Measurement of low interfacial tensions from the intensity of the light scattered by liquid interfaces

Jean Lachaise, Alain Graciaa, A. Martinez, A. Rousset

Classification
Physics Abstracts
68.10 — 78.35 — 82.70

Measurement of low interfacial tensions from the intensity of the light scattered by liquid interfaces

J. Lachaise, A. Graciaa, A. Martinez, A. Rousset

Laboratoire de Thermodynamique des Etats Métastables et de Physique Moléculaire,
Institut Universitaire de Recherche Scientifique, 64000 Pau, France

(*Reçu le 18 juillet 1979, révisé le 17 septembre 1979, accepté le 28 septembre 1979*)

Résumé. — On décrit une méthode destinée à la mesure des tensions interfaciales de l'ordre de la millidyne/cm en partant de l'intensité de la lumière diffusée par réflexion, lorsque les interfaces sont éclairés près de l'angle limite. Cette méthode est utilisée pour mesurer la tension interfaciale optimale de microémulsions de toluène et d'eau salée en équilibre simultanément avec une phase aqueuse et une phase organique.

Abstract. — We describe a method for the measurement of interfacial tensions in the millidyne/cm range by measuring the diffuse part of the total internally reflected light produced when the interfaces are illuminated close to the critical angle. This method has been used to measure the optimal interfacial tension in toluene-brine micro-emulsions in simultaneous equilibrium with the oil and aqueous phases.

In the oil/brine/surfactant/alcohol systems low interfacial tensions can be obtained with a proper choice of salt concentration, type and concentration of surfactant and alcohol [1]. Thus, when a microemulsion is in equilibrium with the oil and aqueous phases, tensions of the two interfaces can fall to values in the millidyne/cm range [2, 3]. When a thin pencil-ray of light strikes these interfaces, a very important scattering of the reflected ray is observed and, from the measurement of the relatively high ratio of scattered intensity to unscattered reflected light intensity, deduction of the low interfacial tensions values may be made.

1. **Light scattering by liquid interfaces.** — During the past ten years, the theory of the light scattering by the free surface of a liquid and its experimental verification, and the spectral composition of the scattered light, have been discussed in numerous papers by the research workers of the Laboratory of Hertzian Spectroscopy at the Ecole Normale Supérieure [4 to 9] and also by Katyl and Ingard [10]. For the calculation of the intensity of the reflected light, we have used their following results.

The amplitude ζ of the surface roughness, generated by thermal motion and responsible for the scattering can be resolved in terms of a continuous series of sinusoidal waves which as such constitute diffraction gratings. For a given direction, the intensity of the scattered beam is that of the first order spectrum of the grating the wave vector q of which fulfils the relation :

$$q^2 = k_0^2(\sin^2 \theta_0 + \sin^2 \theta - 2 \sin \theta \sin \theta_0 \cos \varphi) \quad (1)$$

(θ_0, incident angle ; θ, angle between the scattered ray and the normal ; φ, angle between the incident and the scattering planes ; k_0, wave vector of the incident radiation).

The roughness formation is opposed by the forces of gravity and capillarity. Thus, the mean square amplitude by unit surface $\langle | \zeta_q |^2 \rangle$ which is a function of the wave vector q in terms of g and γ is given by :

$$\langle | \zeta_q |^2 \rangle = \frac{k_B T}{\gamma q^2 + g\rho} \quad (2)$$

(k_B, Boltzmann's constant ; T, absolute temperature ; γ, surface tension ; g, gravity acceleration ; ρ, liquid density).

On passing from the free surface case to that of the interface it is sufficient, in the preceeding equation to denote the interfacial tension by γ and to replace ρ by the difference $\Delta\rho$ between the densities of the two superimposed liquids.

La traduction en français de cet article a été acceptée aux Comptes Rendus de l'Académie des Sciences et elle est insérée dans le n° du 16 juillet 1979, série B.

The scattered flux $d\Phi$ in the solid angle element $d\Omega$ around the θ direction is given by :

$$d\Phi = \Phi_r \frac{k_0^4}{4\pi^2} \frac{k_B T}{\gamma q^2 + g \Delta\rho} f(\theta_0, \theta, N, \varphi) \, d\Omega$$

(N, relative index, Φ_r, reflected flux).

When $\theta = \theta_0$, and $\varphi = 0$, the function $f(\theta_0, \theta, N, \varphi)$ is reduced to $4(\cos\theta_0)^3$. The expression of $d\Phi$ becomes :

$$d\Phi = \Phi_r \frac{k_0^4}{\pi^2} \frac{k_B T \cos^3\theta_0}{\gamma q^2 + g \Delta\rho} d\Omega . \quad (3)$$

When the measurement of the very narrow bandwidth of the scattered ray is required, scattered light must be collected within a very small solid angle (10^{-6} str.) in order to eliminate an unwanted device bandwidth, and in directions making small scattering angles (a few minutes) in order to increase the intensity of the collected light [7]. The parasitic light is then very important and it is used as a local oscillator when spectral analysis is performed by photon correlation with the heterodyne method [7].

When it is simply necessary to measure the scattered intensity, without spectral analysis, one may collect light from a larger solid angle and make measurements at larger scattering angles ; thus parasitic light will represent a very small fraction of the total collected. From the preceeding considerations, we have designed the apparatus described in the following section and represented in figure 1*a*.

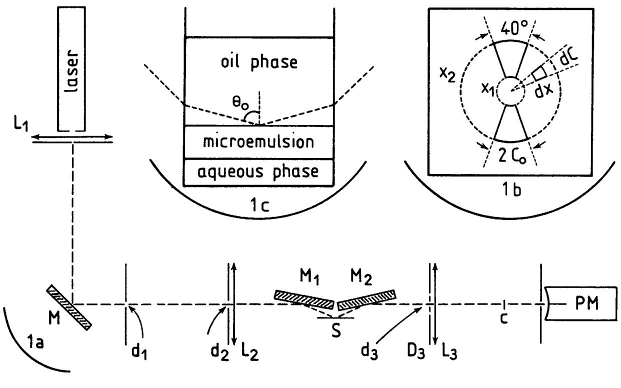

Fig. 1. — Experimental apparatus for the measurement of the intensity of the light scattered by liquid interfaces.

2. **Experimental apparatus.** — The light provided by a low power He-Ne laser (0.1 mV) is concentrated on a circular aperture d_1 of 0.1 mm diameter, located at the image focus of lens L_1 the focal length of which is 1 m. A quasi-cylindrical beam is obtained by locating d_1 with the object focal plane of a lens L_2 of 0.5 m focal length. L_2 is stopped with an aperture d_2 of 1 mm diameter. With the two swivelling mirrors, M_1 and M_2, the beam is again made horizontal after a total internal reflection on the interface S. A lens L_3, the focal length of which is 0.25 m gives a vertical image in real size of the impact of the incident beam on the interface ; this image is centered on a circular aperture of 2 mm diameter, located in front of the photomultiplier (P.M).

In front of the lens L_3, is applied a diaphragm D_3 (Fig. 1*b*), the uncovered parts of which are a 3 mm diameter circular aperture d_3, which can be closed, and two circular quadrants of internal radius x_1 and external radius x_2 opened at $2\,C_0$.

We have fixed x_1 to 4 mm and the distance d from the impact of the beam on the interface to the lens L_3 equal to 50 cm, so that for our experiments, the scattered rays collected by the P.M. are inclined at more than one third of a degree to the reflected beam. We thus reduce the parasitic light produced by the impact of the incident and the reflected beams on the mirrors and the lenses, light which is mainly found in the reflected beam direction. We have taken $x_2 = 10$ mm because of the steep decrease of the scattered intensity around the direction of the reflected ray. As we are operating with total internal reflection, close to the critical angle, $f(\theta_0, \theta, N, \varphi)$ becomes equal to $4(\cos\theta_0)^3$. Moreover, θ_0 and θ are large enough for the solid angle element $d\Omega$ subtended by the surface $dS = x\,dx\,dC$ on L_3, and the corresponding wave vector q to be given by :

$$d\Omega = \frac{dS}{n^2 d^2} = \frac{x\,dx\,dC}{n^2 d^2} \quad (4)$$

$$q^2 = k_0^2 \frac{x^2}{n^2 d^2} (1 - \sin^2\theta_0 \cos^2 C) \quad (5)$$

where n is the index of the liquid inside of which the reflection is produced.

When the capillary forces are very much greater than the forces due to gravity, the relations (3), (4) and (5) allow us to easily calculate the ratio of the scattered flux to the reflected flux :

$$\frac{\Delta\Phi}{\Phi_r} = 4 \frac{k_0^2}{\pi^2} \frac{k_B T}{\gamma} \cos^2\theta_0 (\ln x_2/x_1) \operatorname{Arc\,tg} (\operatorname{tg} C_0/\cos\theta_0) . \quad (6)$$

For $\theta_0 = 80°$, when C_0 varies from $\pi/2$ to $\pi/9$, the relation (6) shows that $\Delta\Phi$ decreases by 28 %, while the uncovered surface of L_3, source of parasitic light, decreases by 78 %. For this reason, we have taken $C_0 = \pi/9$.

If the incident and reflected beams were only cylinders of 1 mm in diameter, to obtain $\Delta\Phi/\Phi_r$, it would be sufficient to compare the currents of the P.M. when d_3 is closed and open [11]. In reality, the diffraction through d_2 produces a central spot surrounded by rings on the lens L_3. Only the rings which are nearer to the center are eliminated with the central spot when d_3 is closed. However, the other rings will not reach the P.M. if a 1.5 mm diameter circular disc c is located on the image of d_2 given by L_3 (33 cm behind this lens). This cover does not cut off the scattered rays which have passed through the quadrants.

3. **Calculation of γ from $\Delta\Phi/\Phi_r$.** — As the interfacial tensions that we want to measure are very low, the gravity forces involved are not generally negligible with respect to the capillary forces. The integration of the complete relation (3) performed with the expressions (4) and (5) leads to :

$$\Delta\Phi/\Phi_r = A \int_0^{C_0} \ln \frac{x_2^2(1 - \sin^2\theta_0 \cos^2 C) + a}{x_1^2(1 - \sin^2\theta_0 \cos^2 C) + a} \times \frac{dC}{1 - \sin^2\theta_0 \cos^2 C} \quad (7)$$

with :

$$A = \frac{2 k_0^2}{\pi^2} \frac{k_B T \cos^3\theta_0}{\gamma} \quad \text{and} \quad a = \frac{g \Delta\rho}{\gamma} \frac{n^2 d^2}{k_0^2}.$$

As an example, we have calculated $\Delta\Phi/\Phi_r$ for an interface characterized by $\theta_0 = 80°$, $n = 1.4$ and $\Delta\rho = 0.1$ g/cm³. The variation of $\Delta\Phi/\Phi_r$ *versus* γ is shown in the figure 2. When γ is higher than 10^{-1} dyne/cm, the relation (6) is verified, while when the capillary forces become negligible $\Delta\Phi/\Phi_r$ is directed towards the limit :

$$\Delta\Phi/\Phi_r = 2 C_0(x_2^2 - x_1^2) k_B T \frac{k_0^4}{\pi^2 n^2 d^2} \frac{\cos^3\theta_0}{g\Delta\rho} = 2.6 \times 10^{-3} \quad (8)$$

γ is determined by an interpolation method using the measured value of $\Delta\Phi/\Phi_r$ on the curve representing the variation of $\Delta\Phi/\Phi_r$ with γ as deduced from relation (7).

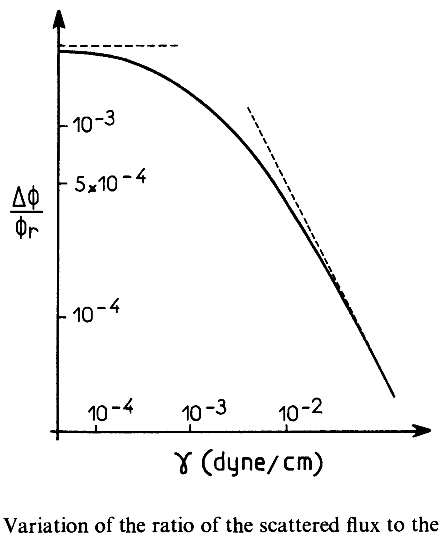

Fig. 2. — Variation of the ratio of the scattered flux to the reflected flux as function of the interfacial tension for an interface characterized by $\theta_0 = 80°$, $n = 1.4$, $\Delta\rho = 0.1$ g/cm³.

4. **Applications to Microemulsions.** — We have used the method and the apparatus previously described to determine the optimal interfacial tension γ^* of the quaternary system whose weight composition is : toluene 43.1 %, brine 49.5 %, sodium dodecylsulfate (S.D.S.) 4.95 %, butanol-1 2.45 %.

For salinities S between 45 g and 60 g of NaCl per liter of water, this system presents three phases : the microemulsion which is the middle phase, a lighter oil phase and a more heavy aqueous phase (Fig. 1*c*).

For the optimal salinity S^*, the middle phase contains equal volumes of brine and oil ; then the interfacial tension, optimal, is the same for its two interfaces [2].

We have obtained S^* from the measurement of the specific refraction $r = (n^2 - 1)/(n^2 + 2)\rho$ of the three phases, deduced from measurements of density and of refractive index. For numerous systems, E. S. Derderian *et al.* [12] have verified that when the optimal salinity is reached, the specific refraction r^* of the middle phase is equal to the arithmetic mean of the specific refractions of the two other phases. Our mean agrees with the measured value $r^* = 0.268$ for a mixture whose salinity is $S^* = 53.5$ g/l. This S^* value has been found again by directly measuring the volumes of brine and oil solubilized within the middle phase.

Table. — *Measured values of $\Delta\Phi/\Phi_r$ and calculated values of γ for various microemulsions systems.*

$S_{g/l}$	40	45	50	55
$\Delta\Phi/\Phi_r$	9.3×10^{-4}	1.67×10^{-3}	2.65×10^{-3}	3.22×10^{-3}
γ (dyne/cm)	1.8×10^{-2}	8.3×10^{-3}	4.0×10^{-3}	2.7×10^{-3}

In the above table, we have reported $\Delta\Phi/\Phi_r$ measurements relating to the oil phase/microemulsion interfaces of a diphase system ($S = 40$ g/l) and of triphase systems. These measurements are corrected

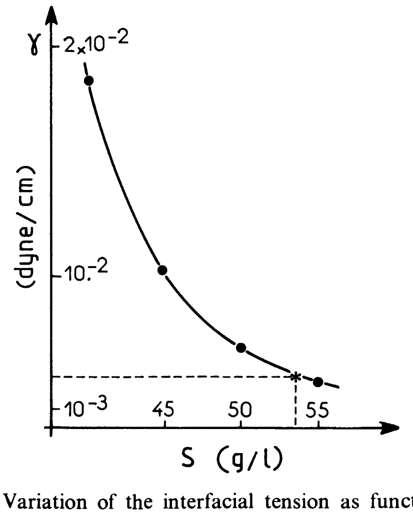

Fig. 3. — Variation of the interfacial tension as function of the salinity deduced from light scattering measurements.

for the parasitic flux evaluated to be $1.8 \times 10^{-4} \Phi_r$. In the same table are reported the values of γ deduced from the relation (7).

The curve of the variation of γ *versus* S (Fig. 3) allows us to obtain the optimal interfacial tension γ^* by an interpolation at $S = S^*$. We find that :

$$\gamma^* = 2.8 \times 10^{-3} \text{ dyne/cm} .$$

Thus, the measurement of the intensity of the light scattered from the interfaces, and the measurements of refractive indexes and of densities permit the determination of the optimal salinity *and* interfacial tension in microemulsions. This method can be extended to the systems of higher phase which are homogeneous and transparent.

References

[1] CAYIAS, J., SCHECHTER, R. S., WADE, W. H., *J. Colloid Interface Sci.* **59** (1977) 31.

[2] HEALY, R. N., REED, R. L., STENMARK, D. G., *Soc. Pet. Eng. J.* **16** (1976) 147.

[3] As this property is linked to the efficiency of the microemulsions for improved oil recovery, this work has been subsidized by D.G.R.S.T. and S.N.E.A. (P).

[4] BOUCHIAT, M. A., MEUNIER, J., BROSSEL, J., *C.R. Hebd. Séan. Acad. Sci.* Paris, **B 266** (1968) 255.

[5] BOUCHIAT, M. A., MEUNIER, J., *C.R. Hebd. Séan. Acad. Sci.* Paris, **B 266** (1968) 301.

[6] BOUCHIAT, M. A., MEUNIER, J., in *Polarisation, Matière et Rayonnement* (Presses Universitaires, Paris) 1969.

[7] MEUNIER, J., Thèse, Paris (1971).

[8] LANGEVIN, D., MEUNIER, J., in *Photon Correlation Spectroscopy and Velocimetry* (Plenum Press) 1977.

[9] BOUCHIAT, M. A., LANGEVIN, D., *J. Colloid Interface Sci.* **63** (1968) 193.

[10] KATYL, R. H., INGARD, U., *Phys. Rev. Lett.* **20** (1968) 248.

[11] To measure Φ_r, it is necessary to put an absorbent cell of known optical density close to 3 in front of the photomultiplier.

[12] DERDERIAN, E. J., GLASS, J. E., BRYANT, G. M., *J. Colloid Interface Sci.* **68** (1979) 184.