emulsions in which both oscillatory and steady-state measurements are given. It was found that the apparent viscosity of emulsions scaled with the droplet size, the viscosities of the two phases and the interfacial tension. The results for the oscillatory measurements were less clear, however the moduli appeared to scale with the interfacial tension and droplet size.

The applicability of Eq. (1) will be investigated in this paper through measurement of the rheological properties of PVA stabilized O/W emulsions as a function of droplet volume fraction both in the presence and absence of sodium dodecyl benzene sulphonate (NadDBS). Anionic surfactants are known to associate with PVA in solution and at interfaces to form poly-electrolyte type complexes and to reduce the interfacial tension [14, 15].

Experimental

Materials

The poly(vinyl alcohol) was GL05 (88% hydrolysed with Mw ca. 28,000, ex Nippon Gohsenai) and the oil used was Isopar *M*, a commercial paraffinic oil (ex Exxon). Both were used as received. Two grades of sodium dodecyl benzene sulphonate (NaDBS) were used, Nansa 1169P (ex Allbright and Wilson), which is composed primarily of linear dodecyl chain isomers and <0.4% sodium sulphate, and GPR grade (ex BDH) which contains up to 20% (w/w) sodium sulphate. The Nansa 1169P was supplied as a 30% (w/w) aqueous solution, and both surfactants were used as received. The Nansa 1169P was used for all of the experiments except for the storage stability tests.

Emulsion preparation

For the rheological measurements a stock emulsion of isopar *M* in a 3.14%(w/w) PVA solution at an oil volume fraction of 0.8 was prepared by stepwise addition of the oil whilst mixing with a high speed mixer (Ystral). The emulsion was sized using a Malvern Mastersizer (Malvern Instruments, Malvern, UK). The average sizes obtained were: volume mean radius ($R_{4,3}$) = 3.21 μm and surface (Sauter) mean radius ($R_{3,2}$) = 1.09 μm. The specific mean area was found to be 3.5 $m^2 g^{-1}$. The concentration of unadsorbed PVA was measured using a colorimetric technique [16] giving the concentration of unadsorbed polymer as 1.6% (compared to the original concentration of 3.14%) corresponding to an adsorption of around 1.6 $mg\,m^{-2}$.

Rheological measurements

Low shear oscillatory measurements were made using a Bohlin VOR rheometer (Bohlin UK, Cirencester, UK).

Strain sweeps were made at a frequency of 1 Hz using a cone and plate geometry over a strain range of 0.001–0.2. Storage (G') and loss moduli (G'') were determined in the usual manner [2, 3, 12]. This measurement enabled the linear viscoelastic region (where the rheological properties were independent of applied strain) to be determined where the moduli of the emulsions were independent of the applied strain. A frequency sweep was then carried out at a strain within this region in the range 0.01–20 Hz. The measurements were made at 20 °C. All moduli reported here were obtained at strains within the linear viscoelastic region.

In the measurement of the rheological properties of highly concentrated emulsions the possibility of wall slip must not be ignored [8, 17, 18]. To check for wall slip the stock PVA stabilized emulsion ($\phi = 0.8$ and most likely to show wall slip) was measured as a function of plate separation in a parallel plate geometry (pp 30) and also in the cone and plate geometry (cp 5/30). Strain sweeps were made at separations of 0.25–2 mm; if wall slip was present then the modulus would systematically decrease with decrease in plate separation. The strain sweeps are shown in Fig. 1. No systematic decrease in modulus was seen with decrease in separation, suggesting that wall slip was not present. All curves agreed to within ± 5% within the linear visco-elastic region. Some differences were seen in the non-linear region, but this had no effect since all measurements reported were in the linear region. The cp 5/30 geometry agreed well with the other data and was used for all further measurements.

The stock emulsion was diluted with a variety of 1.6% PVA (to maintain its concentration in the aqueous phase) + NaDBS (Nansa 1169P) solutions to give a range of NaDBS concentrations at an isopar *M* volume fraction of 0.775. These were used as the stock emulsions for the rheological measurements. These emulsions were then diluted to give a range of isopar *M* volume fractions between 0.65 to 0.775, the volume fractions of the emulsions were calculated from the weight percentages of the oil in the aqueous phase. These dilutions were made with aqueous solutions of PVA (1.6%) + NaDBS, the composition of these solutions are described below.

Adsorption isotherm

In order to maintain a constant interfacial tension as a function of volume fraction for each of the NaDBS concentrations, the dilution of the stock emulsion had to be made with a solution of the same composition as the aqueous phase of that stock emulsion. Thus, it was necessary to know the extent of adsorption of NaDBS on the droplets so that the composition of the aqueous phase could be calculated for any total NaDBS concentration. The adsorption of NaDBS (Nansa 1169/P) on to the stock emulsion droplets was determined. 10 g of the stock PVA stabilized emulsion was added to 40 g of various NaDBS solutions covering a range of concentrations. After equilibration the aqueous phases were separated off by centrifugation and the NaDBS concentration determined by UV absorption at 230 nm. The results are shown below as amount adsorbed (Γ) as a function of equilibrium aqueous phase NaDBS concentration ($[\text{NaDBS}]_{\text{eq}}$).

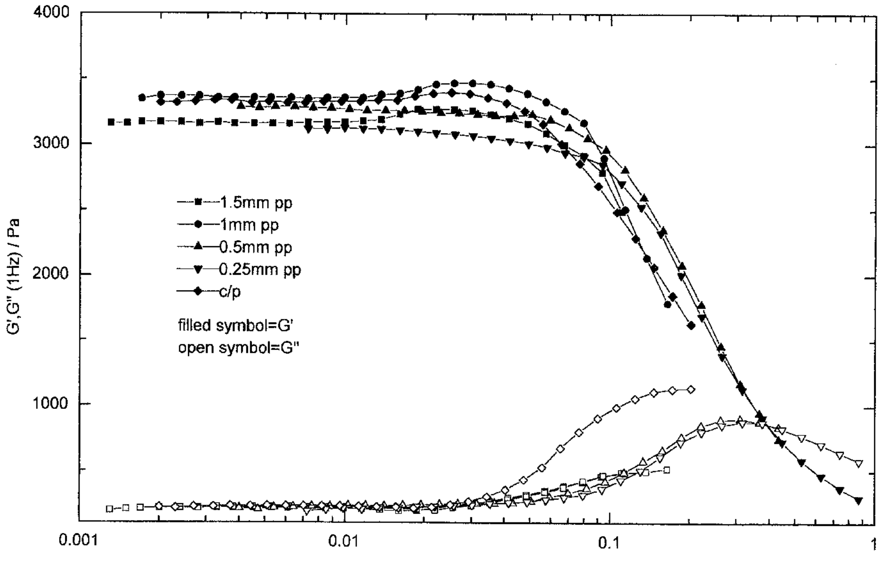


Fig. 1 Strain sweeps (storage modulus, G', as a function of applied strain, γ) at a frequency of 1 Hz for the stock PVA stabilized emulsion ($\phi = 0.8$) at various gap settings in a parallel plate geometry and also in a cone and plate (cp 5/30) geometry

The equilibrium concentration of NaDBS at any volume fraction ϕ could then be estimated using the above data for a given total NaDBS content. Thus, a plot of total NaDBS concentration versus $[\mathrm{NaDBS}]_{\mathrm{eq}}$ was made for a volume fraction of 0.775 from which the aqueous phase equilibrium NaDBS concentration allowing the composition of the aqueous phase for any particular emulsion to be determined.

Interfacial tension measurements

The interfacial tension between the isopar *M* and 1.6% PVA/NaDBS solutions was determined using the static Wilhelmy plate method. The apparent increase of mass of a roughened platinum plate in contact with the O/W interface was measured using Robal microbalance (CI Electronics, sensitivity 10 μg). The plate was cleansed with chromic acid and thoroughly washed with distilled water and finally flamed. Care was taken to ensure that the plate was wetted by the aqueous phase prior to immersion in the oil phase. The measurements were made at 20 °C.

To avoid any spurious effects from any surface-active impurities, the isopar *M* was cleansed with activated charcoal and a silica gel (sorbsil) and the PVA solutions were repeatedly foamed and the foam separated off to remove possible surface active impurities. A 13.37% NaDBS/1.6% PVA solution was mixed with a small amount of the stock PVA stabilized emulsion. The emulsion was added to remove any surface active impurities from the solution. The aqueous phase was separated off, diluted to the required NaDBS concentrations with the PVA solution and used in the interfacial tension measurements. Any impurity would have disproportionately large effect in the measurement of the interfacial tension due to the small interfacial area. In the emulsions systems where the interfacial area was very large they would have a much smaller effect.

Zeta potential measurements

The effect of addition of NaDBS on the zeta potential of isopar *M* in PVA (aq) emulsions was investigated using a Malvern Zetamaster Malvern Instruments, UK). The emulsions were prepared at various PVA concentrations at a volume fraction of ca. 2% by sonication with a sonic probe (Branson, UK). These emulsions were then diluted into various PVA/NaDBS solutions to give a range of NaDBS concentrations in 0, 100, 200 and 1000 ppm PVA. NaCl was also added to maintain a constant Na^+ concentration of 0.01 M. The zeta potential was calculated using the Smoluchowski equation.

Storage stability

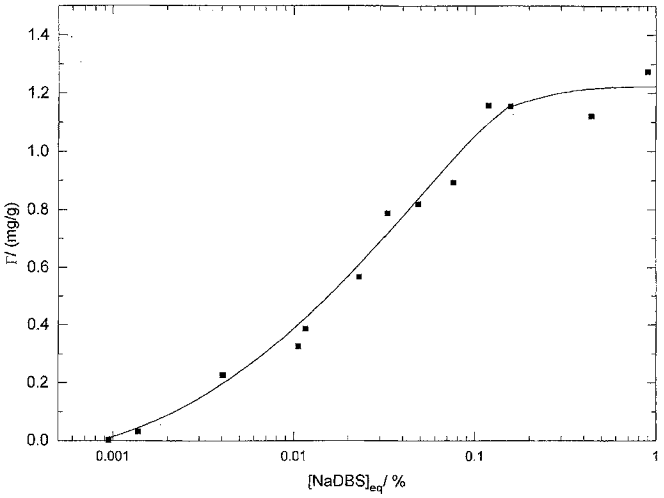
A stock emulsion was prepared with $\phi = 0.8$ isopar *M* in 3.14% PVA, this was then diluted to $\phi = 0.775$ with various NaDBS solutions to give a range of concentrations. The NaDBS used here was BDH GPR grade. The storage modulus, G' (0.1 Hz), and the volume average diameter, D_v (obtained with a Coulter TAII, Coulter UK) were measured as a function of time of storage at 40 °C.

Results

The adsorption isotherm obtained for NaDBS on the emulsion droplets is shown in Fig. 2. The shape of the adsorption isotherm is typical for reversible (Gibbsian) adsorption and shows a sigmoidal shape as a function of equilibrium NaDBS concentration (on a logarithmic scale). The plateau adsorption of around 1.3 $\mathrm{mg\,g^{-1}}$ corresponded to an area per molecule of 1.56 nm^2. This isotherm was used to estimate the equilibrium aqueous concentrations of NaDBS in the stock emulsions used in the rheological experiments. It was assumed that the adsorption was essentially independent of the volume fraction of the emulsion.

Plots of the storage modulus (G') at a frequency of 1 Hz are shown in Fig. 3 as a function of isopar *M* volume fraction at various initial NaDBS concentrations. The storage modulus (G') was found to increase linearly with volume fraction for all of the NaDBS concentrations studied, as suggested by the Princen equation [8]. Moreover, the observed linearity suggested that the interfacial

Fig. 2 Adsorption isotherm for NaDBS on the PVA stabilized emulsion droplets at an oil volume fraction of 0.2. Adsorbed amount expressed as mass adsorbed per unit mass of oil



tension was constant for each set of data suggesting that the estimated NaDBS equilibrium aqueous concentrations were close to the true values. The addition of NaDBS at a total concentration of 1.81% (corresponding to an aqueous phase concentration of 1.48%) was found to decrease the moduli by a factor of around 5–6. The linearity of *G'* with volume fraction suggests that the viscoelastic properties of the emulsions are, at least in part, the result of the stretching of and subsequent storage of energy at the interface. Linear regression of the data showed that the curves all interested the x-axis at a volume fraction of 0.665–0.672, allowing for the error in the measurement of *G'* and in the volume fraction all of the curves intersected at effectively the same volume fraction.

A typical strain sweep is shown in Fig. 4, where *G'*, *G''* and the phase angle δ are shown as a function of the applied strain for the stock PVA stabilized emulsion ($\phi = 0.8$). Below a certain strain (the critical strain) the moduli were essentially independent of strain, this is the linear visco-elastic region where the stress induced in the sample is linearly dependent upon the strain. At strains above the critical strain the moduli decreased as the

Fig. 3 Storage modulus (at 1 Hz) as a function of oil volume fraction at various equilibrium concentrations of NaDBS in the aqueous phase

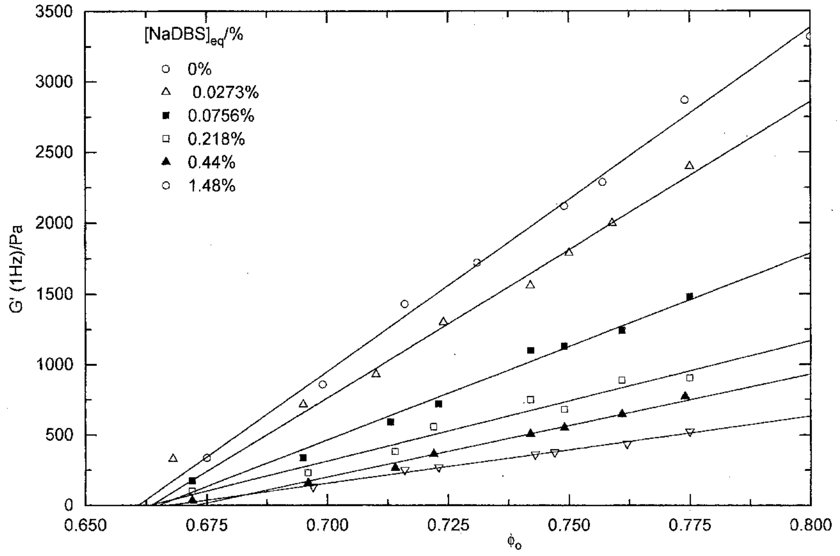
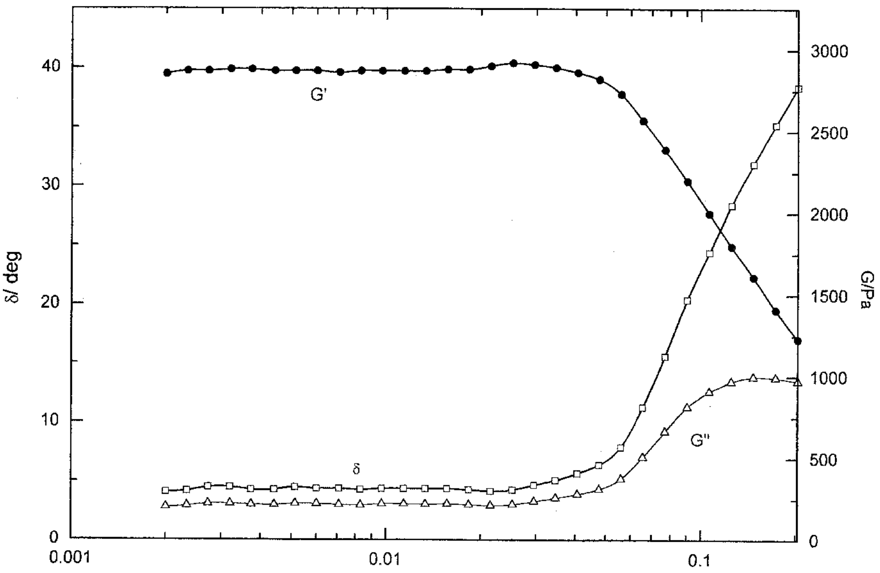
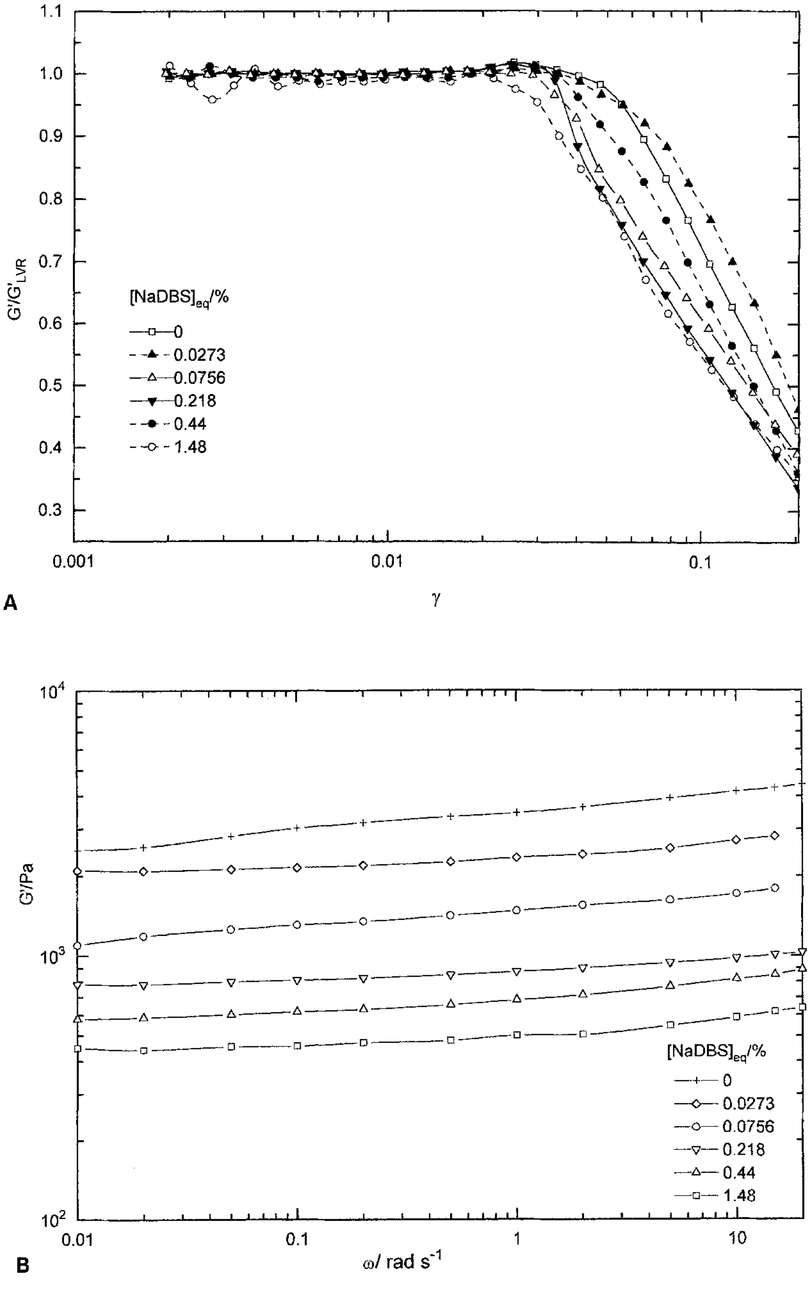


Fig. 4 Strain sweep for the stock emulsion ($\phi = 0.8$, no added NaDBS)



emulsion began to show nonlinear viscoelastic behaviour. In this region the emulsion structure was being perturbed to such an extent that the deformed droplets were hopping from one configuration to another resulting in a much reduced stress in the sample. This process has been described by Princen [7]: at low strain an applied strain deforms the emulsion structure, pushing together two adjacent vertices of the polyhedral structure, eventually these will meet and the structure becomes unstable. To alleviate this the droplets jump to their original configuration, except that adjacent layers have moved relative to another by one droplet diameter. This process reduces the stress in the system and thus results in a reduced modulus. The critical strain was found to be slightly dependent on oil volume fraction, however the results were inconclusive and no conclusions can be made. Above the critical strain the emulsions became progressively more liquid like in response, with an increase in G'' and a decrease in G' as the structure was disturbed. Eventually G'' reached a maximum and then decreased as the applied strain further perturbed the structure. The critical strain decreased slightly with decreasing

Fig. 5A Storage moduli as a function of strain at $\phi = 0.775$ at various NaDBS concentrations, moduli are normalized to their respective values in the linear viscoelastic region.
B Storage moduli as a function of frequency at $\phi = 0.775$ at various NaDBS concentrations



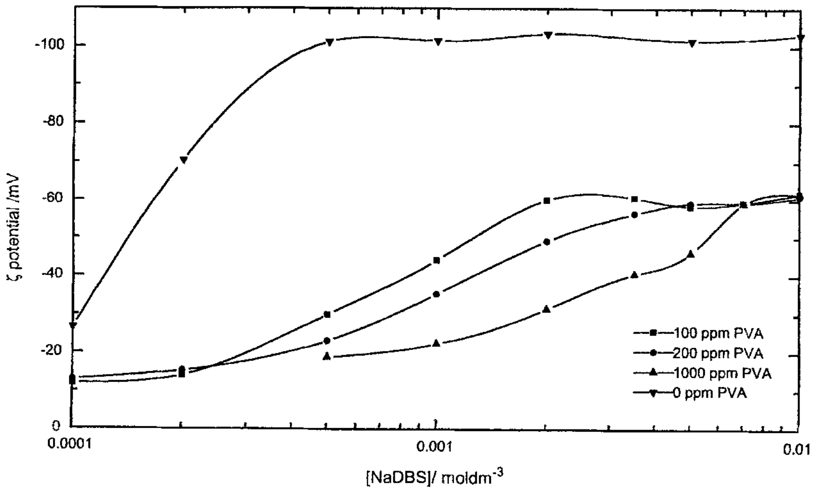
volume fraction, this has been predicted by the theory of Princen [8]. This decrease in critical strain in concentrated emulsions has recently been noted by Pons et al. [18].

The addition of the NaDBS was found to change the form of the strain sweeps to a small extent, Fig. 5a. In Fig. 5a the strain sweeps are plotted as G' divided by its value in the linear viscoelastic region (G'_{LVR}) at an isopar *M* volume fraction of 0.774. The onset of nonlinearity in the rheological response appeared to fall to slightly lower strains in the presence of NaDBS. The critical strain at which nonlinearity occurred was in the range 0.02–0.04 for all of the systems. Whilst the model of Princen suggests that the linear region should be dependent on volume fraction, it is not clear why the addition of the surfactant should affect the critical strain, though the change in the form of the interparticle potential may have some effect. The addition of the NaDBS is modifying the rheology of the system to a greater degree than that predicted, suggesting that it may be having an effect other than simply reducing the interfacial tension. It is interesting to note that addition of NaDBS to PVA stabilized poly(styrene) dispersions also reduces the moduli by a significant amount. Here the particles are not deformable and the reduction is due to the formation of a charged surface rather than the original uncharged steric layer [19]. The reduction in modulus in this case is due to the change in particle–particle interaction. Polyelectrolytes are also known to stabilize suspensions to a greater degree that nonionic polymers. Ufoxane 3A (a lignosuphonate) has been found to reduce the moduli of aqueous coal suspensions to much lower values than nonionic polymers such as synperonic F108 [19].

Within the linear viscoelastic region the emulsions were found to be predominantly elastic in nature ($G' \gg G''$), this was true for all of the emulsions in the frequency range 0.01–10 Hz. Frequency sweeps for emulsions at $\phi = 0.774$ are shown in Fig. 5b for each of the NaDBS concentrations used, the emulsions showed very little frequency dependence in their rheological properties. In general, they behaved as viscoelastic solids with relaxation times greater than 16 s showing that the rheology was dominated by the elastic properties of the deformed droplets and not any viscous effects due to the viscous nature of the aqueous phase. The frequency sweeps began to show greater frequency dependence as the volume fraction fell to values close to ϕ_0.

The results obtained from the microelectrophoresis measurements agreed well with those obtained by Tadros for a similar NaDBS/PVA systems at both the O/W interface and at the ethirimol (a commercial pesticide)/water interface [14, 20]. The PVA emulsions all showed a zeta potential of around -12 mV in the absence of NaDBS, however, addition of NaDBS markedly increased this up to a plateau value of around -60 mV as the NaDBS adsorbed onto the PVA layer on the droplets, Fig. 6. This plateau was significantly less than that in the absence of PVA, which showed a value around -100 mV. This reduction in the presence of PVA was probably due to two factors [14, 20], i) the surface concentration of NaDBS in the presence of PVA may have been lower than in its absence, ii) the PVA may shift the shear plane further from the interface and so reduce the zeta-potential. It is clear from these results that the addition of NaDBS will significantly modify the droplet–droplet interaction in the emulsions from a purely steric interaction to one of an electrosteric nature. This change in interaction is the

Fig. 6 Zeta potential of emulsion droplets as a function of NaDBS concentration in 0,100 200, and 1000 ppm PVA



predominant factor in the rheology of suspensions, where it is found that addition of NaDBS to a PVA stabilized dispersion of poly(styrene) in water markedly reduces the moduli [21], but in emulsions this is not so. The dominating factor here is the change in interfacial tension brought about by the formation of the PVA/NaDBS complex at the O/W interface.

The interfacial tension (Table 1) showed the same basic trend as a function of NaDBS concentration as found by Tadros [14] for an 88% hydrolyzed PVA sample (MW 42000) and NaDBS at the liquid paraffin/water interface. The presence of the polymer causes the plot of interfacial tension versus the logarithm of NaDBS concentration to deviate from the normal well defined behaviour. The sharp discontinuity at the CMC (1.6×10^{-3} moldm^{-3}) is no longer seen as a result of the formation of the polyelectrolyte type complex between the PVA and NaDBS at the interface. At high surfactant concentration the interfacial tension is dominated by the surfactant and approaches the equilibrium value found in the absence of polymer.

Table 1 Characterization of the various emulsions, including total and equilibrium NaDBS concentrations, interfacial tensions average mean radii, and the slope and critical volume fractions obtained from the linearized Princen equation

$[\mathrm{NaDBS}]_{\mathrm{tot}}$ /%	[NaDBS] /%	γ/mNm^{-1}	R_{32}/μm	Slope	ϕ_0
0	0	13.2	1.18	2.17	0.658
0.185	0.0273	11.1	1.17	2.29	0.668
0.336	0.0756	9.0	1.09	1.75	0.662
0.637	0.218	7.0	1.10	1.46	0.663
0.907	0.44	4.9	1.18	1.78	0.672
1.81	1.48	3.6	1.14	1.55	0.664

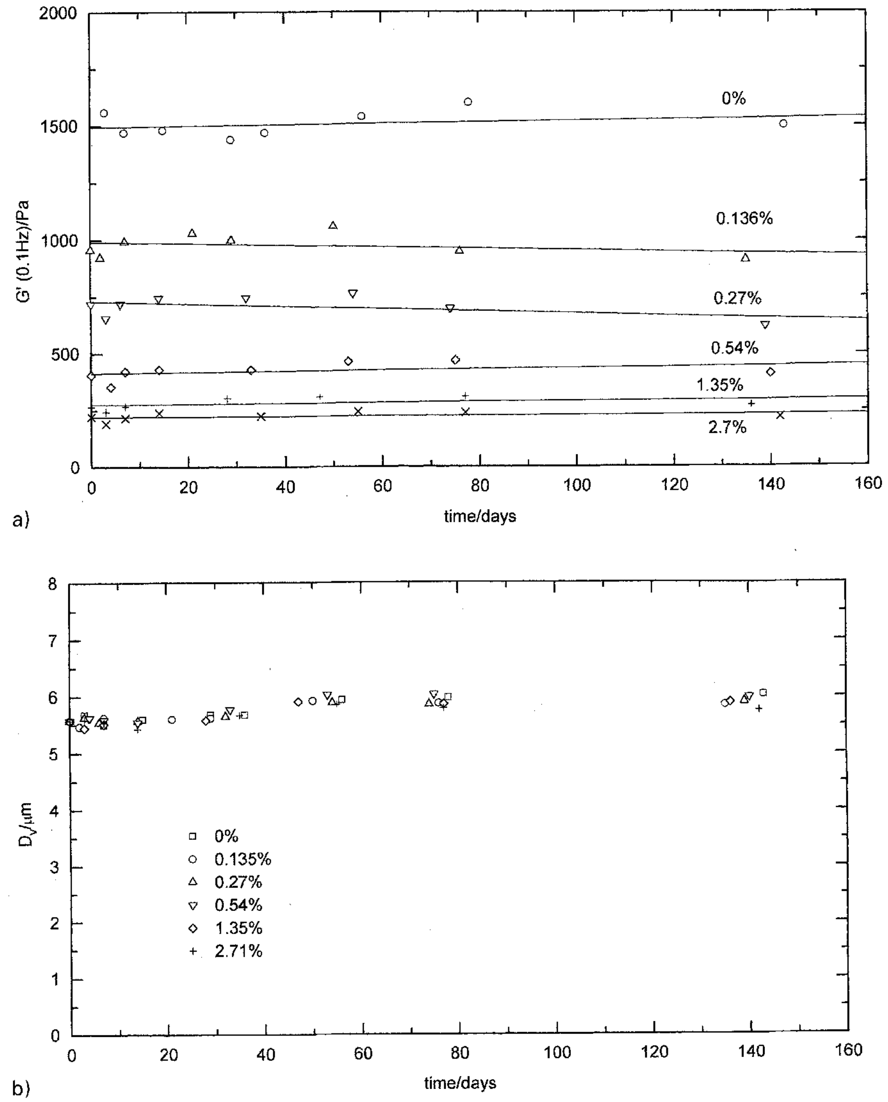


Fig. 7 Storage stability results (at 40 °C) at various total NaDBS concentrations a) storage modulus as a function time and b) volume mean diameter as a function of time

The results obtained from the storage stability tests are shown in Figs. 7a and 7b, as volume mean diameter and storage modulus as a function of time. Over a period of ca. 140–150 days little change was noted in either the volume average diameters of the storage moduli of the emulsions, this might be expected since PVA is known to be a good O/W emulsion stabilizer [14]. However after a further period of 3 years at 25 °C the above emulsions showed different results. The emulsion containing 0% NaDBS showed no free oil, but there was an increasing amount of free oil with increasing NaDBS content, with total breaking at 2.7% NaDBS.

Discussion

The results obtained show that the addition of an anionic surfactant to an emulsion stabilized significantly affects the rheological responses of that emulsion. The linearity of the plots of storage modulus against volume fraction (Fig. 3) strongly suggest that the rheology of these emulsions is dominated by the interfacial tension between the droplets and the aqueous phase. To test this the Princen equation (Eq. (1)) was linearized such that $G' \cdot R_{32}/\gamma\phi^{1/3}$ was plotted as a function of volume fraction. The values for the interfacial tensions and the droplet sizes are given in Table 1 for each equilibrium NaDBs concentration. Also listed are the critical volume fractions and slopes obtained from the linearized Princen plots shown in Fig. 8.

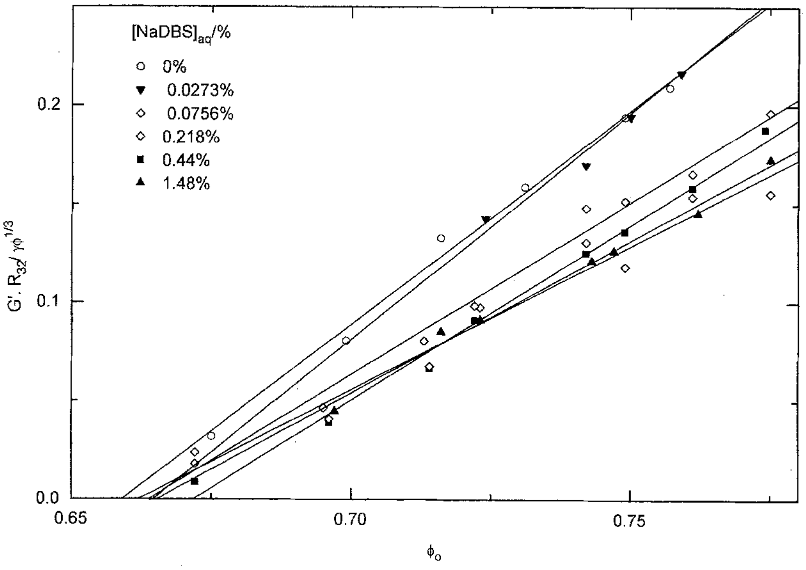
The plots were all found to be linear within experimental error, but there was a slight variation in the slope with NaDBS concentration. The slopes and x-axis intercepts, ϕ_0, are in Table 1. The form of the dependence of $G' \cdot R_{32}/\gamma\,\phi^{1/3}$ on volume fraction is very similar to that given by Princen [8], and suggests that the analysis is valid for polymeric stabilized emulsions. However, minor deviations were seen. At the two lowest concentrations of NaDBS the two parameters obtained for each set of data are very similar, however as the concentration of NaDBS increased the slope in the main decreased whilst ϕ_0 remained essentially constant.

The values obtained for the intercept are lower than that reported by Princen [8], the intercept essentially is a measure of the effective volume fraction of the emulsions. Princen's value of 0.71 was obtained for a much smaller surfactant than PVA, and the reduction in intercept is a measure of the increased thickness of the interfacial barrier formed by PVA. For a monodispersed emulsion the intercept would have a value of 0.74, the limit for hexagonal close packing and the volume fraction at which the droplets would begin to deform and show a measurable modulus. We may approximate the layer thickness, δ, from this reduction in ϕ_0 using [3]:

$$\frac{0.74}{\phi_0} = \left(1 + \frac{\delta}{R}\right)^3 . \qquad (2)$$

Taking the average value obtained for ϕ_0 of 0.665 and an average radius R, of 1.1 μm (the R_{32} average) we obtain a value for δ of around 39 nm for the PVA layer. This value is in reasonable agreement with that obtained from other techniques (though slightly high). It should be noted that the value of 0.74 may be modified by the polydispersity of the emulsion droplets but the extent of the modification is not known. If Princen's value of 0.71 is used then a layer thickness of 24 nm is obtained, this is in much better

Fig. 8 Linearized Princen plot showing $G'R_{32}/\gamma\phi^{1/3}$ as a function of volume fraction



agreement with that reported in the literature. Garvey et al. [22] obtained adsorbed layer thickness for a fractionated sample of PVA (narrow molecular mass range, MW = 28 000, 88% hydrolyzed) on polystyrene particles (165 nm radius) of 22.2 nm by Photon Correlation Spectroscopy, 18 nm by ultracentifuge and 37 nm by microelectrophoresis. Strictly speaking, it is dangerous comparing results from either l/l and the s/l interfaces but the value obtained here of 24 nm is of the correct order of magnitude, however, the range seen in the thicknesses indicates the difficulty in unambiguously defining the layer thickness.

The change in slope seen with varying NaDBS concentration is hard to explain. Pons [23] has suggested that the change in the form of the interaction potential upon addition of an ionic surfactant to a nonionic polymer stabilized emulsion may account for the change in the extent of the viscoelastic linear regions. Zeta-potential measurements have shown that the presence of the NaDBs significantly increases the charge on the droplets, as it both adsorbs on any free interface and also complexes with the acetate groups on the PVA molecule [24]. It may also partially desorb some of the polymer. Thus, the interaction potential is transformed from a simple steric interaction to one resembling an electrosteric interaction as produced by a polyelectrolyte. How this change in interaction may affect the rheology is as yet unclear. Cates and Buzza [25] have suggested that the contribution to the osmotic pressure by a charged interfacial layer would have a negligible effect on the rheological properties of the emulsion.

It should be noted that the change in slope may be due to uncertainties in the interfacial tension, polymer surfactant systems are complex systems and prone to uncertainties. In addition the effect of any impurity in the surfactant and or the polymer may have been underestimated, however such differences are expected to be small in comparison to the changes in overall interfacial tension. The order of addition of polymer and surfactant may also have a bearing on the measured interfacial tension. Adsorption from a mixed solution of PVA and NaDBS onto a clean interface (as in the measurement of the interfacial tension) will be dominated by the NaDBS (especially at higher NaDBS concentrations) due to its higher diffusion coefficient in aqueous solution. In the emulsions studied here the NaDBS was adsorbed onto an interface already saturated with PVA, and so the interfacial composition may be different in the two cases.

In summary, the Princen equation adequately describes the low shear rheology of these polymerically stabilized emulsions. The variation in the slope of the Princen plot was relatively small, and may be within experimental error. The variation found was much less than that found by Pons et al. [12] who found values ranging between 5 and 13 for O/W emulsions stabilized by PEO–PPO–PEO block copolymers.

The storage stability of the emulsions was clearly affected by the addition of the NaDBS. Whilst no apparent change was noted in storage modulus or volume mean diameter over a period of 150 days at 40 °C, after 3 years, at 25 °C, complete breaking of the emulsion was seen at the highest surfactant concentration. The NaDBS may have been displacing the individual adsorbed segments of the PVA at the interface, eventually displacing most or all of the adsorbed PVA. This may explain why initially no differences were noted, in that to destabilize the emulsion droplets a certain fraction of the PVA would have to be displaced from the interface; prior to this point the remaining PVA would still stabilize the emulsion. The surfactant alone would not be as good a stabilizer as the PVA and so coalescence would have resulted. Tadros [14] has found that the coalescence rates in NaDBS (stabilized liquid paraffin in water emulsions fell in the presence of PVA (even at very low levels, eg. 200 or 1000 ppm) compared to that of the NaDBS alone. The rates of coalescence in the presence of NaDBS + PVA were, in fact, lower than those obtained for PVA alone. Thus, it appeared that the mixture of the two stabilizers gave an enhanced stability, however it should be noted that the kinetics of coalescence were studied only over a short period and these results do not preclude the possibility of displacement of the PVA by the NaDBS over a longer period of time. Moreover, the use of very low polymer concentrations would have resulted in much lower emulsion stability compared to the concentrations used here. Alternatively, the increase in sodium sulphate concentration with NaDBS concentration may have destabilized the emulsion. However, at the highest NaDBS concentration may have destabilized the emulsion. However, at the highest NaDBS concentration its concentration was 0.043 M which was probably below its critical flocculation concentration and so may be expected not to aid coalescence. Tadros [26] has reported that the critical flocculation concentration (CFC) of sodium sulphate for poly(styrene) lattices stabilized by PVA (MW = 45,000) at 25 °C was 0.15 mol dm^{-3}, which is well above the concentration found here. Moreover, if the sodium sulphate had been having a significant effect on the emulsions studied here, the greater effect would have been seen during the storage period at 40 °C, where the sodium sulphate would have been closer to its CFC, whereas no significant differences were noted during this period.

Acknowledgments The author wishes to thank ZENECA PLC for permission to publish this work. Thanks go to R. Pons and Th.F. Tadros for many useful discussions and ideas.

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