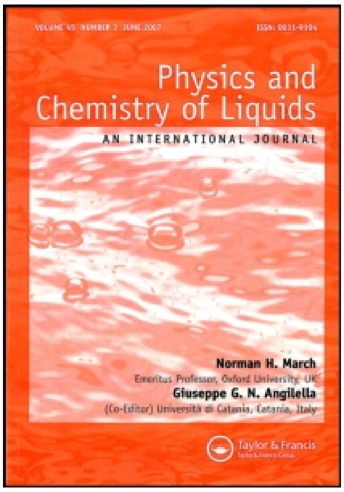
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Measurements of the Kerr Effect in W/O Microemulsions up to the Proximity of a $W_{II} \rightarrow W_{III}$ Transition

M. Bisceglia[a]; D. H. Kurlat[a]; J. P. Chéret[a]; B. Ginzberg[a]
[a] Departamento de Física, Facultad de Ingeniería (UBA), Buenos Aires, Argentina

To cite this Article Bisceglia, M. , Kurlat, D. H. , Chéret, J. P. and Ginzberg, B.(1993) 'Measurements of the Kerr Effect in W/O Microemulsions up to the Proximity of a $W_{II} \longrightarrow W_{III}$ Transition', Physics and Chemistry of Liquids, 25: 2, 127 — 134
To link to this Article: DOI: 10.1080/00319109308030353
URL: http://dx.doi.org/10.1080/00319109308030353

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 1993, Vol. 25, pp. 127–134
Reprints available directly from the publisher
Photocopying permitted by license only

© 1993 Gordon and Breach Science Publishers, S.A.
Printed in the United States of America

Downloaded At: 08:25 28 January 2011

LETTER

Measurements of the Kerr Effect in W/O Microemulsions up to the Proximity of a $W_{II} \rightarrow W_{III}$ Transition

M. BISCEGLIA, D. H. KURLAT, J. P. CHÉRET and B. GINZBERG

Facultad de Ingenieria (UBA), Departamento de Física, Paseo Colón 850, 1063-Buenos Aires, Argentina

(Received 15 December 1991)

The Kerr effect in W/O microemulsions has been studied. The Kerr constant (B) and the relaxation time $\langle\tau\rangle$ as a function of the volume fraction of dispersed water in oil (ϕ) ($0.049 \leq \phi \leq \phi_t$; where ϕ_t = phase transition point) have been determined.

The B values are very high, even for small values of ϕ, as its range of values varies from a third of the Kerr constant of the nitrobenzene to values in between 2 and three orders of magnitude of this constant. As from $\phi > 0.12$, B grows abruptly. The different factors transient aggregates, droplet strain, cluster formation and density fluctuations are analyzed.

KEY WORDS: Induced birrefringence, microemulsions dispersions

INTRODUCTION

The study of the physico-chemical properties of microemulsions presents many problems which have not been solved yet. One of these problems is their behavior in the proximity of phase transition points. As it is well-known, these systems presents different types of phase equilibria which have been coined as[1].

Winsor I(W_I), or "lower": the microemulsion phase is in equilibrium with the hydrocarbon (two phases).

Winsor III(W_{III}), or "middle": the microemulsion phase is in equilibrium with the aqueous and hydrocarbon phases (three phases).

Winsor II(W_{II}), or "upper": the microemulsion phase is in equilibrium with the aqueous phase (two phases).

From the microscopic point of view, it is generally accepted that the "lower" microemulsion corresponds to droplets of hydrocarbon in water (O/W), the upper one to the inverse structure (W/O), and the middle one to an intermediate structure which are not well understood yet. It is particularly interesting to come to know the microemulsion properties in the proximity of phase transition points. Owing to reasons which will be explained below, in this work we will limit ourselves to the study of W/O microemulsions when the system approaches the $W_{II} \rightarrow W_{III}$ transition by increasing the water content dispersed in hydrocarbon. As the concentration of the dispersed phase increases, clusters are formed. The abrupt increase in electric conductivity evinces this phenomenon, which has been explained as a percolative process by several authors[2–5].

Therefore, the increase of water concentration in hydrocarbon brings about the occurrence of these structures in upper microemulsions. Moreover, there exists spontaneous density fluctuations in the proximity of phase transition points.

Now, the Kerr effect, that is the occurrence of birrefringence induced by an electric field, is specially sensitive to the presence of non-isotropous structures. Consequently, the aim of this work has been the study of the physical magnitudes which characterize this effect, when the system approaches the phase transition points, and their relation to the microscopic structure of the dispersed system under study. While there are some works which have dealt with the Kerr effect near phase transition temperature[6,7], as far as we know, there are no systematic studies similar to the one we present here. In this study we approach the phase transition point by means of the volume fraction of brine in microemulsions (ϕ).

Downloaded At: 08:25 28 January 2011

EXPERIMENTAL

The microemulsions were prepared using dodecane (hydrocarbon), tri-ethanol amine dodecyl benzene sulfonate (surfactant), *n*-amyl alcohol (cosurfactant) and brine.

Special care was taken so that the samples could have low specific conductivity, even in the proximity of the phase transition point. This condition must be fulfilled so that the ohmic resistance should be compatible with the charge which can be accepted by the high voltage source, as well as to prevent electrophoretic effects. Hence, we used the lowest possible concentrations of surfactant and electrolyte, since these are elements which contribute to conductivity to the greatest extent.

The water/hydrocarbon ratio (1.25 in volume) and the brine concentration (0.25% in weight) were held fixed, while the surfactant concentration (1.189% – 1.33% in volume) and the alcohol one (18.67% – 27.67% in volume) were varied.

We have observed that the brine volume dispersed in hydrocarbon phase can be regulated very easily if we diminish the surfactant concentration and increase that of alcohol.

The samples were dipped in a thermostatic bath (25 ± 0.1°C) until the phase volumes became constant. This stabilization process took from 2 to 4 weeks.

The experimental set-up used to study the Kerr effect has been explained well enough in the literature dealing with this subject[8]. We will therefore limit ourselves giving just a brief description of the equipment used. A laser beam ($\lambda = 632.8$ nm; 5 mW) polarized by means of a Glan-Thomson type polarizer passes through a cell where the liquid sample to be measured has been placed. This cell is composed of an optical cuvette (Hellma QS-5000; L = 50 nm) and two electrodes separated by a distance of 2.9 mm. Both electrodes are connected to a high voltage source which generates pulses up to 850V, and of a duration of as long as 1.2 ms, which causes the occurrence of birrefringence in the sample. The cell temperature is held constant

(25 ± 0.1°C) by means of a thermostatic bath. On leaving the cell, the beam goes through another polarizer (analyzer). The optical axes of the polarizer and analyzer are 45° and 135° repectively from the direction of the electric field. A quarter-wave plate is intercalated between the cell and the analyzer. The extinction coefficient, defined as Ir/Io is in the order of 10^{-5}, being Ir the light intensity measured with the polarizer and analyzer in crossed position, and Io is the light intensity when their optical axis are parallel among them. The light signal is detected in a photomultiplier (Hammamatsu R968), visualized in a digital oscilloscope and registered in a XY recorder. The light intensity detected on the photomultiplier is related to:

$$\Delta n = n_{\|} - n_{\perp}$$

where $n_{\|}$ and $n_{\perp}$ are parallel and perpendicular refraction indices with respect of the direction of the polarizing field (**E**), and in turn

$$\Delta n = \lambda B E^2$$

where B is the Kerr constant of the liquid being studied. Calibration of the equipment was achieved by measuring the Kerr constant of nitrobenzene and acetone.

We have obtained the following values (for $T = 25 \pm 0.1$°C):

$$B_{\text{acetone}} = 2.2 \cdot 10^{-14}\,\text{mV}^{-2}$$

$$B_{\text{nitrobenzene}} = 2.7 \cdot 10^{-12}\,\text{mV}^{-2}$$

The results being in reasonable agreement with other authors[9,10–13] taking into account the dispersion that exists in the literature data. The lowest B value that our experimental set-up was able to measure was about $10^{-15}\,\text{mV}^{-2}$, and the relative error of each measurement was estimated to be 10%.

The electrical conductivity was measured at 25°C in calibrated cells connected to an a.c. bridge (1 KHZ).

DISCUSSION

The experimental results for the stationary regime are shown in Figure 1, where the Kerr constant has been represented as a function of ϕ. We can divide B behavior in two zones:

$$0.04 \le \phi \le 0.12 \text{ and } 0.12 \le \phi \le 0.18$$

$$(\phi_t \simeq 0.2)$$

Even for the first zone B(ϕ) has a high value

$$10^{-12}\,\text{mV}^{-2} \le B \le 3 \cdot 10^{-11}\,\text{mV}^{-2}$$

Downloaded At: 08:25 28 January 2011

Downloaded At: 08:25 28 January 2011

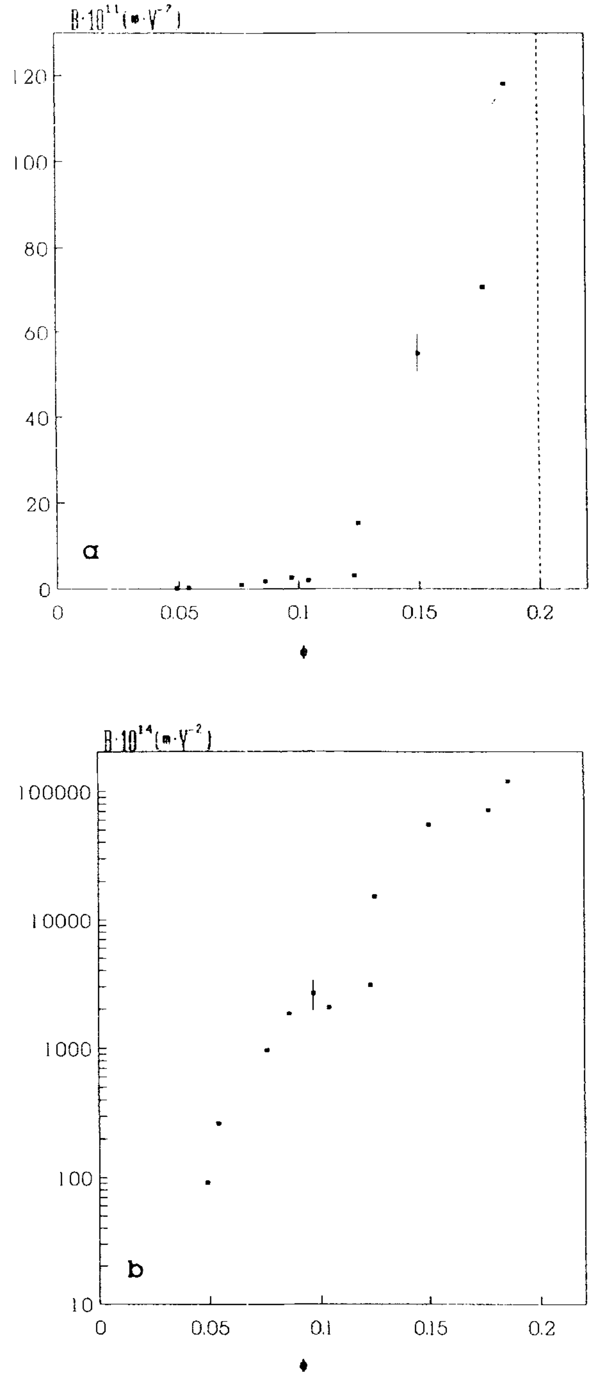


Figure 1 (a) Variation of Kerr constant, B vs. water volume fraction ϕ. (b) Variation of log. Kerr constant, B vs. water volume fraction ϕ.

Although we can not confirm which type of law is followed by $B(\phi)$, it has been observed that for $\phi \leq 0.12$ its behavior can approach that of a linear law.

In the interval $0.12 \leq \phi < 0.18$, B changes its slope abruptly. We should point out that for $\phi > 0.18$ we can not measure B owing to the high values of the electrical conductivity.

The birrefringence analysis with time in field absence provide us with the information concerning the relaxation time of the samples.

If microemulsions were very diluted ($\phi < 10\%$) and monodispersed, the law provided by birrefringence as a function of time, in the absence of a polarizing field would be:

$$\Delta n = \Delta n_0 e^{-t/\tau}$$

When the microemulsion is not monodisperse, curve $\Delta n(t)$ is no longer exponential and, in general (always in diluted dispersions), the following equation should occur:

$$\Delta n = \sum_i \Delta n_{oi} e^{-t/\tau_i}$$

where: (Δn_{oi}) = birrefringence at $t = 0$, owing to the i-drops. It has no sense to adjust our curves of $\Delta n(t)$ to a sum of two or more monoexponentials. Therefore it is more reasonable to define the mean value of τ as[14]

$$\langle \tau \rangle = \frac{1}{\Delta n_o} \int_0^{\infty} \Delta n(t)\, dt$$

For $\phi < 10\%$, we can apply the above model, while for $\phi > 10\%$ it is clear that we could not do so. However, and considering the absence of a consistent theory, we decided to apply the above analysis in order to have a semiquantitative idea of the behavior of measured parameters.

The values of $\langle \tau \rangle$ as a function of ϕ are shown in Figure 2.

It is striking that the Kerr constant should have such high value even for small brine concentrations which are far from the phase transition point. Now the usual theory of the Kerr effect accounts for the occurrence of optical polarizabilities in the parallel and perpendicular directions to the applied electric field.

Obviously, if we are in the presence of spherical droplets dispersed in hydrocarbon, as it is generally admitted in the case of W/O microemulsions, the phenomenon cannot be explained. Other measurements of $B(\phi)$ for low droplet concentration in microemulsions W/O have been reported[15–18]. The authors suppose that transient aggregates are formed by collisions, which would result in the formation of anisotropic structures. Nevertheless, this model must follow a $B(\phi^2)$ law, which does not hold with our experimental result.

Another cause which may be possibly account for the high value of the Kerr effect could be the strain of the droplets by the electrical field.

Downloaded At: 08:25 28 January 2011

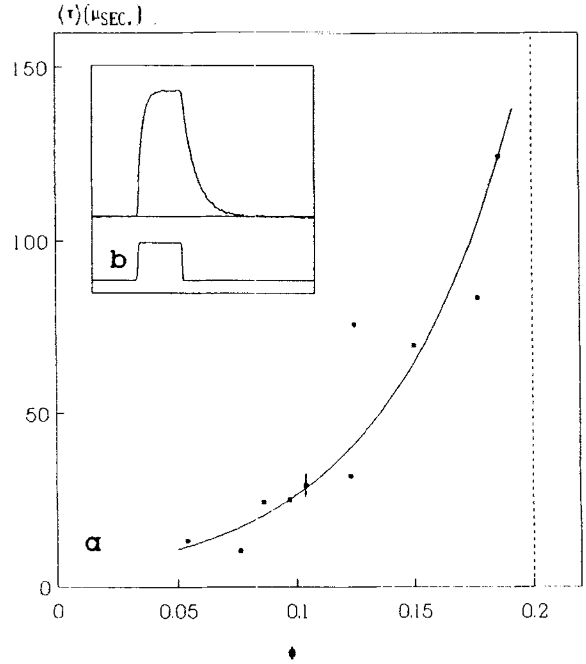


Figure 2 (a) Variation of mean relaxation time ⟨τ⟩, vs. water volume fraction ϕ. (b) Transient birrefringence signal vs. time and applied pulse.

Downloaded At: 08:25 28 January 2011

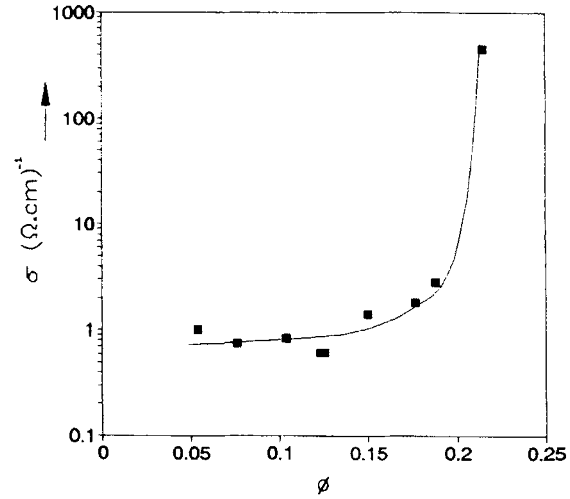


Figure 3 Variation of conductivity σ, vs. water volume fraction ϕ.

Unfortunately, a rigorous calculation of this process is extremely complex. Nevertheless, a theoretical analysis of the Kerr effect in microemulsions has been proposed, taking into account the strain of the droplets by the electric field. The eccentricity of the spheroids has been found by minimizing the deformation energy, which is obtained by the addition of the electromagnetic and the curvature energies[19]. Afterwards[20], the contribution due to the interfacial tension has been added, though this term may be considered negligible because of the ultralow value of this physical magnitude in these systems.

The Kerr constant so calculated is a function of several variables—the spontaneous curvature, the droplet radius, the thickness of the surfactant layer which surrounds the droplet, the dielectric constants of the water and the polar and non-polar parts of the surfactant (or their respective refraction indices) and the temperature.

The authors[20] have applied their theory to the case of 3-component microemulsions—Surfactant (AOT), Water and Oil—. Due to the relative simplicity of the system and the understanding of the physico-chemical characteristics of the components, an adequate check of the proposed formulae using experimental results was carried out. Unfortunately it is difficult for us to make a similar calculation because we work with a 5-component microemulsion, in which the characteristics of the components are not well-known.

In the interval $0.12 \leq \phi \leq 0.18$, $B(\phi)$ changes its slope abruptly.

The causes which bring about this phenomenon are the following:

—As we have seen above, clusters are formed, as it is envinced by the abrupt increase of $\sigma(\phi)$. This type of variation of electrical conductivity is a process which has been widely studied. The anisotropy of the medium obviously increases due to the non-spherical structure of the clusters. As ϕ grows, the clusters increase both in number and size, and therefore B grows. This correspondence between the formation of clusters and the increase of B is limited by the fact that, if the clusters become too big, the electric field finds it very difficult to orientate them and as a consequence, their contribution to the Kerr effect is either less or even null. The hypothesis concerning the formation of structures of this type is supported by the shape of $\langle \tau(\phi) \rangle$ curve, since for $\phi > 0.12$ also changes its slope, increasing in an order of magnitude.

—Moreover, in the neighborhood of the $W_{II} \rightarrow W_{III}$ transition, the occurrence of spontaneous density fluctuations can be expected; these play the role of non-spherical molecules[21].

In the present state of the theory of the Kerr effect it is not possible to discriminate separately the influence that the two processes described above have.

Finally, we want to point-out that, because it is not possible to measure B or ϕ near the phase transition point, it does not make any sense to put them under scale law form.

Downloaded At: 08:25 28 January 2011

References

1. *Microemulsions* Ed. L. M. Prince, Acad. Press, (1977).
2. M. J. Lagües, R. Ober and C. Taupin, *J. de Phys.* (Lettres) **39**, L-487 (1978).

3. M. J. Lagües, *J. de Phys.* (Lettres) **40**, L-331 (1979).
4. D. Langevin, *Mol. Cryst. Liq. Cryst.* **138**, 259 (1986).
5. M. Moha-Ouchane, J. Peyerlasse and C. Boned, *Phys. Rev. A* **35**, (7), 3027 (1987).
6. R. Hilfiker, H. F. Eicke, S. Geiger and G. Furker, *J. of Colloid and Interface Science*, **105** (2), 378 (1985).
7. V. Degiorgio and R. Piazza, *Phys. Rev. Letters*, **55**, (3), 288 (1985).
8. *Electric Dichroism and Electric Birrefringence*, E. Fredericq and C. Houssier, Oxford (1973).
9. *Molecular Electro-Optics*, C. T. O'Konski (Ed.), N.Y. (1978).
10. M. Angel, *Diplomarbeit*, Bayreuth (1981).
11. M. S. Beevers and G. Khanarian, *Austr. J. Chem.* **32**, 263 (1979).
12. N. Okubo, Y. Mori, R. Hayakawa and Y. Wada; *Japan J. Appl. Phys.* **19**, 2271 (1980).
13. H. F. Eicke and Z. Markovic, *J. of Coll. and Interf. Science*, **79** (1), 151 (1981).
14. H. Watanabe, K. Yoshioka. Physical principles and techniques of protein chemistry (ed. S. J. Leach), Pt. A, Chap. 7, Academic Press, N. Y., 1969.
15. A. M. Cazabat in *Colloids et Interfaces*, Aussois, Les Editions de Physique, (1984).
16. A. M. Cazabat in *Physics of Amphiphiles: Micelles, Vescicles and Microemulsions*, North Holland (1985).
17. P. Guering—These—Paris (1985).
18. P. Guering and A. M. Cazabat, *Europhys. Letters*, **2** (12), 953 (1986).
19. E. v.d. Linden, S. Geiger and D. Bedeaux, *Physica A* **156**, 130 (1989).
20. E. v.d. Linden, *Determination of the interfacial rigidity in microemulsions using the Kerr effect*, Thesis, Leiden University, 1990.
21. W. Pyzuk, *Chem. Phys.* **50**, 281 (1980).

Downloaded At: 08:25 28 January 2011