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The Effect of an Electric Field on the Critical Opalescence.

1. Introduction.

Concentration fluctuations in liquid mixtures, which
may be observed by means of light scattering, include also
fluctuations of the dielectric constant. If an electric
field is applied, the fluctuations of the dielectric constant
cause changes of the electric energy density, which is
connected with the dielectric constant and the field strength
by the relation

$$W = \frac{\varepsilon}{8\pi} E^2 \tag{1}$$

In the expression for the free energy of a binary liquid
system an additional term due to the electric energy has
to be added to the term representing the work involved in
concentration changes. The work necessary to create a
given amplitude of concentration fluctuations is usually
rather big, and it is only in the vicinity of the critical
point that it becomes small enough to become comparable to
the electric work involved.

In calculating the possible effect of an electric field
on the concentration fluctuations one has to consider, that
both the dielectric constant and the field strength are
functions of the geometrical distribution of the concentration
fluctuations.

2. Concentration Fluctuations and Electric Energy.

The energy density of a parallel plate condenser is

given by

$$W = \frac{\varepsilon}{8\pi} E^2$$

ε is the dielectric constant of the medium and E is the field strength of the applied electric field.

Concentration fluctuations create fluctuations of the dielectric constant. Observing the fluctuations by means of light scattering and accepting Brillouins interpretation of the fluctuations as a superposition of sonic waves, we may write for one of the components

$$\varepsilon = \varepsilon_0 + \eta \sin K (\vec{S}, \vec{\pi}) \qquad (2)$$

The vector $\vec{\pi}$ defines the position of the point in which the dielectric constant is measured. The unit vector $\vec{S}$ has the direction of propagation of the sound wave. $K = \frac{2\pi}{\Lambda}$ in which Λ is the wavelength of the wave and η is the amplitude of the fluctuation of the dielectric constant.

The field strength may be expressed as the gradient of a potential ϕ: $\quad E = - grad\ \phi \quad$ This potential ϕ is a function of the position defined by the vector $\vec{\pi}$. We develop it in powers of η and obtain

$$\phi = \phi_0 + \eta\,\phi_1 + \eta^2\,\phi_2 \qquad (3)$$

For an electrostatic field we always have the relation

$$div\,(\varepsilon\,\vec{E}) = 0$$

Substituting from eq. (2) and ϕ from eq. (3) we obtain after arrangement according to powers of η.

$$div \left\{ \begin{array}{l} \varepsilon_0\,grad\,\phi_0 + \eta\,\varepsilon_0\,grad\,\phi_1 + \eta^2\,\varepsilon_0\,grad\,\phi_2 \\[4pt] + \eta \sin K(\vec{S},\vec{\pi})\,grad\,\phi_0 + \eta^2 \sin K(\vec{S},\vec{\pi})\,grad\,\phi_1 \end{array} \right\} = 0$$

neglecting all terms containing higher powers of η than the

second. So the equations necessary to find ϕ_0, ϕ_1, ϕ_2 are

$$\triangle \phi_0 = 0 \qquad (4a)$$

$$(4) \qquad \triangle \phi_1 = -\frac{1}{\varepsilon} \, div \left[\sin K(\bar{S}, \bar{\pi}) \, grad \, \phi_0 \right] \qquad (4b)$$

$$\triangle \bar{\phi}_2 = -\frac{1}{\varepsilon_0} \, div \left[\sin K(\bar{S}, \bar{\pi}) \, grad \, \phi_1 \right] \qquad (4c)$$

We now assume the electric field to be applied in the z-direction. Then we may write

$$(5) \qquad \phi_0 = -A_z$$

Now calculating grad ϕ_0 from equ. $(4a)$ and substituting this value in equ. $(4b)$ we obtain $\triangle \bar{\phi}_1$ and grad ϕ_1, and repeating this operation with ϕ_1 we also obtain grad ϕ_2.

First we have

$$grad_x \, \phi_0 = 0 \quad , \quad grad_y \, \phi_0 = 0 \quad , \quad grad_z \, \phi_0 = -A$$

which gives

$$\triangle \phi_1 = \frac{A}{\varepsilon_0} \frac{\partial}{\partial z} \left[\sin K(\bar{S}, \bar{\pi}) \right] = \frac{A}{\varepsilon_0} K \gamma \cos K(\bar{S}, \bar{\pi})$$

supposing that the 3 components of the unit-vector $\bar{S}$ are

$$\alpha, \beta, \gamma .$$

From this it follows that we can take for ϕ_1 the expression

$$\phi_1 = -\frac{A}{\varepsilon_0} \frac{\gamma}{K} \cos K(\bar{S}, \bar{\pi})$$

which yields

$$grad_x \, \phi_1 = \frac{A}{\varepsilon_0} \gamma \alpha \, \sin K(\bar{S}, \bar{\pi})$$
$$grad_y \, \phi_1 = \frac{A}{\varepsilon_0} \gamma \beta \, \sin K(\bar{S}, \bar{\pi})$$
$$grad_z \, \phi_1 = \frac{A}{\varepsilon_0} \gamma^2 \, \sin K(\bar{S}, \bar{\pi})$$

Proceeding now to the calculation of ϕ_2 we have

$$\triangle \phi_2 = -\frac{A}{\varepsilon_0^2} \gamma \left(\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y} + \gamma \frac{\partial}{\partial z} \right) \sin^2 K(\bar{S}, \bar{\pi})$$

or $\qquad \triangle \phi_2 = -\frac{A}{\varepsilon_0^2} K \gamma \, \sin 2K(\bar{S}, \bar{\pi})$

which gives

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$$\ddot{\Phi}_2 = \frac{A\gamma}{\varepsilon_0^2} \frac{1}{4K} \sin 2k(\bar{S},\bar{\pi})$$

So finally, in second approximation, we have

(6)
$$\Phi = -Az - \eta \frac{A\gamma}{\varepsilon_0 K} \cos K(\bar{S},\bar{\pi}) + \eta^2 \frac{A\gamma}{4\varepsilon_0^2 K} \sin 2K(\bar{S},\bar{\pi})$$

From this expression for the potential we derive the field-strength E by calculating the 3 components of the gradient and obtain

$$E_x = -\eta \frac{A\gamma}{\varepsilon_0}\alpha \sin K(\bar{S},\bar{\pi}) - \eta^2 \frac{A\gamma}{2\varepsilon_0^2}\alpha \cos 2K(\bar{S},\bar{\pi})$$

(6')
$$E_y = -\eta \frac{A\gamma}{\varepsilon_0}\beta \sin K(\bar{S},\bar{\pi}) - \eta^2 \frac{A\gamma}{2\varepsilon_0^2}\beta \cos 2K(\bar{S},\bar{\pi})$$

$$E_z = A - \eta \frac{A\gamma}{\varepsilon_0}\gamma \sin K(\bar{S},\bar{\pi}) - \eta^2 \frac{A\gamma}{2\varepsilon_0^2}\gamma \cos 2K(\bar{S},\bar{\pi})$$

Finally we have to calculate the energy-density

$$W = \frac{\varepsilon}{8\pi} E^2$$

by substituting for ε expressions from eq.(2) and for the 3 components of E their expressions from (6'). The result up to the second power of η is

$$8\pi W = \varepsilon_0 A^2 - \frac{\eta^2}{\varepsilon_0} A^2\gamma^2 \sin^2 k(\bar{S},\bar{\pi}) + \text{terms which contain only first}$$

powers of the periodic functions.

Since the phase of the wave must be arbitrary we can average over the periodic function and obtain

(7)
$$W = \frac{\varepsilon_0 A^2}{8\pi}\left[1 - \frac{1}{2}\left(\frac{\eta}{\varepsilon_0}\right)^2 \gamma^2\right]$$

This means that in such a fluctuation only the component of the applied electrical field in the direction of propagation of the supersonic wave is efficient.

3. Critical opalescence in an electric field

For a binary liquid mixture of two components 1 and 2 occupying a volume V in which the fluctuations of the volume fraction φ_2 of component 2 have an amplitude ζ, the free

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energy F, as changed by those fluctuations, can be represented by the expression

(8)
$$\frac{F}{VkT} = \frac{F_0}{VkT} + \frac{1}{4}\left(\frac{\zeta}{\varphi_2}\right)^2 \varphi_2 \frac{\partial}{\partial \varphi_2}\left(\frac{P}{kT}\right)$$

This holds as long as there is no external field and was derived in the article on the "Angular Dissymmetry of the Critical Opalescence in Liquid Mixtures" J. Chem. Phys. 31, 680 (1959) . It is equation (24) of that article in which the dissymmetry-effect has been neglected. This is sufficiently correct for the estimate we are going to make of the expected order of magnitude of the electrical field effect.

It is obvious that in the presence of a field A we will have to add to the right-hand side of equation (8) the additional electrical energy calculated in eq.(7) divided by kT. In this way we obtain

(8')
$$\frac{F}{VkT} = \frac{F_0}{VkT} + \frac{1}{4}\left(\frac{\zeta}{\varphi_2}\right)^2 \varphi_2 \frac{\partial}{\partial \varphi_2}\left(\frac{P}{kT}\right) - \frac{\varepsilon_0 A^2 \gamma^2}{16\pi kT}\left(\frac{\eta}{\varepsilon_0}\right)^2$$

We substitute the concentration c for the volume fraction of the second component. Since

$$\frac{\eta}{\varepsilon} = \frac{\zeta}{\varphi}\left(\frac{\varphi}{\varepsilon}\frac{\partial \varepsilon}{\partial \varphi}\right) = \frac{\zeta}{\varphi}\left(\frac{c}{\varepsilon}\frac{\partial \varepsilon}{\partial c}\right)$$

we now can write instead of eq. (8')

(8'')
$$\frac{F}{VkT} = \frac{F_0}{VkT} + \frac{1}{4}\left(\frac{\zeta}{\varphi_2}\right)^2\left[c\frac{\partial}{\partial c}\left(\frac{P}{kT}\right) - \frac{\varepsilon_0 A^2 \gamma^2}{4\pi kT}\left(\frac{c}{\varepsilon}\frac{\partial \varepsilon}{\partial c}\right)^2\right]$$

In the case $A = 0$ eq (25) of the paper in the J.Chem. Phys. loc. cit. gives the scattered intensity. It is clear that when $A \neq 0$ we will have to substitute for the denominator in this formula the expression in bracket of eq.(8'')

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Suppose now that the experiment is performed at the critical concentration. In this case it follows from equations (22) (22') and (26) in J.Chem. Phys. loc cit. that

$$c \frac{\partial}{\partial c} \left(\frac{P}{kT} \right) = \frac{1}{\omega_2} \left(\frac{T}{T_c} - 1 \right)$$

in which ω_2 is the volume occupied by one molecule of the second component. Since the reciprocal scattered intensity is proportional to the expression in brackets of eq. (8''') it follows in essence that we can expect an observable effect by the application of a field A if we can make the electric energy content of a volume equal to that occupied by one molecule of the second component of the same order as

$$kT \left(\frac{T}{T_c} - 1 \right)$$

The chances of an observable effect therefore increase with diminishing temperature distance of the critical temperature. At the same time the minus-sign in the bracket indicates that under the influence of an applied field the scattered intensity should increase.

This can be expressed in a quantitative way by comparing the intensity for $A = 0$ to the intensity after application of the field. It follows that

$$(9) \quad \frac{I_{A=0}}{I_{A=A}} = \frac{\Delta T / T_c - \left(\frac{c}{\varepsilon} \frac{\partial \varepsilon}{\partial a} \right)^2 \frac{\omega_2 \varepsilon A^2 \gamma^2}{4\pi} / kT}{\Delta T / T_c}$$

if we call the temperature distance $T - T_c = \Delta T$. Another feature of the expected effect is that it is proportional to $A^2 \gamma^2$, which means that only the component of the field perpendicular to the front of the reflecting supersonic wave is effective.

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4 Example (Methanol in Cyclohexane)

The dielectric constants of cyclohexane and methanol are $\varepsilon_1 = 2.0$ and $\varepsilon_2 = 32.6$. The molar volumes are 107 and $40.5\ cc$, making $\omega_1 = 177 \cdot 10^{-24}$ and $\omega_2 = 67.3 \cdot 10^{-24}\ cc$. This makes $x = 0.37$ and the critical molfraction

$$(\varphi_2)_{crit} = \frac{1}{1 + \sqrt{x}} = 0.62$$

Assuming linear dependences of the dielectric constant on the volume fraction, which should be good enough for our immediate purpose, the dielectric constant at the critical concentration comes out to be 21.0 and

$$\left(\frac{c}{\varepsilon} \frac{\partial \varepsilon}{\partial c} \right)^2 = 0.81$$

If we now suppose the experiment of being performed by the observation of the scattered light under 90° with the primary beam and the field to be in the direction of the secondary beam we have $\gamma = \frac{1}{\sqrt{2}}$ and for an applied field strength of $30\,000 \frac{Volts}{cm} = 100\ e.s.$ units we obtain with $k = 1.37 \cdot 10^{-16}\ ergs$:

$$\left(\frac{c}{\varepsilon} \frac{\partial \varepsilon}{\partial c} \right)^2 \frac{\omega_2 \varepsilon A^o \gamma^2}{4\pi k} = 3.3 \cdot 10^{-3}$$

Since the temperature of observation will be very near the critical temperature this result has to be compared with the temperature-distance ΔT from the critical temperature. So if observation would be made at $\Delta T = 0.03^\circ C$, the effect would be 11% of the primary intensity and 1.1% if the experiment is performed at $\Delta T = 0.3\ ^\circ C$.

Examining different mixtures, which were all chosen to have as one component a polar substance (which obviously is helpful because of the relatively high dielectric constant of polar

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substances) it turned out that all mixtures had relatively
high electrical conductivities. The measured specific resistance
was sometimes as low as 10^{-8} ohm cm. In this case the heating
effect is rather large and it is estimated that under these
circumstances the heating rate might be as high as $5°/sec$.
Obviously it is therefore necessary to apply a pulse technique
which allows the field to be applied in short bursts of the
order of 100 micro sec.

The experimental setup
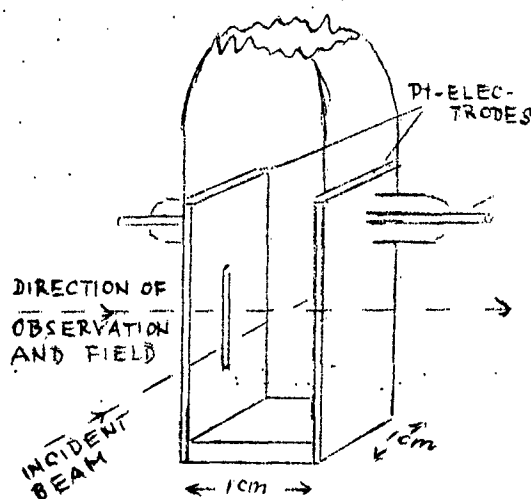
The design and the dimensions of
the measuring cell are shown in
the figure.

It consists of a rectangular polished
Pyrex cell, the molten in platinum
electrodes are 1 cm apart from each
other. The small slit through which
the scattered light is observed by
means of a photomultiplier should
not disturb the homogeneity of the
field.

The cell is fixed in a temperature
bath which allows to control the temperature within $.005°$.
The refractive index of the oil used in the temperature bath is
the same as the refractive index of the glass in order to
avoid reflections. The electrodes are connected with the

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high voltage power supply by heavily isolated cables.
Temperature bath, measuring cell and phototube are placed
in a black painted box, which is mounted on a optical bank, the
light from a 500 Watt projection lamp enters through a system
of slits.   The photocurrent is measured by means of an
oscilloscope.

As a power supply a high voltage pulse generator is used
which delivers rectangular pulses up to 30 000 volts with
a variable pulse width up from 100 microseconds.

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