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ON THE CRITICAL OPALESCENCE

EX AEDIBVS ACADEMICIS IN CIVITATE VATICANA



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THE EFFECT OF AN ELECTRIC FIELD ON THE CRITICAL OPALESCENCE

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SUMMARIVM — Ex novis quibus experimentis describitur quomodo lucis diffusio in duorum liquidorum mixtura, cuius caloris index proximus sit calori critico mixtionis, magis vel minus intensa fiat propter vim alicuius campi electrici.

Near the critical mixing point of two liquids one observes the so called critical opalescence: a strong scattering of light passing through the liquid, which increases in intensity if one approaches that critical point. This effect is due to the existence of concentration-fluctuations coupled with fluctuations of the refractive index, which become large in amplitude near that point just before the separation in two phases occurs. Here the mixture of the two liquids is in a not very stable condition. Therefore it may be expected that in this region observable changes in the scattering may be induced say by the application of an electric field. Right from the beginning it has to be expected that the applied field will have to be strong, when one realises that in order to explain say the heat of vaporisation of benzene by so called London-forces it is necessary to

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accept in the interior of the liquid the natural existence of molecular fields of the order of 100 million Volts/cm.

It also is to be anticipated that in actual experiments where strong electric fields are applied a disturbing effect will be the Joule-heating due to the conductivity of the mixture even if this conductivity is small. This disturbing heating effect will have to be counteracted by the application of the field in pulses of short duration.

In collaboration with K. KLEBOTH we have submitted mixtures of 2-2-4-trimethyl-pentane and nitrobenzene to pulsed fields of up to 50000 Volts/cm in pulses of a duration of the order of 100 μ sec. Such mixtures have a dielectric constant which varies from 2 to 34 by increasing the amount of nitrobenzene from 0 to 100%. The critical concentration is at a volume-fraction of nitrobenzene of 0.381 and the critical temperature is 29.15°C. It was observed that submitting such mixtures at their critical concentration and at a temperature 0.1°C above their critical temperature to pulses of 45000 Volts/cm decreases their natural turbidity, which itself is already of the order of 1cm^{-1} , by about 10%.

The dependence of this new effect on the field-strength and on the temperature-distance from the critical temperature were investigated. The effect is proportional to the square of the field-strength and increases in magnitude by approaching the critical temperature. It is proportional to the reciprocal of the square of that temperature distance for larger distances.

The effect can be described as a depression of the critical temperature, proportional to the square of the field-strength and in our case being about 0.01°C for a field of 45000 Volts/cm.

A theory of the effect along classical lines can be built up on an expression for the free energy of liquid mixtures as used for instance by HILDEBRAND (See J.H. HILDEBRAND and R. L. SCOTT: *Solubility of nonelectrolytes*, Reinhold Press, New York, 1950). Such a theory can only be expected to yield semi-quantitative results. As a matter of fact it predicts the

order of magnitude and the observed temperature-dependence correctly. It also predicts the sign of the effect (decrease or increase of the apparent turbidity by the application of the field) which depends on the sign of the curvature of the curve for the dielectric constant of the mixture as a function of composition. In our case the curvature is positive. If this is so more work has to be done to excite concentration-fluctuations when the field is present than without the field. Then, as observed, the turbidity decreases by the application of the field.

The effect itself is interesting from two points of view:

a) it provides an opportunity to measure thermodynamic quantities directly in terms of electrical units;

b) it is interesting in connection with a large number of recent theoretical speculations about non-classical anomalies to be expected near the critical point (For a survey see for instance the article of MARSHALL FIXMAN « The Critical Region » in *Advances in Chemical Physics*, vol. VI, 1964, edited by I. Prigogine, Interscience Publishers, New York). These speculations do not prove but make it probable that such deviations exist. From the experimental point of view it then becomes important to find out how near the critical point has to be approached to make such deviations observable. Experiments so far seem to indicate that this temperature-range is of the order of a few hundredths of a degree centigrade.

