

Electrical properties of bitumen emulsions

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The complex dielectric constant (permittivity) of water-in-bitumen emulsion was measured for emulsions with water volume fractions ranging from 0 to 0.5, in steps of 0.1. Significant departure from theoretical calculation was observed, and was attributed to the presence of polar components in the bitumen. Owing to the presence of salt in the water phase, the interfacial relaxation was found to be > 1 MHz. Low-frequency measurements can therefore be used to estimate the water volume fraction in laboratory emulsion flow experiments.

(Keywords: bitumen; emulsions; permittivity)

The flow of emulsions in porous media is a physical phenomenon important to the petroleum industry in mobility control¹ and in enhanced oil recovery processes such as chemical flood² or cyclic steam stimulation³. The interest in the present case is to understand the flow behaviour of water-in-bitumen emulsion in Imperial Oil Resources Limited (IORL)'s operation in Cold Lake, Alberta. Under certain experimental conditions, it was found necessary to be able to monitor the individual volume fractions without phase separation. Electrical measurement, being a fairly well understood technique and easily adaptable to the experimental set-up, was chosen for this purpose.

The initial concept was based on the fact that the dielectric constants (permittivities) of bitumen and water are sufficiently different for a dispersion of one phase in the other to take intermediate values. The only requirement appeared to be the establishment of a one-to-one relation between the dielectric constant of an emulsion and its phase volume. Obviously, the dielectric dispersion of heterogeneous material is a potential problem that might interfere with data interpretation. The primary objective of this study was to understand the electrical properties of water-in-bitumen emulsions to achieve better interpretation of laboratory data.

Workers in other industries have used dielectric measurements to monitor the quality of emulsions. The electrical properties of emulsions have been studied extensively^{4,5}. In the literature there have been many independent verifications of Hanai's equation⁴ relating the complex dielectric constant of an emulsion to its component dielectric properties and its dispersed-phase volume. A significant departure from this equation is found in bitumen emulsions. This may be due to the polar components in the bitumen. Although the discrepancy between theory and experiment may be of theoretical interest, the lack of understanding of this phenomenon does not impede the use of dielectric

measurements to estimate water volume fractions in the laboratory.

THEORY

The problem of calculating the dielectric constant of a heterogeneous system from the component properties and volume fractions was considered as early as the last century by Maxwell and Rayleigh⁴. More recent studies^{4,5} showed that the equation developed by Bruggeman and later applied to emulsions by Hanai⁴ gives the best fit to a number of experimental data. In this equation, the complex dielectric constant, ϵ^* , is given by

$$\left(\frac{\epsilon^* - \epsilon_d^*}{\epsilon_c^* - \epsilon_d^*} \right)^3 \frac{\epsilon_c^*}{\epsilon^*} = (1 - \phi)^3 \quad (1)$$

where ϕ is the volume fraction of the dispersed phase, and the subscripts d and c denote the dispersed and continuous phases respectively.

For water-in-oil emulsions, the conductivity of the dispersed phase is much higher than that of the continuous phase, so the low- and high-frequency dielectric constants ϵ_l and ϵ_h can be approximated by

$$\epsilon_l = \epsilon_c \frac{1}{(1 - \phi)^3} \quad (2)$$

and

$$\left(\frac{\epsilon_h - \epsilon_d}{\epsilon_c - \epsilon_d} \right)^3 \frac{\epsilon_c}{\epsilon_h} = (1 - \phi)^3 \quad (3)$$

respectively. In these regions ϵ is a simple function of ϕ and the component dielectric constants. In between, interfacial relaxation reduces the low-frequency value given by Equation (2) to the high-frequency value given by Equation (3); ϵ is a strong function of the frequency there. It is therefore necessary to choose a frequency outside this range so that either of these equations may be used to estimate ϕ .

Experiments by a number of authors have verified

Hanai's equation for water in oils such as Nujol weighted with carbon tetrachloride⁶, kerosene, transformer oil and terpene⁷, and vaseline⁸. Those workers all used distilled water as the dispersed phase, and the relaxation frequency was determined to be ~ 100 kHz.

EXPERIMENTAL

Bitumen

The bitumen used was produced by cyclic steam stimulation in Cold Lake. The crude produced is always in the form of water-in-oil emulsion, with suspended fines as well. The water was removed by vacuum distillation at 220°C. The light ends evaporated in this process were collected and remixed with the bulk oil. This treatment eliminated only water from the crude. Dissolved salts in the water remained as crystals suspended in the bitumen. The fines stayed suspended as well. These solids were removed by centrifuging and further filtering the top portion with 7 and 2 μm filters.

Both the measured dielectric constant and the conductivity of bitumen at 20°C are almost linear on a log-log plot, as shown in Figure 1. The scatter in the data at both ends of the spectrum was due to limitations of the equipment. The value of ϵ_0 was slightly higher than the 2 to 2.5 obtained for hydrocarbons⁹. A power relation can be fitted to these data:

$$\epsilon_0 = 3.05 f^{-0.016} \quad (4)$$

$$\kappa_0 = 3.14 \times 10^{-14} f^{1.017} \quad (5)$$

Similar behaviour has been observed for an aqueous dispersion of solid particles or macromolecules¹⁰. The exact nature of this power dependence has not been established.

Water

Since the water in the formation is saline, and the injected steam is fresh, the salinity of the water

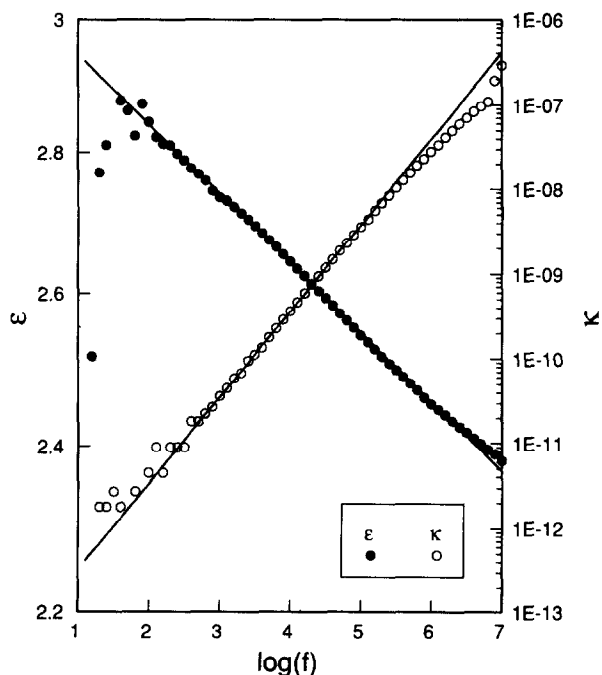


Figure 1 Dielectric constant (*) and conductivity (O) of bitumen at 20°C

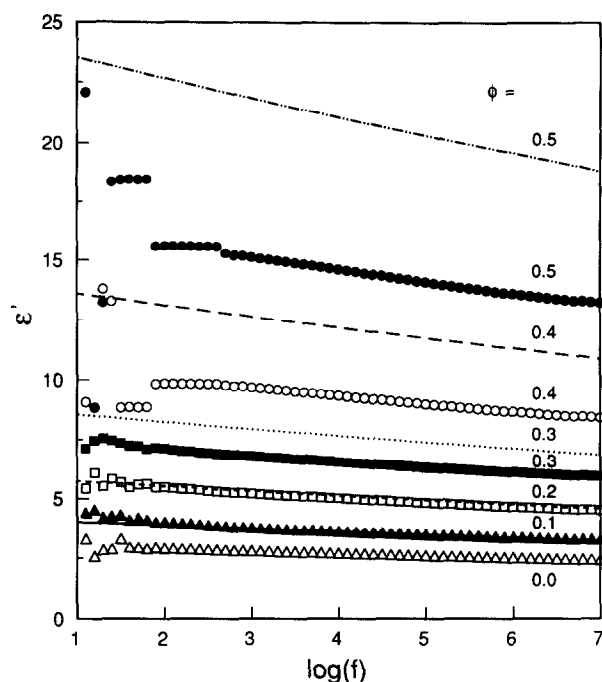


Figure 2 ϵ' of water-in-oil emulsions at different water contents. Experimental data denoted by points, theoretical calculations by lines

produced can vary widely. Both IORL's field data and Abercrombie's¹¹ analysis of the fluid produced showed that the salt content was mainly NaCl, with the more saline samples having a content of 10 g l^{-1} (loosely denoted 1%). There was a small amount of other salts, calcium and magnesium being the next most abundant. The brine used in the present work was made from distilled water with 1% NaCl, 0.03% CaCl_2 , and 0.02% MgCl_2 . The distilled water was simply taken from the tap supply in the laboratory. At 20°C, ϵ_w is 80, and κ_w for distilled water and brine are 10^{-5} and 0.02 S cm^{-1} respectively.

Emulsion

The emulsions were prepared by low-speed blending of the components in a Waring blender. Owing to the high viscosity of the bitumen and the nearly equal densities of the two phases, the bitumen emulsion is stable in terms of settling for more than a year under room conditions, allowing ample time for experimentation.

Dielectric measurements

All electrical measurements were made with a Hewlett-Packard 4192A impedance analyser over the frequency range 10 Hz to 10 MHz. The electrodes were four parallel platinum plates connected in pairs. Values of ϵ^* of the base constituents quoted above were used as input to Equations (1)–(3) to calculate the emulsion properties. Comparison of the experimental data with theory revealed important aspects of the bitumen emulsion system that have not been considered in the literature.

RESULTS AND DISCUSSION

Five samples of water-in-bitumen emulsions were made with the brine solution, and their dielectric response measured at 20°C. The water volume fraction, ϕ , of these

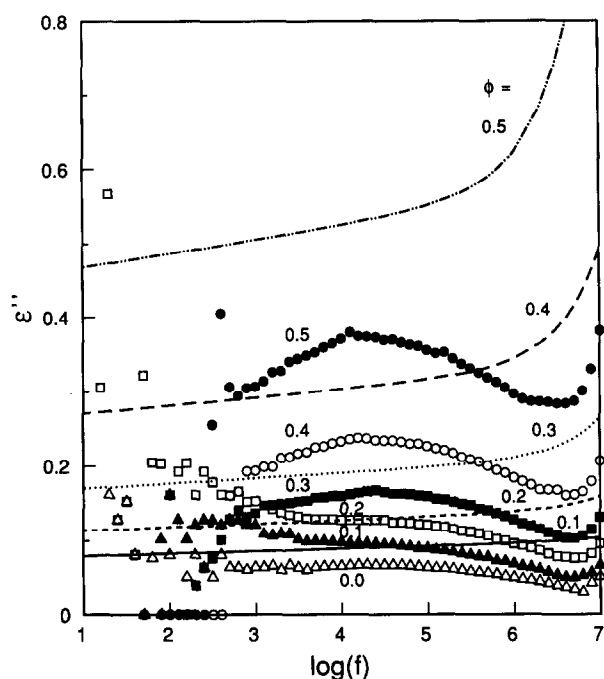


Figure 3 ϵ'' of water-in-oil emulsions at different water contents. Symbols as in Figure 2

samples was varied from 0.1 to 0.5 in steps of 0.1. As shown in Figures 2 and 3, both the real, ϵ' , and the imaginary, ϵ'' , parts increased with the water content. It is seen that the bitumen data lie below the $\phi = 0.1$ data. The lines were calculated from Hanai's formula, Equation (1), using the dielectric properties of bitumen and brine. Except for the low-water fractions, the good agreement between experiment and theory reported in the literature⁶⁻⁸ was not obtained. The following two subsections discuss the disagreement with theory.

Interfacial relaxation

The interfacial relaxation frequency for water-in-oil emulsions reported in the literature is ~ 100 kHz. The humps in Figure 3 at ~ 10 kHz are signs of some form of relaxation, but this frequency is one order of magnitude lower. This relaxation process may not be the interfacial relaxation predicted by Hanai's equation, because that relaxation can be located at higher frequencies if the range of calculation is extended. Plots of ϵ' and ϵ'' for $\phi = 0.3$ emulsions are shown in Figures 4 and 5. In these calculations the conductivity of the water component was varied from 10^{-5} S cm⁻¹ for distilled water to 10^{-2} S cm⁻¹, in increments of a factor of 10. The corresponding relaxation frequencies are 0.1 to 100 MHz, and are linearly dependent on the dispersed-phase conductivity. As the observed relaxation in the data at 10 kHz occurs much below the theoretical value, it is probably due to the polar components in the bitumen, its response being amplified by the dispersed water droplets. A similar amplification effect was observed by Clause¹² for a dispersion of mercury in vaseline.

Besides the humps at ~ 10 kHz in the ϵ'' data, the rise at the high-frequency end of Figure 3 seems to indicate that another relaxation process is starting. However, the limitations of the instrument mean that these data points might be erroneous. To observe the interfacial relaxation frequency within the present measurement range, according to Figures 4 and 5 the emulsion should

be made with distilled water. The relaxation frequency of such an emulsion should be ~ 100 kHz. However, efforts to measure it experimentally failed, owing to trace amounts of salt in the bitumen. In spite of the centrifugation and filtration, micrometre-sized crystals remained suspended in the bitumen, as observed under the microscope.

Low-frequency dielectric constant

It was shown in the previous subsection that the interfacial relaxation frequency for emulsions made with

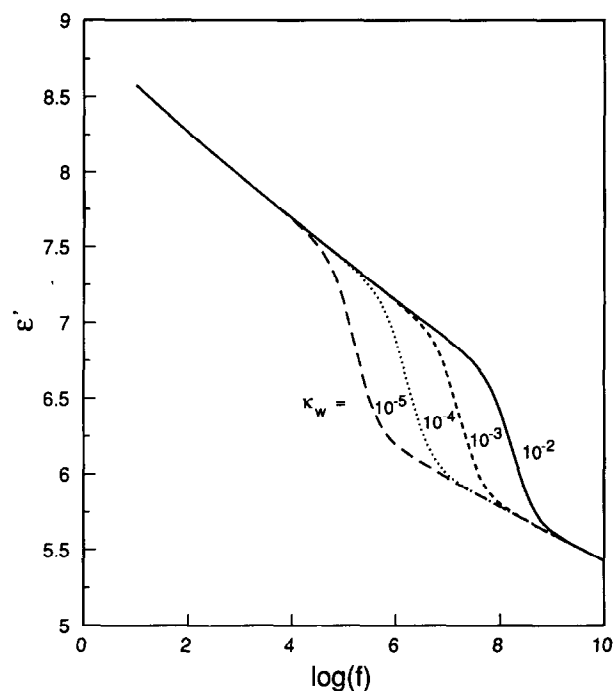


Figure 4 Calculated ϵ' of $\phi = 0.3$ water-in-bitumen emulsions at different water conductivities

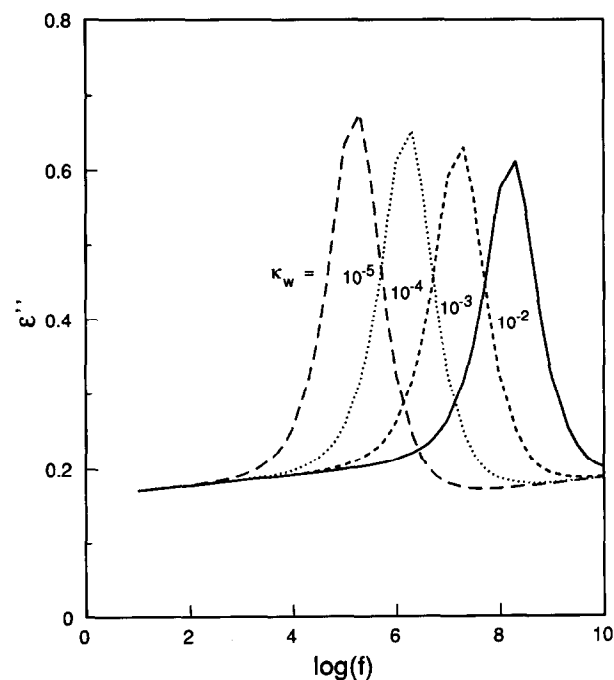


Figure 5 Calculated ϵ'' of $\phi = 0.3$ water-in-bitumen emulsions at different water conductivities

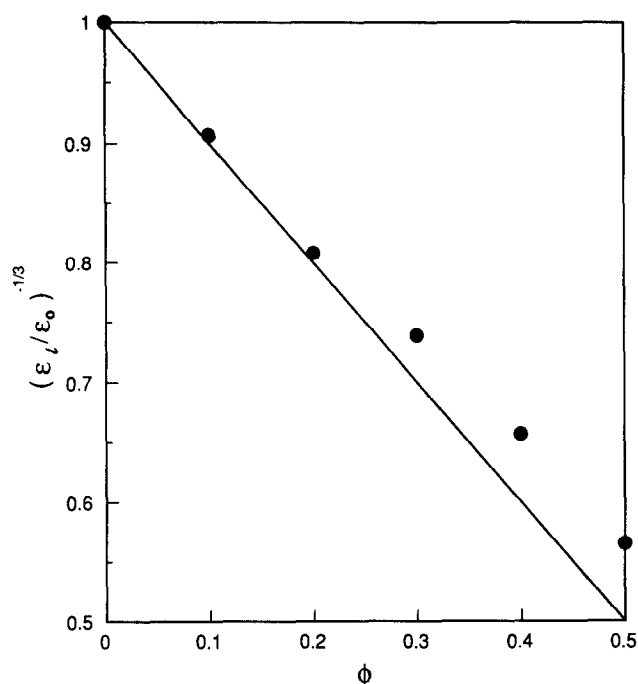


Figure 6 Low-frequency dielectric constant of water-in-bitumen emulsions: ●, experimental data for emulsions made with brine; —, calculated from Equation (2)

brine is > 1 MHz. Below this frequency, the ϵ data should correspond to low frequency values. Instead of being constant as reported in the literature⁶⁻⁸, ϵ'_1 of the water-in-bitumen emulsions followed a similar frequency dependence as did ϵ'_0 of the bitumen. However, the ratio ϵ'_1/ϵ'_0 for each curve calculated from 1 kHz to 1 MHz is fairly constant: the standard deviation is of the order of 10^{-3} . A plot of $(\epsilon'_1/\epsilon'_0)^{-1/3}$ versus volume fraction of the dispersed phase is shown in Figure 6. The deviation of Equation (2) from the data for the brine emulsions ranges from 2% for the low volume fractions to as high as 45% at $\phi = 0.5$.

In most of the water-in-oil experiments reported in the reviews by Hanai⁴ and Clausse⁵, the oils used were non-polar, and distilled water was the dispersed phase. The deviation from theory may therefore be attributed to either the polar compounds in the bitumen or the ions in the water, or both. More recently, Le Petit *et al.*¹³ and Hanai *et al.*¹⁴ considered the effect of KCl concentration in the water phase. The conductivity of the KCl solutions that they used varied from 10^{-3} to 10^{-2} S cm⁻¹. Their oils were mixtures of lanolin and vaseline and of kerosene and carbon tetrachloride. The measurements at different KCl concentrations were similar to those for emulsions with distilled water, except that the relaxation frequency was displaced to the right. Both of these groups found good agreement in measured ϵ_1 and relaxation frequency with theory. As their oils were non-polar, their results imply that it was the interaction between the polar compounds in the bitumen and the dissolved ions in the brine that contributed to the deviation of the present experimental data from theory.

Temperature dependence

In the above discussions only those data obtained at 20°C were used to illustrate the properties of emulsions. However, the effect of temperature must also be considered, because emulsion flow experiments in the authors' laboratory are conducted at temperatures between 60 and 120°C, and the well-head temperatures in Cold Lake are usually $> 100^\circ\text{C}$.

At 20 and 60°C the dielectric constant of water is 80 and 66.2 respectively⁹. Measurements on the bitumen show that there is no significant change in its dielectric constant over this temperature range. The same is true for measurements on emulsions. The higher-temperature data are not shown here, because the plot is almost identical to Figure 2. This result can be understood in the light of the fact that the entire range of measurements was in the low-frequency regime of interfacial polarization. In this range, the dielectric constant of a water-in-oil emulsion can be approximated by Equation (2), which is independent of the dispersed-phase dielectric constant. The observed results are in accordance with Hanai's equation.

CONCLUSIONS

It has been shown that owing to the presence of even a trace amount of salt in the water phase, the interfacial relaxation frequency of water-in-bitumen emulsion is always > 1 MHz. This implies that the relaxation process would not interfere with laboratory measurements if any frequency < 1 MHz is chosen. Although there is significant departure from Hanai's equation at the low-frequency end of the dielectric dispersion, there is still a one-to-one correspondence between the dielectric constant of an emulsion and its water volume fraction. A correlation can easily be established between these quantities and used to estimate the water volume fraction via dielectric measurement.

REFERENCES

- Islam, M. R. and Farouq Ali, S. M. *Can. J. Pet. Technol.* 1989, **28**, 59
- Sharma, M. K. and Shah, D. O. *Enhanced Oil Recovery* 1985, **272**, 149
- Vittoratos, E. Paper to CIM/SPE International Technical Meeting, Calgary, June 1990
- Hanai, T. In 'Emulsion Science' (Ed. P. Sherman), Academic Press, 1968, Ch. 5
- Clauss, M. In 'Encyclopedia of Emulsion Technology' (Ed. P. Becher), Vol. 1, Dekker, New York, 1983, Ch. 9
- Hanai, T. *Kolloid-Z.* 1960, **171**, 23
- Naiki, T., Fujita, K. and Matsumura, S. *Mem. Fac. Ind. Arts, Kyoto Tech. Univ.* 1959, **8**, 1
- Clauss, C. R. *C. R. Acad. Sci. Paris B* 1973, **277**, 261
- Buckley, F. and Maryott, A. A. 'Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions', Circular 589, National Bureau of Standards, Washington, DC
- Fricke, H. and Jacobson, L. E. *J. Phys. Chem.* 1939, **43**, 781
- Abercrombie, H. J. *Appl. Geochem.* 1991, **6**, 495
- Clauss, M. *Colloid Polymer Sci.* 1975, **253**, 1020
- Le Petit, J. P., Delbos, G., Bottreau, A. M., Dutuit, Y., Marzat, C. and Cabana, R. *J. Microwave Power* 1977, **12**, 335
- Hanai, T., Imakita, T. and Koizumi, N. *Colloid Polymer Sci.* 1982, **260**, 1029