Vol. A58 (1980) *ACTA PHYSICA POLONICA* No 5

KERR EFFECT IN THE CRITICAL SOLUTION OF BENZYL ALCOHOL

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(Received February 23, 1980)

In the benzyl alcohol-methylcyclohexane system the Kerr effect changes sign near the critical solubility temperature due to the increasing positive contribution arising from pretransitional processes.

PACS numbers: 78.20.Jq, 64.70.Ja

Studies of strong electric field action on precritical liquid mixtures, initiated by Piekara's pioneering work [1] on the non-linear dielectric effect, including also the electro-optical Kerr effect (EKE), have been intensively continued in the recent years. In the vicinity of the critical solubility point an increase in the Kerr constant B has been observed for mixtures having a positive sign for B, e.g. [2,3]. The aim of this work was to observe the temperature behaviour of benzyl alcohol solutions which are characterized by a negative Kerr constant far from the critical point. Thus, it should be possible to establish whether the precritical field-induced processes really give a positive contribution to EKE, or whether they enhance only the effect without changing its sign.

The method of EKE pulse measurements made at 550 nm has been described elsewhere [3]. The sign of the effect was checked by using the reference cell with nitrobenzene

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in addition to the Kerr cell filled with the liquid to be examined. Materials in our experiment were cyclopentane (99%, Fluka) used without further purification, carbon tetrachloride and methylcyclohexane, both purified by standard methods, and benzyl alcohol (for gas chromatography, Roth) carefully dried and vacuum-distilled over calcium hydride. The alcohol sample gives a critical solution with methylcyclohexane at $T_c = 276.9$ K. Up to 252 K no phase separation or even critical opalescence has been observed for the mixtures with cyclopentane or carbon tetrachloride.

Solutions of almost the same alcohol concentration (in volume fractions, ϕ) have been studied in three different solvents. As seen from Fig. 1 the negative Kerr effect due to hydrogen bond association [4] monotonically decreases with decreasing temperature in

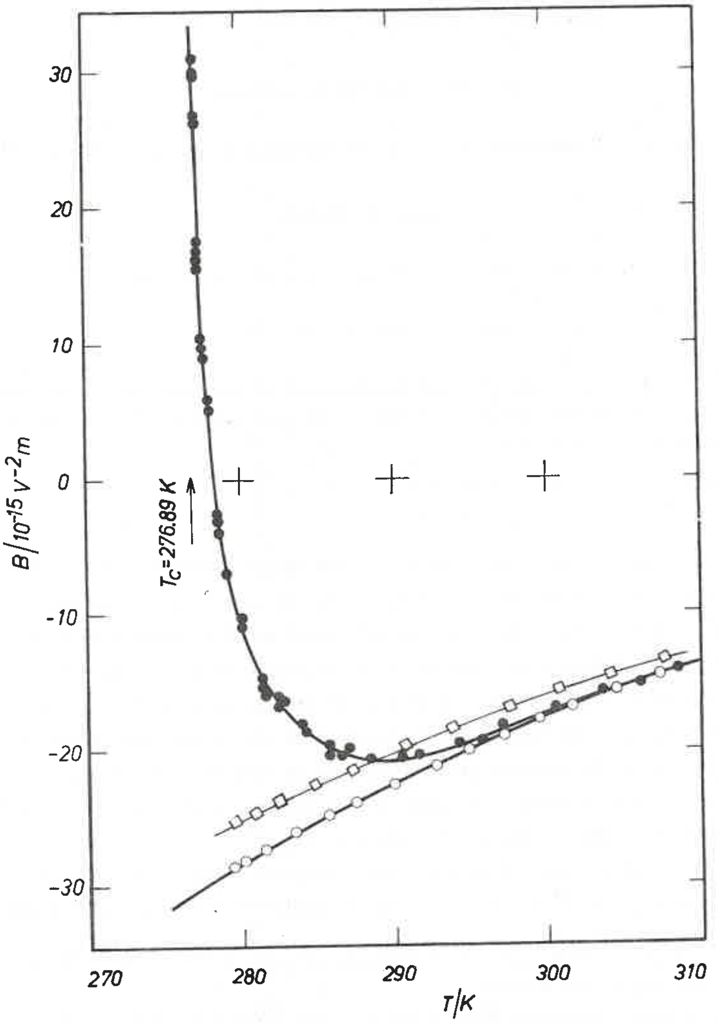

Fig. 1. Kerr constant B vs. temperature T for the solutions of benzyl alcohol in methylcyclohexane (●), $\phi = 0.3066$; cyclopentane (○), $\phi = 0.3068$; and carbon tetrachloride (□), $\phi = 0.3038$

non-critical solutions in carbon tetrachloride or cyclopentane. The solvent slightly influences the association since the effect for both systems differs by about 10%. For the critical solution in methylcyclohexane the Kerr effect exactly follows the behaviour of the solution in cyclopentane, another cyclic hydrocarbon; however, for high temperature only. When approaching the phase separation the precritical contribution to EKE increases, resulting in a change in the sign of the effect and its temperature coefficient by 1.4 K and 12 K above T_c, respectively. Such a behaviour, typical for the non-linear dielectric effect [5, 6], has been for the first time observed for EKE.

Since the studied system has a distinctly pronounced critical opalescence ($\Delta n_D = 0.12$) the EKE anomaly can be due not only to birefringence, but also to conservative dichroism [3, 7]. Although the mechanisms of electric field induced precritical phenomena are not quite clear to-day, it should be noted that the reversal of the sign of both the birefringence and the induced electric permittivity increment as a result of increased molecular interactions was predicted by Piekara as early as 1939 [8]. However, non-molecular macroscopic mechanisms of anomalies near the consolution point also seem to be very important [3, 5, 6].

In all the mixtures examined up to-date (more than ten binary systems) only the positive anomalies of EKE have been observed in the precritical state. This makes the EKE mechanisms near the critical solubility point of binary mixtures different from those near the nematic–isotropic phase transition temperature of pure compounds, where the sign of the anomaly is controlled by molecular parameters and geometry [9].

Detailed analysis of the results for non-linear electric field induced effects, obtained for several phenyl alcohols, in terms of critical parameters will be presented elsewhere.

The advice and interest of Professor A. Piekara in the present work is greatly acknowledged. One of authors (W. P.) is also indebted to Doc. Dr. T. Krupkowski for a critical discussion.

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