

<b>MESURES DE POTENTIELS ZETAS SUR DES EMULSIONS DE BITUME ET DES GRANULATS ROUTIERS</b>			
<b>ZETA POTENTIAL MEASUREMENTS ON BITUMEN EMULSIONS AND ROAD AGGREGATES</b>			
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### RÉSUMÉ

L'analyseur ZétaPlus fabriqué par Brookhaven permet de mesurer rapidement les potentiels zétas de granulats routiers et de gouttes de bitume en émulsion. Nous avons utilisé le ZétaPlus pour mesurer les potentiels zetas d'une gamme d'émulsions dont certaines ont été préparées à partir d'émulsifiants de bitumes disponibles sur le marché et d'autres à partir d'un surfactant pur. Nous avons également comparé des bitumes d'origines différentes. Nous avons étudié les effets du pH et de la composition de la phase continue sur les mesures de mobilité. D'autre part, nous avons essayé d'étudier les gouttes de bitume dans les conditions qu'elles pourraient rencontrer en pratique lors de la réparation des chaussées. De la même façon, nous avons comparé les potentiels zétas de quartz pur et de granulats en présence (par exemple) d'émulsifiants. Les résultats obtenus ont été utilisés pour éclairer les mécanismes de rupture et d'enrobage dans les mélanges émulsion-granulats.

### ABSTRACT

The Brookhaven ZetaPlus zeta potential analyser allows the rapid determination of zeta potentials of bitumen emulsion droplets and road aggregates. The equipment has been used to determine the zeta potentials of a range of emulsions, some prepared using commercially available bitumen emulsifiers and others using a pure surfactant. Bitumens from different crude sources have been compared. The effects of pH and the composition of the continuous phase used in the mobility measurements have been studied and an attempt made to study the bitumen droplets under conditions they might experience in real-life road repair applications. Similarly, both pure quartz and road aggregate have also been studied in the presence of (for example) emulsifier. The results are used to throw light on the breaking mechanism of emulsions and coating in emulsion-aggregate mixes.

## 1. Introduction

Bitumen emulsions are used in many cold processes for road construction and repair. Their use avoids the handling and environmental hazards associated with hot bituminous materials (1). However the strength of road materials made using emulsions develops only when the emulsion breaks or "sets" into a continuous bitumen film (2).

Various mechanisms have been proposed for this "setting" process.

- i) Emulsifier is gradually abstracted from the bitumen-water interface by adsorption onto the aggregate surface. Eventually the remaining emulsifier is insufficient to stabilise the emulsion.
- ii). Emulsion droplets migrate to the aggregate surface under the influence of charge difference (electrophoresis). The concentration of droplets at the surface increases and coagulation occurs.
- iii). The pH of the (cationic) emulsion increases due to the reaction of acid with the aggregate, or adsorption of protons onto the mineral surface. At high pH the cationic emulsifiers are deprotonated and the resulting uncharged emulsifiers cannot prevent coalescence of the bitumen.

In addition, the adsorption onto the aggregate of "free" emulsifier and other ions from the water phase of the emulsion could modify the process. Here we report electrophoretic measurements on bitumen emulsions and minerals. The results allow some conclusions about the setting mechanism to be made.

Most surfaces in contact with an aqueous solution acquire an electrical charge. It is difficult to measure surface charge directly; however it is relatively easy to measure a related quantity known as the zeta potential. According to electrical double layer theory, the potential ( $\psi$ ) in the vicinity of a charged surface in contact with an aqueous solution decreases exponentially with distance from the surface ( $x$ ), i.e.  $\psi = \psi_0 e^{-kx}$  where  $\psi_0$  is the surface potential and  $k$  is a constant whose value depends on the composition of the aqueous solution. The zeta potential is the potential measured at the surface of shear created when a solid or liquid dispersed particle moves relative to the background medium under the influence of an applied electric field (3). Various experimental techniques have been used to measure zeta potentials (4). Early measurements involved direct visual determination of the rate of movement of charged particles under an electric field (microelectrophoresis). More modern equipment such as that employed in the current work carries out the same measurement using laser Doppler shifts to determine the particle mobility. Other approaches include measurement of the electric field generated by passing a sound pulse through the sample (electrokinetic sonic amplitude or ESA) and electroosmosis.

## 2. Experimental details

Samples were prepared for analysis by dispersing bitumen emulsions or minerals in distilled water or water phase removed from the emulsions by high speed centrifugation; the degree of dilution was such that the samples were just cloudy (approximately 0.1% w/w solids). Sample pH adjustment was carried out by addition of hydrochloric acid or sodium hydroxide solution. Zeta potentials were determined using the Brookhaven Instruments ZetaPlus equipment, which measures mobility in opposite directions by reversing electrode polarity and then takes the average result. All the results presented here represent the average of at least three separate determinations.

## 3. Results and Discussion

The results of zeta potential measurements for minerals and bitumen emulsions are summarised in Figures 1-6. The emulsifiers are coded as follows: CTAC = hexadecyl (cetyl) trimethyl ammonium chloride, E-9 = N-tallow-1,3-diaminopropane, E-11 = N,N,N',N'-pentamethyl-N-tallow-1,3-propanediammonium chloride (50% active in IPA/water), E-4868 = formulated cold mix emulsifier. The bitumen types are Venezuelan (Ven), Mexican (Mex) and Middle Eastern (ME) 200 pen.

### 3.1. Minerals

The zeta potentials measured in distilled water for quartz and La Meilleraie aggregate are negative in sign, indicating that the minerals are acidic. However the zeta potentials measured in centrifuged water phases are predominantly neutral or weakly positive as a result of adsorption of cationic emulsifier from the solution (Figure 1). The differences between the two sets of data show that the correct choice of diluent is very important if zeta potential results are to give useful information on behaviour in applications. In practice, analysis of run-off water from compacted emulsion-aggregate mixes has shown very little free surfactant left in the continuous phase; it is believed that most of the residual emulsifier is mopped up very quickly by the fines in the aggregate mix. Thus it can be argued that the values measured in distilled water are more realistic. In addition the ratio of free emulsifier:aggregate surface area is usually much lower in practice than that experienced here and thus charge reversal of the aggregate does not normally occur.

The zeta potentials of minerals dispersed in either distilled water or centrifuged water phase were found to vary with time, only stabilising after a period of several hours. Two factors are involved: adsorption of emulsifier (if present) from solution and drift in pH due to surface hydrolysis, adsorption of ions, dissolution etc. Studies employing surfactant-sensitive ion-selective electrodes have demonstrated that adsorption of cationic emulsifiers onto aggregate is usually very rapid (time scale of seconds or less) (5). The other processes involving the aggregate itself are much slower and were typically found to take 5-6 hours to reach equilibrium. The zeta potentials for minerals presented here were all determined under equilibrium conditions.

Figure 1. Zeta potential measurements for minerals dispersed in distilled water and emulsion water phases removed by centrifugation.

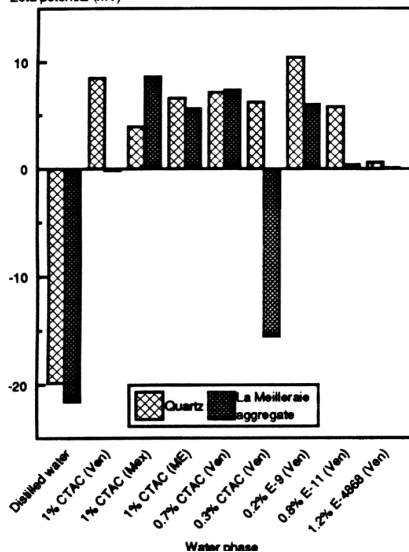
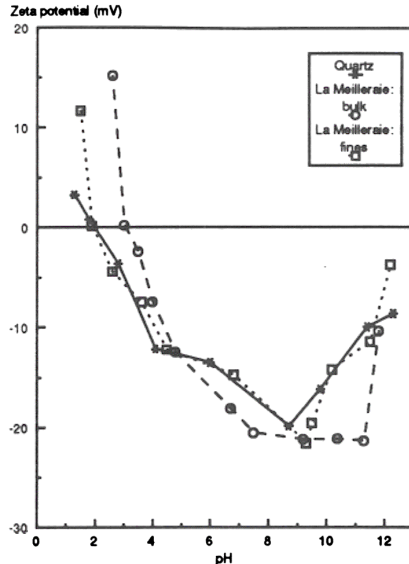


Figure 2. Effect of pH on the zeta potentials of quartz and La Meilleraie aggregate dispersed in distilled water.



Minerals in contact with water are positively charged at low pH and negatively charged at high pH. The pH at which the net charge is zero (in the absence of electrolyte other than that required to adjust the pH) is called the point of zero charge (p.z.c.) (6). For acidic minerals such as quartz and La Meilleraie aggregate (predominantly diorite), the p.z.c. is low, so that under conditions experienced in road making they carry a negative charge (Figure 2). The fines component ( $<75\mu$ ) in La Meilleraie consists mainly of quartz and this is neatly illustrated by the close similarity between the two relevant zeta potential-pH curves. Acidic minerals have a strong affinity for cationic emulsifiers and hence tend to exhibit good adhesion when mixed with cationic bitumen emulsions. Certain aggregates such as limestone are known to be "difficult", giving poor adhesion between bitumen and stone; one reason for this is that such minerals have high p.z.c. values and thus are neutral or even positively charged at the pH of the emulsion-aggregate mix.

### 3.2. Emulsions

The zeta potentials measured in distilled water and centrifuged water phases are, with one exception, positive in sign (Figure 3). The effect of changing the diluent from distilled water to water phase is generally to reduce the magnitude of the zeta potential, mainly as a result of the increase in ionic strength experienced by the emulsion droplets (3). The decrease in magnitude of zeta potential (positive or negative) with increasing ionic strength is further demonstrated by the data in Table 1 which shows the effect of diluting an emulsion or aggregate with 0.01M aqueous sodium chloride solution.

When studying the zeta potentials of bitumen emulsions in order simply to characterise them, it is most appropriate to dilute the emulsions with centrifuged water phase since this does not change the environment experienced by the droplets. However when investigating the interaction of emulsions with mineral aggregates during mixing it is more realistic to consider the values measured in distilled water for the reasons explained earlier.

Sample	pH	Distilled water		0.01M NaCl	
		Zeta pot. (mV)	Conductance ( $\mu$ s)	Zeta pot. (mV)	Conductance ( $\mu$ s)
1% CTAC (Ven)	6.0	+49.7	60	+11.9	1160
La Meilleraie	9.3	-21.5	180	-13.2	2100

Table 1: Effect of diluent ionic strength on zeta potential

For the bitumen emulsions prepared from commercial surfactants, the zeta potentials measured in distilled water at natural (unadjusted) pH decrease in the order 0.2% E-9 > 0.8% E-11 > 1.2% E-4868 (actually negative). This ranking correlates with the speed of breaking of the emulsions when mixed with aggregate; the emulsifiers are classified as rapid, medium/slow and very slow setting. Therefore first indications suggest that the more positive the zeta potential of a bitumen emulsion, the faster it breaks on mixing; however further studies are needed before this rule can be accepted as general.

Initially it was believed that the zeta potentials of the bitumen emulsions studied were stable with respect to dilution, i.e. there was no noticeable change in zeta potential with time from the first value measured after diluting. However standard experimental procedure allowed up to 10 minutes to elapse after diluting the emulsion before the zeta potential result was generated; thus any change in zeta potential within this time would not be detected. Attempts to monitor the system during this initial period have suggested that there is a significant decrease in zeta potential in the first few minutes after diluting with distilled water; however this is not accompanied by an increase in aqueous phase conductance, which would be expected if emulsifier was leaving the bitumen-water interface. Evidently further experiments are required in order to determine whether rapid redistribution of emulsifier takes place on dilution.

Figure 3. Zeta potential measurements for bitumen emulsions diluted with distilled water and water phases removed by centrifugation.

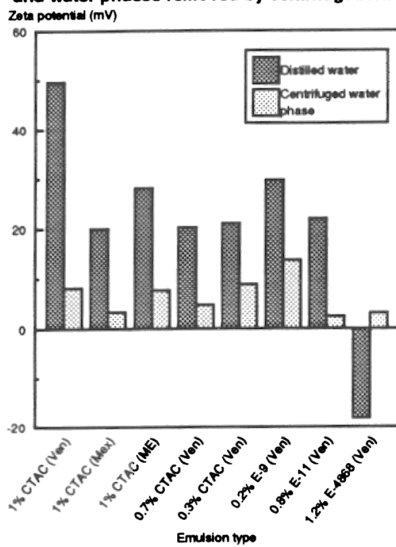
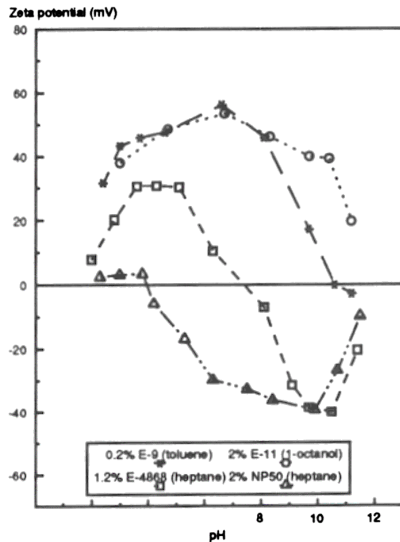


Figure 4. Effect of pH on the zeta potentials of emulsions prepared from non-ionisable oils diluted with distilled water.



Bitumen typically contains a range of acidic functional groups which ionise at high pH; thus the zeta potential of a "cationic" bitumen emulsion comprises contributions from both the emulsifier (positive) and the bitumen droplets (negative). Hence when determining the effect of pH on the zeta potentials of bitumen emulsions, initial experiments were carried out in which emulsions were prepared from non-ionisable oil phases such as toluene, 1-octanol and heptane in order to measure the zeta potential contribution of the emulsifiers alone (Figure 4). The emulsion stabilised by E-9 is cationic under acidic and neutral conditions but loses its charge (and becomes unstable) at high pH due to deprotonation of the amine groups on the emulsifier. In contrast the emulsion prepared using E-11 remains strongly cationic across the entire pH range because of the permanent positive charges on the emulsifier. The E-4868 emulsion is cationic at low pH but undergoes charge reversal at high pH; this is a result of the amphoteric nature of the emulsifier. Surprisingly the "nonionic" emulsion prepared from nonyl phenol 50 mole ethoxylate (NP50) is actually strongly anionic under all but the most acidic conditions. Since the oil phase (heptane) cannot ionise and thus does not contribute to the zeta potential, we are forced to the conclusion that the "nonionic" emulsifier can become negatively charged at neutral and high pH (7).

The relationship between zeta potential and pH for bitumen emulsions depends on the balance between the charge on the emulsifier and the negative charge on the bitumen. The extent of ionisation of the bitumen and hence the negative charge increases with increasing pH. The acid values of the three bitumens studied decrease in the order Venezuelan > Mexican > Middle Eastern (typically 2.5, 0.2 and 0 mg KOH/g respectively). Thus the magnitude of the negative charge at any given pH decreases in the same order. This is illustrated by the zeta potential data for NP50 bitumen emulsions (Figure 5). The majority of the negative charge is due to the emulsifier (c.f. Figure 4); however the depths of the zeta potential minima decrease in the order of the bitumen acid values.

Figure 5. Effect of pH on the zeta potentials of 2% NP50 bitumen emulsions diluted with distilled water.

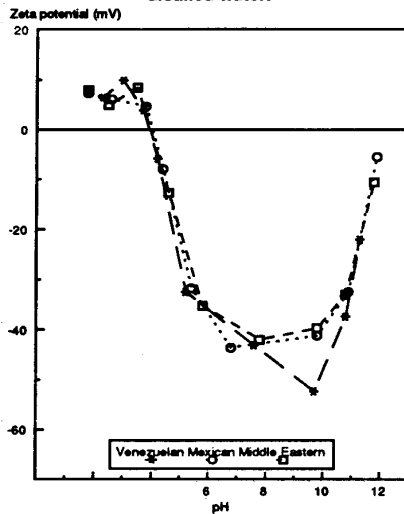
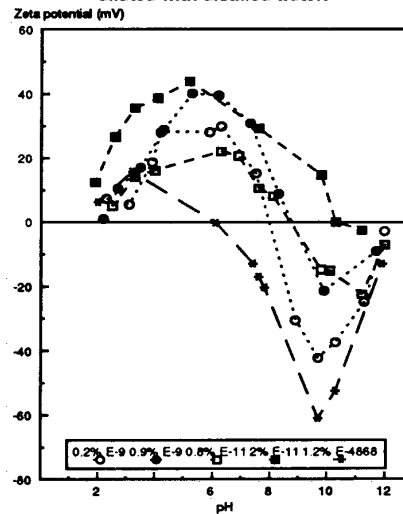


Figure 6. Effect of pH on the zeta potentials of emulsions prepared from Venezuelan bitumen diluted with distilled water.



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Figure 6 shows the effect of emulsifier type and addition level on the pH dependence of zeta potential for emulsions prepared from Venezuelan bitumen. E-9 emulsions were found to be cationic at low pH but deprotonation of the amine groups plus ionisation of the bitumen led to a net negative charge at high pH; increasing the level of emulsifier made the zeta potential of the emulsion more positive (or less negative) across the whole pH range. In the case of E-11, the negative charge on the bitumen was sufficient at the lower emulsifier level to generate a net negative zeta potential at high pH, but at the higher emulsifier level the emulsion remained cationic up to pH 10. The curve for the emulsion prepared from the amphoteric E-4868 has the same shape as that for the corresponding heptane emulsion (Figure 4); the acidity of the bitumen shifts the p.z.c. to a lower pH and increases the depth of the minimum.

#### 4. Conclusions

The following conclusions may be drawn from the results described above concerning the mechanism of emulsion setting:

- Free surfactant in the water phase adsorbs very rapidly onto the aggregate; this process is probably diffusion controlled.
- Some of the surfactant present at the bitumen-water interface may leave quickly on dilution; it has not yet been established whether this loss is large enough to destabilise the emulsion.
- A feasible mechanism for breaking is rapid adsorption of free surfactant onto the aggregate followed by electrophoresis of droplets under the influence of the (new) charge on the mineral particles to the aggregate surface. The speed at which typical bitumen droplets move to a typical aggregate surface has been calculated from mobility data to be of the order of a few minutes; the exact rate, and thus the "speed of break", would depend on the relative zeta potentials of the emulsion and aggregate. The final stage would then be adsorption and spreading of the droplets.

#### 5. References

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