Pramāṇa – J. Phys., Vol. 28, No. 3, March 1987, pp. 269–275. © Printed in India.

The dielectric constant of the binary liquid system *n*. heptane + methanol near its critical temperature

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MS received 11 June 1986; revised 8 January 1987

Abstract. The electrical capacitance of the binary liquid mixture *n*. heptane + methanol at its critical composition is studied in both one-phase and two-phase regions. The two-phase capacitance data are used with the known functional forms for the order parameter and the diameter to obtain T_c and c_c with greater precision. This helps in reducing the number of unknown parameters in the functional form for the one-phase capacitance. The data show consistency with an alpha (α) exponent for dc/dt in the one phase region.

Keywords. Critical phenomena; binary liquids; critical exponents; critical temperature; critical capacitance.

PACS No. 64·70

1. Introduction

The dielectric constant of binary liquid mixtures is expected to show a singular behaviour near the critical solution temperature of phase separation (Mistura 1973; Stell and Hoye 1974; Goulan *et al* 1979; Sengers *et al* 1980). The dielectric constant behaviour at the critical point is expected to behave as

$$\rho^{-1}\varepsilon = \rho_c^{-1}\varepsilon_c(1+\varepsilon_1 t^{(1-\alpha)}+\varepsilon_2 t+\varepsilon_3 t^{(1-\alpha+\Delta)}+\ \ldots), \tag{1}$$

where ε = the dielectric constant of the mixture, ε_c = dielectric constant at the critical temperature T_c, $t = (T-T_c)/T_c$, ρ = density of the system, ρ_c = density of the system at the critical temperature, α = specific heat exponent = 0·11 and Δ = Wegner correction term = 0·5. This implies a density anomaly always hidden along with the intrinsic ε anomaly. However the study of the density of a few systems has shown that the density anomaly contribution is small compared to the intrinsic dielectric constant anomaly (Greer and Jacobs 1980; Theon *et al* 1981). In the absence of a density anomaly the functional form is

$$\varepsilon = \varepsilon_c + A(1)t^{(1-\alpha)}+A(2)t+A(3)t^{(1-\alpha+\Delta)}, \tag{2}$$

where $A(1) = \varepsilon_c\varepsilon_1$ and so on.

Experimental studies on the dielectric constant in binary liquids have indeed shown an anomalous behaviour above the background at the critical temperature. The early literature is reviewed by Arkhangelskii and Semencheko (1967). Jacobs and Greer (1981) report a decrease in ε as $t \to 0$ in the system polystyrene + cyclohexane. Theon