The Dielectric Constant and Electric Polarization of Mixtures in the Neighborhood of the Critical Point

There exist many mixtures of liquids, chiefly organic liquids, which disclose critical phenomena in the system liquid-liquid. As a result of a long series of experiments, I am able to state that the most suitable medium for dielectric tests is the pair of liquids: hexane-nitrobenzene, the critical temperature of dissolution of which is 16.9°, and the critical concentration 51.4%. The object of the present work was to test the behavior of the dielectric constant ϵ, the density d, the gram polarization of the mixture P_{gr}, and the molecular polarization P of the dissolved nitrobenzene, when approaching the critical point where, as is well known, considerable fluctuations of density take place, manifesting themselves by the critical opalescence.

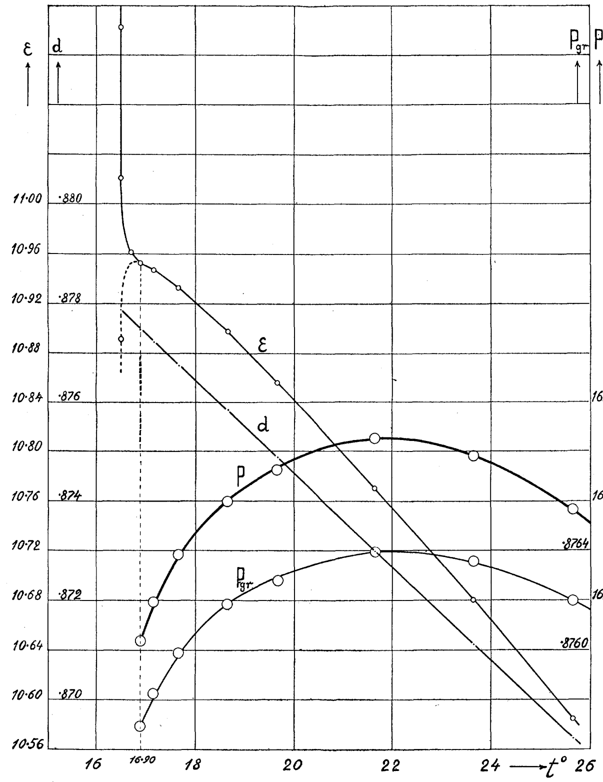

Fig. 1.

The measurements of the dielectric constant were conducted as in the recently published research A. Piekara, Nature **130**, 93 (1932). The measurements of the density were carried out in the dilatometer. The condenser and the dilatometer were placed in a specially constructed thermostat enabling the maintenance of any constant temperature between −4° and +60°C.

The results obtained for the mixture having the critical concentration are shown in Fig. 1. With the fall from higher temperatures to the critical temperature, the dielectric constant increases, but at a decreasing rate; the corresponding curve is bent downwards, which does not occur at other concentrations. The molecular polarization of nitrobenzene at first increases, but from 22° it decreases more and more rapidly. It is obvious that the density fluctuations are responsible for such a considerable decrease of the polarization of nitrobenzene. The critical opalescence begins at 18.7°. It is interesting that even above 18.7°, where no opalescence can be detected, the fluctuations of density, although very feeble, cause the decrease of polarization.

At the temperature of 16.9° the separation of phases occurs. The dielectric constant increases rapidly, in connection with the production of the emulsion hexane-nitrobenzene.

Mixtures were also tested having concentrations lower, and higher, than the critical concentration, especially in the neighborhood of the point at which the separation of phases takes place. The dielectric constant undergoes a rapid fall if the emulsion nitrobenzene-hexane is formed, or a rapid increase if the emulsion hexane-nitrobenzene is produced.

The detailed results of these investigations will be published later in the Bull. Acad. Polonaise (Cracovie).

A. Piekara

Physical Laboratory,
Sulkowski Gymnasium,
Rydzyna, Poland,
September 12, 1932.

The Electric Moment of the Molecule of Nitrobenzene

Recently there have been published a number of investigations establishing the fact that in the neighborhood of 9.6° nitrobenzene undergoes some, as yet not clearly understood, modification (M. Wolfke and J. Mazur, Zeits. f. Physik **74**, 110, 1932; G. W. Stewart, Phys. Rev. **39**, 176, 1932; H. Trotter, Phys. Rev. **40**, 1052, 1932). At the same time, however, there the temperature point of 9.6°. Already the first measurements have been shown that such change does not occur. Now I am able to give more accurate data concerning this matter.

I experimented with dilute solutions of nitrobenzene in hexane. Both substances have been carefully purified and dried. Fig. 1 shows the

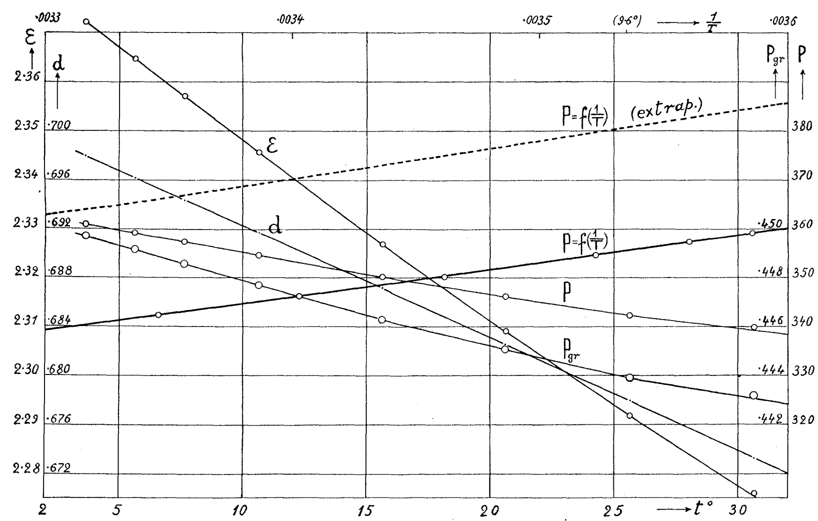

Fig. 1.

appeared publications denying the existence of these allotropic forms of liquid nitrobenzene (M. Wolfke and S. Ziemecki, Acta Phys. Polonica **1**, 271, 1932; Massy, Warren and Wolfenden, Nature **129**, 441, 1932; J. N. Friend, Nature **129**, 471, 1932; A. Piekara, Nature **130**, 93, 1932). Studying the problem of the critical point of dissolution—chiefly on the mixtures of nitrobenzene and hexane—I resolved to derive profit from the occasion and to examine if the electric moment μ and the polarizing ability γ of the molecule of nitrobenzene undergo any change when passing graphs of the dielectric constant ϵ, density d, gram polarization

$$P_{gr} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d},$$

and the molecular polarization of nitrobenzene P, for one of the solutions tested, having a concentration (by weight) $c = 0.04034$. P is to be computed from the formula

$$P = \frac{M}{c}[P_{gr} - (1 - c)P_{gr}']$$

where P_{gr}' is the gram polarization of the pure solvent, and M is the molecular weight of