Acoustic and Electroacoustic Spectroscopy of Water-in-Diluted-Bitumen Emulsions

Alejandro Magual, Géza Horváth-Szabó,* and Jacob H. Masliyah

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB T6G 2G6, Canada

Water-in-oil emulsions of Athabasca bitumen diluted with toluene have been studied using the latest advances in acoustic and electroacoustic spectroscopy. From the sound attenuation spectra of emulsions, the water droplet size distribution is measured. The electrical surface charge density of the water droplets is obtained from the colloid vibration current. In the case of freshly prepared water-in-oil emulsions, the droplet size increased while the surface charge density decreased with time. The time-dependent relaxation of the surface charge ranges from several hours to 3 days, and it is probably due to the slow adsorption/desorption kinetics of bituminous components at the water—oil interface. This study illuminates the contribution of the electrostatic interactions to the stability of water-in-oil emulsions.

Introduction

Oil sands deposits in northern Alberta are mixtures of bitumen, silica sands, and fine clays.[1] Bitumen is a form of heavy oil which needs to be upgraded to obtain commercial fuels. The lesser deep oil sands ores typically contain 9% to 13 wt % bitumen, which is recovered through surface mining operations, followed by a water-based extraction process.[1] At some stage of the process, the extracted bitumen is in the form of bitumen froth, containing about 60% bitumen, 30% water, and 10% solids.[1] Water and solids must be separated from the bitumen prior to upgrading (in order to avoid serious corrosion and plugging problems in upgrading plant operations), and this is done through the addition of an organic solvent (diluent) to the bitumen froth, to lower the density and viscosity of the oil phase.[1] Such a mixture of bitumen froth with organic solvent forms a water-in-oil emulsion. They are referred to as water-in-diluted-bitumen emulsions.

Asphaltenes, fine solids, and natural surfactants present in bitumen have been identified as stabilizing compounds of water-in-diluted-bitumen emulsions. Among them, asphaltenes and fine solids are recognized as the main emulsion stabilizers.[2] They tend to gather at the water—oil interface, resulting in a film which acts as a structural barrier to the coalescence of the water droplets. Most experimental work, to date, suggests that the stability of water-in-diluted-bitumen emulsions is mainly due to a steric repulsion mechanism. Repulsive electrical interactions might have a role in the emulsion stability,[1] as was suggested for instance by Marinova et al.[3] and Karraker and Radke[4] who described electric charge generation at water—oil interfaces. However, the electrical repulsion mechanism has been clearly not sufficiently experimen-

tally investigated. The advent of commercially available ultrasound based techniques during the past decade offers a new opportunity for studying water-in-diluted-bitumen emulsions. They can provide information about size distribution and electrosurface properties of particles or droplets dispersed in nontransparent and nonpolar media, in moderately concentrated dispersions.[5–7] The theory of electroacoustic spectroscopy by Shilov and co-workers based on measurements of the colloid vibration current (CVC) provides the surface charge density of the dispersed phase under the assumption of strongly overlapped double layers.[8–10] Acoustic spectroscopy derives the particle size distribution from measurements of the sound attenuation in the dispersion.[5,11–15] These features are incorporated in the DT-1200 Acoustic and Electroacoustic Spectrometer from Dispersion Technology Inc.[5] The purpose of the present study is to investigate the surface charge density of water droplets dispersed in diluted bitumen by means of this technique and associated theory.

There are few studies reported in the literature relevant to the study of water-in-diluted-bitumen emulsions using the electroacoustic technique, as can be appreciated in two recent review articles written by Hunter.[6,7] Isaacs and co-workers demonstrated that the electroacoustic technique based on colloid vibration potential (CVP) is effective to monitor the rate and extent of coalescence in water-in-crude oil emulsions, and to evaluate the effectiveness of additives to break the emulsion and optimize

---

* Corresponding author. E-mail: ghszabo@usa.net. Fax: 1-780-492-2281.

(1) Czarnecki, J. In *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001; p 497.

(2) Yan, Z.; Elliott, J. A. W.; Masliyah, J. *J. Colloid Interface Sci.* **1999**, *220*, 329–337.

(3) Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Velev, O. D.; Petsev, D. N.; Ivanov, I. B.; Borwankar, R. P. *Langmuir* **1996**, *12*, 2045–2051.

(4) Karraker, K. A.; Radke, C. J. *Adv. Colloid Interface Sci.* **2002**, *96*, 231–264.

(5) Dukhin, A. S.; Goetz, P. J. *Ultrasound for Characterizing Colloids: Particle Sizing, Zeta Potential, Rheology*, 1st ed.; Elsevier Science: New York, 2002.

(6) Hunter, R. J. *Colloids Surf. A* **1998**, *141*, 37–65.

(7) Hunter, R. J. In *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001; p 169.

(8) Dukhin, A. S.; Goetz, P. J. *Colloids Surf. A* **2005**, *253*, 51–64.

(9) Dukhin, A. S.; Goetz, P. J. Dispersion Technology, Inc. Newsletter, Feb 2004. www.dispersion.com.

(10) Shilov, V. N.; Borkovskaja, Y. B.; Dukhin, A. S. *J. Colloid Interface Sci.* **2004**, *277*, 347–358.

(11) Dukhin, A. S.; Goetz, P. J. *Colloids Surf. A* **2001**, *192*, 267–306.

(12) Dukhin, A. S.; Goetz, P. J.; Hamlet, C. W. *Langmuir* **1996**, *12*, 4998–5003.

(13) Wines, T. H.; Dukhin, A. S.; Somasundaran, P. *J. Colloid Interface Sci.* **1999**, *216*, 303–308.

(14) Babick, F.; Hinze, F.; Ripperger, S. *Colloids Surf. A* **2000**, *172*, 33–46.

(15) Dukhin, A. S.; Goetz, P. J. *Langmuir* **2000**, *16*, 7597–7604.

---

their concentration.[16-18] do Carmo Marques and co-workers studied the electrical charging of oil droplets due to asphaltene adsorption in toluene-in-water miniemulsions, using the electroacoustic technique based on electrokinetic sonic amplitude (ESA).[19] After establishing a direct relationship between the ESA signal and the asphaltene content, they concluded that the contribution of asphaltenes to the emulsion stability is based, in principle, on both mechanisms: steric and electrostatic. Dukhin and Goetz studied the stability behavior of water-in-kerosene/SPAN 80 surfactant emulsions and evaluated the surface charge density of the water droplets from measurements of CVC.[8]

The first part of the present study dealt with the investigation of the electroacoustic phenomenon in water-in-diluted-bitumen emulsions. Heavy water (deuterium oxide) was used instead of water with the aim of increasing the magnitude of the electroacoustic signal. We conducted experiments which demonstrate that CVC always exhibits time dependent behavior. CVC also strongly depends on the method of emulsion preparation, particularly on the intensity of water dispersion. In principle, this transient behavior might be due to changes in the water droplet size (inertia effect), concentration of charge carriers in diluted bitumen, and/or water droplet surface charge. Acoustic spectroscopy provided the water droplet size distribution evolution in time. Emulsion conductivity was measured as indicator of the concentration of charge carriers in diluted bitumen. Finally, in the second part of the study, the water droplet surface charge density was evaluated from CVC using Shilov et al. electroacoustic theory. To our best knowledge, this is the first study in the field of electroacoustics which investigates the electrosurface properties of water-in-diluted-bitumen emulsions using Shilov et al. theory.

Theory

The electroacoustic technique is based on the measurement of electroacoustic phenomena. If particles (or droplets) dispersed in a liquid medium are electrically charged, and if the mass densities of the particle and the liquid are different, the application of an acoustic field generates an alternating electric field in the bulk of the dispersion. Similarly, the application of an alternating electric field generates sound waves at the boundaries of the dispersion with its container. Due to the presence of charged particles in a liquid medium, these two acoustic and electric phenomena are coupled together. Any of the two fields can act as the driving field, thus generating a response in the other field which can be measured and ultimately related to the electrosurface properties of the particles in the dispersion.[5-7,10,11,20-25]

Depending on the nature of the response field, the electroacoustic phenomenon is classified in two categories.[5-7] The first category corresponds to the case of applied acoustic field, and the electroacoustic effect is called colloid vibration potential (CVP) if the response is measured as an electric potential between two electrodes, or colloid vibration current (CVC) if an electric current is measured between the two electrodes. The second category corresponds to the case of applied electric field, where the

associated acoustic response is called electrokinetic sonic amplitude (ESA).

The theory of electroacoustics has been under development since 1933 when Debye first predicted this effect.[26] Presently, there are two independent theoretical approaches to electroaocustics: O'Brien's approach[6,7,22-24] and Shilov et al. approach.[5,10,11,20,21] Unfortunately, these two approaches have not merged into a unified electroacoustic theory as yet. O'Brien's approach has been applied to the ESA effect, while Shilov et al. approach has been applied to the CVC effect.[5]

For dispersions in hydrocarbon media such as water-in-diluted-bitumen emulsions, the Shilov et al. approach offers the latest theoretical development for the calculation of the droplet surface charge density in the frame of the quasihomogeneous model.[8-10] Hydrocarbon medium is characterized by low conductivities and, therefore, low ionic concentration. This results in large Debye lengths or $\kappa a \ll 1$ (where "a" is the particle radius and "κ" is the inverse Debye length), to an extent that the double layers are assumed to strongly overlap, irrespective of the dispersed phase concentration. This, in turn, results in a homogeneous charge distribution in the liquid medium, which is the basic assumption of the quasihomogeneous model. The condition of strong overlap of double layers is not restricted to $\kappa a \ll 1$. For any intermediate values of κa, no significant deviation from the homogeneous charge distribution occurs in the liquid medium if the particles are sufficiently close, so that the interparticle distance is smaller than the electric double layer thickness.[8,9] When "d" denotes the interparticle distance, this last condition can be expressed[8] by $\kappa d \ll 1$. The condition $\kappa d \ll 1$, however, is concentration dependent, and there is a minimum concentration of the dispersed phase above which strong overlap of double layers occurs.

We have followed references[5,8] in order to summarize the formulas in the frame of the Shilov et al. theory as follows. The colloid vibration current of the dispersion (CVC) is experimentally found by subtracting the measured CVC signal of the liquid medium (CVC_{medium}) to the measured CVC signal of the dispersion ($CVC_{dispersion}$):

$$CVC = CVC_{dispersion} - CVC_{medium} \qquad (1)$$

Equation 1 is a vector subtraction, as the CVC is mathematically represented by a complex number, having magnitude and phase. The CVC-phase refers to the phase lag between the acoustic perturbation (applied field) and the electric current (electroacoustic response). The details of the component parts and measuring circuit electronics of the DT-1200 electroacoustic probe are discussed by Dukhin and Goetz.[5] The probe includes a transmitting transducer for the generation of 3 MHz sound pulses, and a receiving transducer (consisting of a two-element antenna) for sensing the colloid vibration current.

The dynamic electrophoretic mobility (μ_d) is directly related to the ESA effect, defined as the ratio between the particle (or droplet) velocity and the electric field strength.

(16) Babchin, A. J.; Chow, R. S.; Sawatzky, R. P. *Adv. Colloid Interface Sci.* **1989**, *30*, 111–151.
(17) Isaacs, E. E.; Huang, H.; Babchin, A. J.; Chow, R. S. *Colloids Surf.* **1990**, *46*, 177–192.
(18) Isaacs, E. E.; Chow, R. S. 1992. *Adv. Chem. Ser.* **1992**, *231*, 51–77.
(19) do Carmo Marques, L. C.; de Oliveira, J. F.; González, G. *J. Dispersion Sci. Technol.* **1997**, *18*, 477–488.

(20) Dukhin, A. S.; Shilov, V. N.; Ohshima, H.; Goetz, P. J. *Langmuir* **1999**, *15*, 6692–6706.
(21) Dukhin, A. S.; Shilov, V. N.; Ohshima, H.; Goetz, P. J. *Langmuir* **2000**, *16*, 2615–2620.
(22) O'Brien, R. W. *J. Fluid Mech.* **1988**, *190*, 71–86.
(23) O'Brien, R. W.; Garside, P.; Hunter, R. J. *Langmuir* **1994**, *10*, 931–935.
(24) O'Brien, R. W.; Jones, A.; Rowlands, W. N. *Colloids Surf. A* **2003**, *218*, 89–101.
(25) Marlow, B. J.; Fairhusrt, D.; Pendse, H. P. *Langmuir* **1988**, *4*, 611–626.
(26) Debye, P. *J. Chem. Phys.* **1933**, *1*, 13–16.

Both particle and electric field are characterized by amplitude and phase. Consequently, μ_d is also represented by a complex number. The dynamic electrophoretic mobility can also be related to the other electroacoustic effects (CVP and CVC) by means of a reciprocal relation.[5,22]

$$\mu_d = CVC\left[C_{ant}\frac{2Z}{Z_{ant} + Z}\varphi\left(\frac{\rho_p - \rho_m}{\rho_m}\right)\right]^{-1} \quad (2)$$

Equation 2 shows how μ_d can be derived from quantities accessible to measurement: CVC, liquid medium and particle densities (ρ_m, ρ_p), volume fraction of the dispersed phase (φ), and the acoustic impedances of the electroacoustic probe (Z_{ant}) and dispersion (Z), this latter is approximated as the product of the dispersion density (ρ_s) and sound speed (c_s) as shown by eq 3:

$$Z = \rho_s c_s \quad (3)$$

C_{ant} in eq 2 is a constant evaluated by equipment calibration with a dispersion of known electrosurface properties (i.e., for which μ_d is known). Finally, the surface charge density of particles (σ) is calculated from μ_d as shown by eq 4:

$$\sigma = \mu_d\left[\frac{2a}{3}\frac{\rho_m}{\rho_s\eta_m\Omega + j\omega(1 - \varphi)\frac{2a^2}{9}\rho_p\rho_m}\right]^{-1} \quad (4)$$

for $\kappa a \ll 1$ and/or $\kappa d \ll 1$.

The variables involved in eq 4 which have not been mentioned earlier includes dynamic viscosity of liquid medium (η_m), drag coefficient (Ω), and frequency of the electroacoustic phenomenon (ω). j indicates the complex unit. The calculation of the drag coefficient is discussed by Dukhin and Goetz based on the Kuwabara cell model.[5] When the condition $\kappa d \ll 1$ rather than $\kappa a \ll 1$ applies, the minimum theoretical volume fraction required for strong overlap of double layers (φ_{min}) is given by eq 5:

$$\varphi_{min} \approx \frac{0.52}{\left(1 + \frac{1}{\kappa a}\right)^3} \text{ for } \kappa d \ll 1 \quad (5)$$

In the case of strong overlap of double layers, the formula for σ (eq 4) does not include electrodynamic parameters such as electric conductivity and dielectric permittivity of particle and liquid medium, because the homogeneous distribution of ions eliminates polarization charges induced by the liquid motion.[8] In this case, the nature of the electroacoustic effect is not due to the polarization of double layers but to the generation of a current associated to the oscillating motion of charged particles.[8] Apart from the surface charge density, the generation of the CVC effect is purely hydrodynamic. As demonstrated by Babchin et al.,[16] when the density of the particle is larger than the density of the liquid, the motion of the particle lags behind the fluid in amplitude and phase. Dependence of the electroacoustic effect on particle size (also called inertia effect) is important when $\omega/\omega_{hd} \geq 1$, where ω is the frequency of the driving acoustic field and ω_{hd} is the characteristic hydrodynamic frequency[5-7] which is given by eq 6:

$$\omega_{hd} = \frac{\eta_m}{a^2\rho_m} \quad (6)$$

The condition $\omega/\omega_{hd} \geq 1$ implies that the transfer of momentum through viscous coupling between particles (or droplets) and liquid medium has a characteristic time equal or higher than the period of oscillation in the acoustic field. Considering a fixed frequency of oscillation and surface charge density of particles, the inertia effect would manifest as a reduction in the magnitude of the dynamic electrophoretic mobility and CVC as the particle size increases.[5-7] Currently, Shilov's theory is under development in order to extend to the case where double layers do not overlap strongly.[10] The latter situation is an intermediate case between the two limiting cases of strongly overlapped double layers ($\kappa a \ll 1$ or $\kappa d \ll 1$) and thin double layers ($\kappa a \gg 1$). The second part of the published paper[10] already contains a theory for any κa, but restricted in frequency. It assumes that frequency of measurement is much higher than Maxwell Wagner frequency. Conductivity does not play any role at this condition.

Experimental Section

Materials for the preparation of water-in-diluted-bitumen emulsions include Diluent Recovery Unit bitumen feed from Suncor Energy Inc. (a mixture of 0.7 naphtha to 1.0 Athabasca bitumen by weight), toluene HPLC grade (Fisher Scientific), and deuterium oxide 99.8% atom D (Fisher Scientific).

Calibration of the electroacoustic probe was made with aqueous silica dispersion (10 wt %, ζ-potential -38 mV), prepared by diluting 50 wt % Silica Luddox TM-50 dispersion provided by Dispersion Technology Inc. with 0.01 M KCl (ACS reagent Sigma-Aldrich) electrolyte solution adjusted to pH 10 with KOH (ACS reagent BDH).

Sample Preparation. A stock diluted bitumen solution was prepared by mixing the Diluent Recovery Unit bitumen feed (as received from Suncor) and toluene at a weight ratio of 1:1 for 4 h in a high-speed shaker (200 per minute). Heavy water was used to maximize the density contrast between the continuous and dispersed phases, with the aim of increasing the magnitude of the electroacoustic signal. The heavy water concentration in diluted bitumen was varied from 2% to 30 wt %.

The standard procedure for the emulsion preparation consisted in the addition of known weights of diluted bitumen and heavy water into the spectrometer chamber (approximately 125 mL total volume per emulsion sample), followed by water dispersion for 3 min with a high-speed homogenizer temporarily introduced in the chamber (Fisher Scientific, PowerGen Homogenizer 125 W and 30 000 rpm). The DT-1200 spectrometer is described in detail in reference.[5] It includes a magnetic stirrer device at the bottom of the chamber, which acts as a vortex stirrer and also as a centrifugal pump to circulate fluid from bottom to top of the chamber through the recirculation line (Figure 1). The emulsion sample was kept under gentle stirring after water dispersion to prevent water droplets sedimentation during measurements. The 4th magnetic stirring speed in the scale from 1 (minimum) to 6 (maximum) was selected for all experiments since diluted bitumen and heavy water are introduced into the chamber.

Electroacoustic Measurements. Some instrument improvements were made to the DT-1200 spectrometer chamber. The original chamber is composed of two blocks made of plastic material, tightly joined by thumbscrews (this is illustrated by the two blocks shown in Figure 1). The upper block is attached to the acoustic sensor for sound attenuation measurements. The lower block (where the electroacoustic probe is installed) is removable by unscrewing the thumbscrews. This lower block was replaced by a water-jacketed metallic chamber, which allowed temperature control of the emulsion sample (around 20.7 ± 0.2 °C) by means of a circulating water bath (Fisher Scientific, Isotemp 3016). The spectrometer includes a temperature probe in the chamber for continuous monitoring of the sample temperature. The metallic chamber also functioned as a Faraday shield to the electroacoustic probe, in an attempt to reduce the noise of the CVC signal. The metallic chamber was grounded to the stainless steel shell of the electroacoustic probe. We report
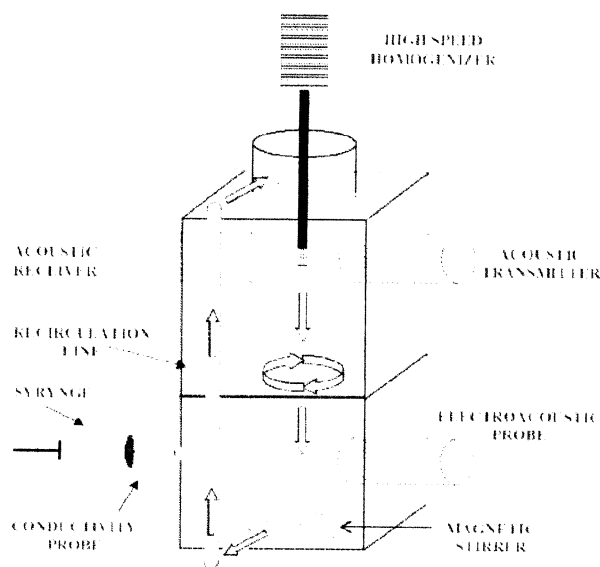
Figure 1. Details of the DT-1200 spectrometer chamber.[27]

the magnitude of CVC as available in the DT-1200 software in all our experiments.

Acoustic Measurements. The DT-1200 spectrometer measures the sound attenuation coefficient of the dispersion sample in the 3–100 MHz range, thus generating and acoustic spectrum. The particle size distribution is then calculated using a suitable predictive theory.[5] Two statistically representative distributions are considered by the spectrometer software: log-normal and bimodal particle size distribution (the later defined as the superposition of two log-normal distributions with the same standard deviation). The results are reported based on the type of distribution that minimizes the fitting error of the predictive theory to the measured acoustic spectrum. The instrument measures the particle size for system containing particles within the 5 nm to 1 mm size range.[5]

In addition to the concentration of the dispersed phase, the most important properties that should be known with accuracy for dispersions with soft particles, such as emulsions, are the density, thermal expansion, intrinsic attenuation coefficient, and sound speed of both phases.[5] These properties were measured[27] at 20 °C, and their values are provided in Table 1. We have measured the attenuation coefficient of emulsions in the 3–100 MHz range in all our experiments, but we have reduced the frequency range for analysis of droplet size down to 3–30 MHz in order to adapt to the long wavelength regime, where theoretical treatment is the most rigorous. The long wavelength regime corresponds to the case where particle size is much smaller than the wavelength of sound.[5,14] According to Dukhin and Goetz,[28] the highest frequency for analysis should be restricted down to at least 30 MHz if the particle size exceeds 10 μm. Considering that the speed of sound in emulsions was in the order of 1380 m/s in all our experiments, the 3–30 MHz frequency range would be appropriate for droplet size below about 50 μm. Microscope observations of freshly prepared emulsion samples revealed the presence of water droplets in the micrometer size range below 50 μm in diameter.[27]

One fundamental limitation of the analysis in the 3–30 MHz range is the inability to detect the presence of very small droplets of the order of tenths of nanometers (<100 nm), because they do not attenuate sound at such low frequencies.[5,28] In view of this fact, it seems that the restriction imposed by the long wavelength regime might prevent the analysis of the complete droplet size distribution of the emulsion. Should a significant fraction of

(27) Magual, A. *Electroacoustic spectroscopy of water-in diluted bitumen emulsions*; Master Thesis. Department of Chemical and Materials Engineering, University of Alberta 2005.

(28) Acoustic and Electroacoustic Spectrometer DT-1200 User Handbook 1999; Dispersion Technology Inc.
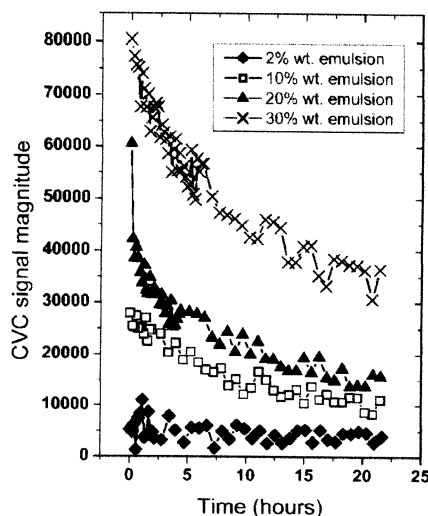
Table 1. Physical Properties of Diluted Bitumen and Heavy Water at 20 °C[27]

	diluted bitumen	heavy water
density [kg·m³] {ρ}	919	1,100
thermal expansion [K⁻¹] {β}	10.8 × 10⁻⁴	1.09 × 10⁻⁴
specific heat [J·kg⁻¹·K⁻¹] {c_p}	1.63 × 10³ ᵃ	4.179 × 10³ ᵇ
dynamic viscosity [Pa·s] {η}	4.9 × 10⁻³	1.32 × 10⁻³
thermal conductivity [W·m⁻¹·K⁻¹] {τ}	0.14	0.6098
sound speed [m·s⁻¹] {c}	1378.0	1386.6
intrinsic attenuation coefficient (dB·cm⁻¹·MHz⁻¹		
{α_{int} 3.0 MHz}	0.181	0.028
{α_{int} 3.7 MHz}	0.192	0.015
{α_{int} 4.5 MHz}	0.191	0.004
{α_{int} 5.6 MHz}	0.215	0.013
{α_{int} 6.8 MHz}	0.247	0.025
{α_{int} 8.4 MHz}	0.260	0.028
{α_{int} 10.3 MHz}	0.293	0.033
{α_{int} 12.7 MHz}	0.327	0.041
{α_{int} 15.6 MHz}	0.363	0.049
{α_{int} 19.2 MHz}	0.408	0.0606
{α_{int} 23.5 MHz}	0.456	0.0714
{α_{int} 28.9 MHz}	0.517	0.0880
{α_{int} 35.5 MHz}	0.590	0.1069
{α_{int} 43.7 MHz}	0.678	0.1321
{α_{int} 53.6 MHz}	0.781	0.1625
{α_{int} 65.9 MHz}	0.898	0.1975
{α_{int} 81.0 MHz}	1.043	0.2455
{α_{int} 99.5 MHz}	1.210	0.301
conductivity [S·m⁻¹] {K_m}	9.4 × 10⁻⁷	

ᵃ Property approximated to toluene. ᵇ Property approximated to water.

nanometer-size water droplets exists (besides the observed micrometer-size fraction), then the smaller fraction might be ruled out from the analysis. However, we have partially addressed the later issue based on the qualitative interpretation of the acoustic spectrum as follows. There are three mechanisms of sound attenuation of importance in emulsion systems:[5,14] intrinsic (α_{int}), thermal (α_{th}), and scattering (α_{sca}). The predictive theory for particle size distribution analysis assumes that the attenuation coefficient of the dispersion (α) is the sum of the individual attenuation mechanisms:[5,14]

$$\alpha = \alpha_{int} + \alpha_{th} + \alpha_{sca} \tag{7}$$

The baseline of the acoustic spectrum is the intrinsic attenuation of the dispersion, which corresponds to the dissipation of acoustic energy on a molecular level associated to the continuous and dispersed phases as homogeneous phases. Any excess attenuation above this level is the part of the spectrum which is truly sensitive to the particle size distribution. The two relevant mechanisms of excess attenuation for emulsions are thermal loss (adsorption of sound energy) and scattering loss (sound redirection).[5,14] As explained by Babick et al.,[14] excess attenuation is mainly due to sound adsorption (thermal loss) in the entire frequency range (3–100 MHz). α_{th} is proportional to a^2 at the low-frequency limit and to a^{-1} at the high-frequency limit.[14] Consequently, thermal loss due to large droplets (micrometer size) would cause excess attenuation at the lower frequencies while very small droplets (nanometer size) would cause excess attenuation at the higher frequencies. The situation is different for the scattering loss mechanism,[11] as it is a strong function of droplet size (a^3), and particularly on frequency (ω^4). Consequently, scattering loss shows up at the higher frequencies only,[14] and it is important for large droplets (micrometer size). According to Dukhin and Goetz,[11] scattering is not important for sizes below 1 μm in the 3–100 MHz frequency range.

From the above discussion it is clear that there is a difficulty (from the perspective of acoustic spectroscopy) in differentiating between a unimodal droplet size distribution in the micrometer range from a bimodal size distribution of large (micrometer size) and very small (nanometer size) droplets. Both cases show excess attenuation at the higher frequencies which creates a two-solution problem when calculating the droplet size distribution from the measured acoustic spectrum in the 3–100 MHz range, even if

Figure 2. The time dependent behavior of CVC of freshly prepared emulsions.

within the long wavelength regime. The qualitative interpretation of the acoustic spectrum, however, might differentiate between these two cases as long as the mechanism of sound attenuation at the higher frequencies is identified. As explained later in the discussion of results, the droplet size distribution that best characterizes the redispergation state of emulsions in our experiments is a unimodal (log-normal) size distribution in the micrometer size range, as calculated from the 3 - 30 MHz analysis. We provide evidence that suggests that scattering loss is the most likely mechanism of sound attenuation at the higher frequencies, which supports the concept of a unimodal droplet size distribution in the micrometer range in our experiments.[27]

Conductivity Measurements. Another instrument improvement was the installation of a conductivity meter (Scientifica, model 627), provided with a stainless steel flow-through probe which was connected to the recirculation line as shown in Figure 1. The conductivity probe could not be installed in the main recirculation line because it caused significant restriction to flow. Therefore, it was installed on a side connection (previously used for chamber drainage). Sample was drawn into the conductivity probe by means of a 3 mL Teflon syringe (Braun Injekt). To get a representative sample, normally 30 strokes were performed to expose the probe to fresh sample before conductivity reading. The full scale of the conductivity meter is 38 to 38 000 picosiemens/cm with an accuracy of 2%. Conductivity is measured at 18 Hz with an applied voltage of 5 V rms, approximately.

Results and Discussion

Surface Charge Determination. Figure 2 shows the CVC signal magnitude of emulsions in the 2% to 30 wt % heavy water content range. The standard procedure for the emulsion preparation consisted of the dispersion of heavy water in diluted bitumen using the high-speed homogenizer for 3 min. The CVC signal magnitude always decreased with time. Further experiments demonstrated that the initial peak value of CVC is sensitive to the intensity of water dispersion. Following the standard protocol of heavy water dispersion, Figure 2 shows that the higher the heavy water content, the higher the magnitude of CVC over the 24 h time span investigated. CVC of the 2 wt % emulsion should be below the limit of detection of the electroacoustic probe, as the measured signal reached the noise level. CVC of diluted bitumen with no added water corresponds to the noise level of the CVC signal expected for any emulsion. Based on 70 measurements of CVC for diluted bitumen,[27] the noise level of CVC is estimated as 5000.

To investigate the relationship between CVC and the dispergation state of emulsion, a further experiment was
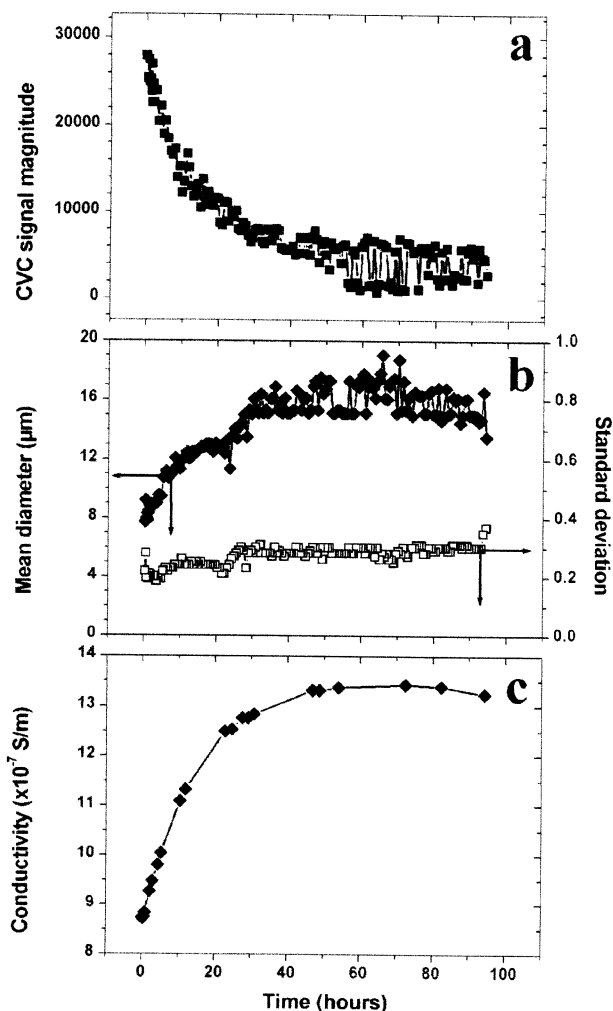

Figure 3. 10 wt % Emulsion: (a) CVC, (b) droplet size distribution, (c) conductivity.

conducted at a fixed heavy water content of 10 wt %. Figure 3 shows the CVC, droplet mean diameter, and conductivity of 10 wt % emulsion for a time span of 4 days. These quantities change on the same time scale. Clearly, a correlation can be observed between CVC, conductivity, and the droplet mean size of emulsion: the higher the droplet size, the lower the CVC magnitude and the higher the emulsion conductivity.

Considering that the frequency of the acoustic field is 3 MHz, the critical droplet diameter above which inertial effects are important is 2.7 μm ($\omega/\omega_{hd} = 1$). The droplet size distribution shown in Figure 3b confirms that the droplet diameter was above this critical value. The droplet mean size started increasing from 8 μm, and it leveled off at 16 μm after 2 days. Considering a standard deviation of 0.25 for the log-normal size distribution, it can be said that the majority of water droplets were in the size range between 2 and 60 μm in diameter during the experiment. Consequently, inertial effects are important and the observed droplet size dependence of CVC is in accordance with theoretical considerations.

Figure 4 shows a 10 wt % emulsion redispersion experiment where the high-speed homogenizer was applied every 24 h after the initial emulsion preparation following the standard protocol. The aim of this test was to investigate the relaxation behavior of CVC. The redispersion of the emulsion brings the system back to
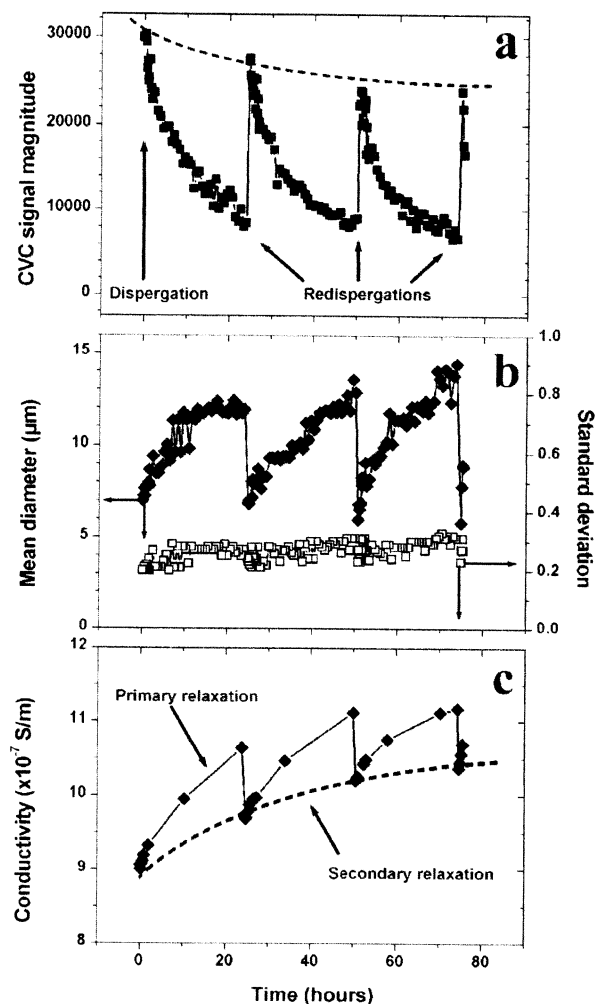
Figure 4. 10 wt % emulsion (redispersion every 24 h after emulsion preparation): (a) CVC, (b) droplet size distribution, (c) conductivity.

the same dispergation state, with an associated partial recovery of the CVC signal. A similar effect is observed for the emulsion conductivity. We have verified that such a fact is indeed reproducible with the only difference being the magnitude of the increase in the emulsion conductivity.[27] Although the transient behavior of CVC and emulsion conductivity are strongly correlated with the droplet size, Figure 4 points out that this is not the only factor. The fact that CVC and emulsion conductivity (highlighted by dashed lines in Figures 4a and 4c) have only a partial recovery cannot be explained in terms of the droplet size alone. Therefore, a superposition of two relaxation behaviors can be distinguished as follows: (i) primary relaxation (or relaxation in the droplet size); (ii) secondary relaxation (or superimposed relaxation due to yet an unknown factor).

The dashed lines in Figures 4a and 4c suggest that the process associated to the superimposed relaxation is characterized by long transients, in the order of several hours or even days before it apparently stabilizes. Recognizing that CVC is related to the electrosurface properties of the emulsion as well as to the droplet size, the observation of a super-imposed relaxation in the CVC signal might well reflect a phenomenon occurring at the water—oil interface. We postulate that such long transients might be attributed to the slow adsorption—

desorption kinetics of bituminous components (such as natural surfactants and asphaltenes) at the water—oil interface.

As demonstrated by Sheu et al.,[29-31] the characteristic time of adsorption of asphaltenes at toluene-water interfaces is in the order of hours, much longer than those of surfactants. Asphaltenes are recognized as main emulsion stabilizers of water-in-diluted-bitumen systems, forming complex adsorption layers with resins, which prevent droplet coalescence or flocculation.[32] (Goual et al. in ref 32 referred to resins as all the surface-active materials present in maltenes.) Consequently, time-dependent properties of such adsorbed layers are to be expected. Combining these things with the fact that adsorbed asphaltenes contribute to the surface charge of the water—oil interface,[19] it is reasonable to postulate that the super-imposed relaxation of CVC is connected to the interfacial adsorption process.

Before discussing the derivation of the water droplets surface charge density from the measured CVC, we need to demonstrate that the electroacoustic phenomenon is indeed related to the presence of the emulsified water drops. Fine solids and entrapped air microbubbles might exhibit surface charge high enough to generate their own electroacoustic effect. As discussed by Chen et al.,[33] toluene can remove natural surfactants adsorbed on fine solids, making them more hydrophilic. This "interfacial washing" effect, which could be strengthened by the vigorous agitation achieved with the homogenizer, might result in a relaxation type behavior too. On the other hand, as discussed by Goetz and El-Aasser,[34] the introduction of air microbubbles after sample dispersion is an issue of concern, because entrapped air bubbles can acquire surface charge by the adsorption of natural surfactants present in bitumen at the air-oil interface. The electroacoustic phenomenon associated with the air bubbles could be higher than the one associated to the water droplets because of the larger density contrast existing between air and diluted bitumen.[34] We have verified that no CVC signal above the noise level can be detected when the high-speed homogenizer is applied to diluted bitumen only (with no added water), following the standard protocol.[27] We wish to emphasize that such a test ruled out the possibility that other components in diluted-bitumen different from water droplets (such as fine solids or air micro-bubbles) are responsible on their own for the observed CVC of emulsions.

We cannot disregard the possibility of electrical charging of water droplets due to the intense shear exerted by the high-speed homogenizer. However, this appears not to be the case since CVC is still measurable for emulsions prepared without the high-speed homogenizer, provided that heavy water concentration is sufficiently high. This is the case when 30 wt % water was dispersed in diluted-bitumen only with a gentle mixing of the magnetic stirrer of the spectrometer chamber at the maximum stirring speed.[27] The fact that no CVC effect can be detected at lower than 30 wt % heavy water concentrations without the application of the high-speed homogenizer could be

(29) Sheu, E. Y.; De Tar, M. M.; Storm, D. A. *Fuel* **1992**, *71*, 1277–1281.

(30) Sheu, E. Y.; Storm, D. A.; Shields, M. B. *Fuel* **1995**, *74*, 1475–1479.

(31) Sheu, E. Y. *J. Phys.: Condensed Matter* **1996**, *8*, A125–A141.

(32) Goual, L.; Horvath-Szabo, G.; Masliyah, J.; Xu, Z. *Langmuir*, in press.

(33) Chen, F.; Finch, J. A.; Xu, Z.; Czarnecki, J. *J. Adhesion Sci. Technol.* **1999**, *13*, 1209–1224.

(34) Goetz, R. J.; El-Aasser, M. S. *J. Colloid Interface Sci.* **1992**, *150*, 436–452.
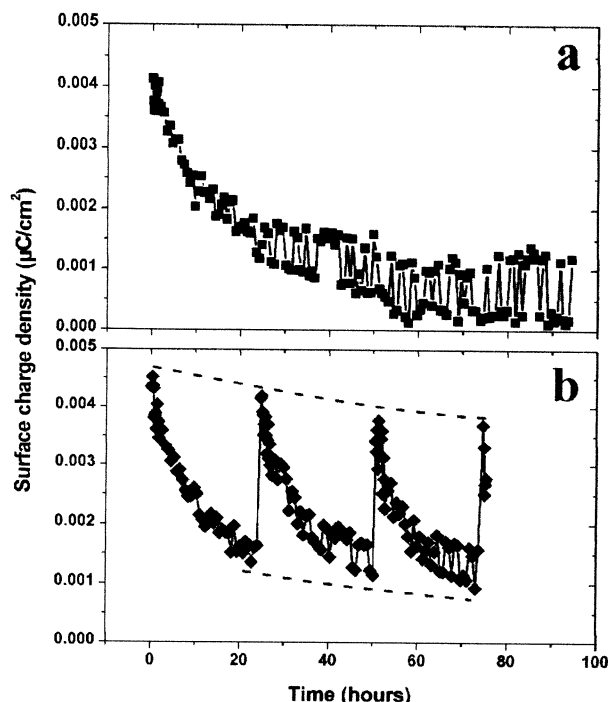
Figure 5. Water droplets surface charge density derived from CVC: (a) 10 wt % emulsion, (b) 10 wt % emulsion with redispersion every 24 h.

explained by inertial effects (the droplet size might be too large for the CVC to be measured).

The nature and concentration of ionic species in bitumen media is still not well understood, and this precludes estimation of the magnitude of the dimensionless inverse Debye length (κa) of the emulsified water droplets in water-in-diluted-bitumen emulsions. The calculation of the water droplet surface charge density by means of the Shilov et al. theory[8-10] assumes strong overlap of double layers, which is the case of most dispersions in hydrocarbon media. This theory allows screening the inertial effect on the CVC signal and then calculating the surface charge density of water droplets. The present state of the theory has been formulated for monodisperse systems only. Figure 5 shows the calculated water droplet surface charge density of the two 10 wt % emulsion experiments discussed earlier (Figures 3 and 4). Similar to the CVC data, the droplet surface charge density shows a transient behavior after the emulsion preparation: it decreases with the same time scale as the scale of increase for droplet size and emulsion conductivity. The diminishing surface charge suggests that inertia effects are not solely responsible for the decrease in the magnitude of CVC of emulsions. There should be an additional contribution due to the decrease in the surface charge density of the water droplets with time.

We have postulated earlier in this work that the well-known adsorption—desorption process of bituminous components at the water—oil interface may be connected to the long transients observed for CVC and the calculated droplet surface charge density. The peak value of the surface charge density might reflect the initial quick adsorption of low molar mass components (resins or natural surfactants) at the interface because of their quick diffusion. In a time scale of hours, however, the high molar mass asphaltenes of low diffusion coefficient compete with resins for the same interface thereby resulting in an eventual and partial replacement of resins with asphaltenes. The suggestion of this mechanism stems from the

general understanding of the competitive adsorption mechanism of components with different molar masses. For the majority of mixed polymer systems studied, the systems arrive at thermodynamic equilibrium after some hours. Usually the lower molecular mass polymers are adsorbed first but are then displaced by the more strongly adsorbed higher molecular mass components.[35] Thus the partial replacement of resins with asphaltenes at the interface might be responsible for the decrease in the droplet surface charge density with time. (We want to stress here that our current results[32] suggest that when asphaltenes adsorb at the oil/water interface from a crude it is the complex unit of resin-stabilized asphaltene which adsorbs at the O/W interface and competes with the free resins for the interface). Such replacement process may also explain why the emulsion conductivity increases for freshly prepared emulsions. When resins, natural surfactants, and asphaltenes are considered as either charge carriers or charge stabilizers in the hydrocarbon media, then the competitive adsorption would result in an eventual and partial release of the higher equivalent conductance components (resins or natural surfactants) from the interface to the oil phase, and the withdrawal of the lower equivalent conductance components (asphaltenes) from the oil phase. The overall effect would be an increase of emulsion conductivity with time, which is in agreement with our experimental findings (Figure 3c). This proposed mechanism also predicts a sudden decrease of emulsion conductivity (Figure 4c) during redispersion because of the temporary removal of charge carriers or stabilizers with high diffusion coefficient. It is because at redispergation, to some extent, new interfaces are formed increasing by this manner the adsorption capability. Since, however, not all the o/w interfacial area are freshly formed, the conductivity cannot descend back exactly to the value corresponding to the previous dispergation step. This can be the very reason of the secondary relaxation of the conductivity. The segment line in Figure 4c shows that with time an increasing portion of the interfacial area is covered with low diffusion coefficient material (asphaltenes) which cannot be removed at the consecutive redispergation step.

Determination of the Size Distribution. To our best knowledge, there is no previous work in the literature dealing with the determination of the droplet size distribution of water-in-diluted-bitumen emulsions by means of acoustic spectroscopy. Published emulsion studies using the DT-1200 spectrometer cover: oil-in-water and water-in-oil cosmetic emulsions,[36] heptane/water/AOT microemulsions,[13] and water-in-kerosene/SPAN 80 emulsions.[8] The theoretical aspects of acoustic spectroscopy are discussed elsewhere.[5,11,12,14,15] In our experiments, the droplet size distribution analysis by acoustic spectroscopy has revealed that the dispergation state of emulsions is characterized by a unimodal (log-normal) size distribution in the micrometer size range (2−60 μm in diameter). As mentioned earlier in the Experimental Section, our measurements of the droplet size are based on the analysis of the acoustic spectrum in the 3−30 MHz in order to adapt to the long wavelength regime.

Besides the restriction imposed by the long wavelength regime, we have also mentioned before the ill-defined problem (two-solution problem) that might arise if our analysis is performed in the whole frequency range (3−100 MHz), which stems from the fact that the two

(35) Kawaguchi, M. Adv. Colloid Interface Sci. 1990, 32, 1−41.
(36) Fairhurst, D.; Dukhin, A. S.; Klein, K. Dispersion Technology, Inc. Newsletter, Apr 2001, www.dispersion.com.
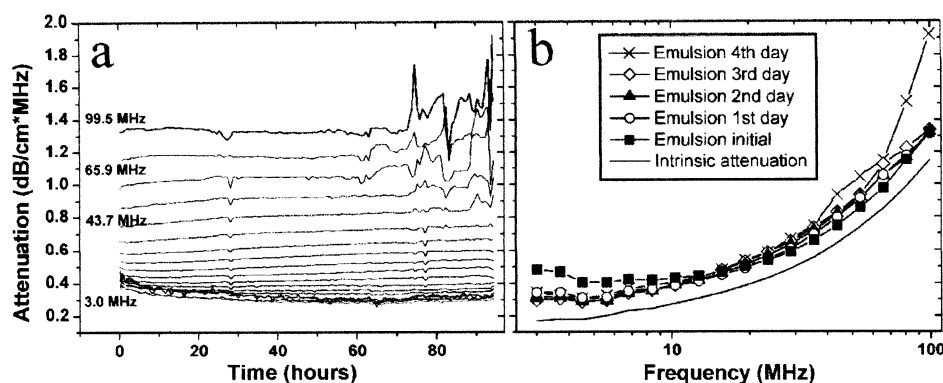
Figure 6. Attenuation coefficient of 10 wt % emulsion as a function of time and frequency: (a) attenuation versus time, (b) attenuation versus frequency.

mechanisms of sound attenuation in the case of emulsions (namely, thermal and scattering losses) scale differently with the droplet size. Excess attenuation at the higher frequencies in the 3–100 MHz range could be due to the presence of large droplets (micrometer size) via scattering loss mechanism, or very small droplets (nanometer size) via thermal loss mechanism. Therefore, we would face a two-solution problem depending on how the predictive theory fits the measured attenuation coefficient in the 3–100 MHz range, particularly at the higher frequencies. Either the calculated droplet size distribution would be unimodal in the micrometer size range (if attenuation at the higher frequencies is taken as due to scattered sound) or bimodal with two fractions in the nanometer and micrometer size range (if thermal loss scattering is assumed at the higher frequencies). We have confirmed the presence of micrometer size water droplets by microscope observations.[27] The logical question is whether a significant second fraction of nanometer size droplets were present in the emulsions as to more accurately characterize it as bimodal.

We think that scattering loss is the most likely explanation of the attenuation behavior at the higher frequencies, which consequently supports the concept of a unimodal droplet size distribution in the micrometer size range as shown in Figures 3b and 4b. Our rationale is based on the qualitative interpretation of the acoustic spectrum. Figure 6a shows the attenuation spectrum as a function of time corresponding to the emulsion experiment shown in Figure 3. Each line in Figure 6a corresponds to the attenuation coefficient at a specific frequency. There are 18 frequencies in total increasing from bottom to top; from 3 to 100 MHz. Figure 6b shows the same attenuation spectrum as a function of frequency; only five measurements are shown with 1 day interval between. The intrinsic attenuation (baseline of the acoustic spectrum) is also shown in Figure 6b.

It can be observed in Figure 6a that attenuation in the whole frequency range changes smoothly with time during the first 3 days. Particularly, attenuation in the 3–30 MHz range used for droplet size calculations changes with time during the first 40 h and then stabilizes. However, after 3 days the attenuation at the higher frequencies (>65 MHz) suddenly increased and showed an erratic behavior. It is important to emphasize that such erratic behavior continued until the experiment ended after 24 h. Also, it is important to recognize that this erratic behavior starts first at the higher frequencies (>65 MHz) and then seems to propagate to the intermediate frequencies (>43 MHz). The same erratic behavior for the higher frequency attenuation was always observed when an

emulsion experiment was conducted for a long period of time (few days). Indeed, supplementary experiments[27] demonstrated that when the water content is increased (20 wt %), such erratic behavior appeared earlier (1 day after water dispersion). Finally, the redispersion of the emulsion with the high-speed homogenizer eliminates this erratic pattern at the higher frequencies, and the attenuation spectra changes again smoothly with time.[27]

The erratic behavior observed for the higher frequency attenuation can be explained in terms of scattering. This erratic behavior occurs one or more days after water dispersion with the high-speed homogenizer, when the droplet mean size has apparently leveled off. A condition of dynamic equilibrium is reached where the rate of aggregation or coalescence of water droplets is comparable to the rate of aggregate disjoin or droplet breakup. Given the fact that sound scattering is very sensitive to droplet size, the oscillatory nature of the high frequency attenuation could be the consequence of the sound scattered by the larger water droplets in the size distribution. The erratic oscillation of attenuation may well reflect the fact that cycles occur where droplets coalesce or aggregate due to droplet collision (thus increasing their effective size), eventually reaching a critical size where shearing forces causes droplet breakup or aggregate disjoin (thus decreasing their effective size again).

The fact that the erratic behavior occurs first at the higher frequencies in the 3–100 MHz spectrum and then seems to propagate to intermediate frequencies is in agreement with the strong frequency dependence of the scattering mechanism. Furthermore, the observation that the erratic attenuation never occurs immediately after water dispersion but with one or 2 days time delay is in agreement with the calculated droplet size evolution in time. After water dispersion with the high-speed homogenizer, it would take time for the droplet size to increase until a significant population of large droplets is formed that would start to scatter sound significantly. Most importantly, the fact that the redispersion of the emulsion eliminates the erratic pattern is to be expected based on the frame of the sound scattering mechanism. The redispersion of the emulsion brings the system back to the initial dispergation state where no erratic behavior was previously observed. The high-speed homogenizer reduces the droplet size to an extent where water droplets are no longer able to significantly and erratically scatter sound.

Conclusions

This study demonstrates that the colloid vibration current (CVC) electroacoustic phenomenon is measurable

for water-in-diluted-bitumen emulsions. The CVC magnitude of emulsions is time dependent with a characteristic time of several hours or even days. Two relaxation behaviors were identified: a primary relaxation in the droplet size where CVC decreases as water droplet size increases, and a super-imposed secondary relaxation which is presumably associated to other factors intervening on CVC such as the surface charged density of water droplets and emulsion conductivity. The calculation of the surface charge density of the water droplets by means of the Shilov et al. theory[8-10] assumes strong overlap of double layers, which is the case of most dispersions in hydrocarbon media. The analysis of the CVC phenomenon in terms of Shilov et al. theory results in a decreasing surface charge density of droplets for freshly dispersed water in diluted bitumen. Such long transients are probably due to the slow adsorption/desorption kinetics of bituminous components at the water–oil interface.