

## LETTERS TO THE EDITOR

DIELECTRIC SATURATION OF NITROBENZENE IN SOME DIPOLAR AND  
NONDIPOLAR SOLVENTS

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Dielectric saturation  $\Delta\epsilon = \epsilon^E - \epsilon$  (where  $\epsilon^E$  and  $\epsilon$  are, respectively, the dielectric permittivity of the medium in the presence and absence of an externally applied electric field  $E$ ) is measured for solutions of nitrobenzene in the nondipolar solvents: benzene, cyklohexane, carbon tetrachloride, and the dipolar solvents toluene, chlorobenzene, *o*-dichlorobenzene.

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*Experimental*

All substances were purified by distillation (at normal or reduced pressure, according to the boiling temperature) and dried over dehydrated  $\text{Al}_2\text{O}_3$ . After purification, the liquids had a conductivity of the order of  $10^{-11}$  to  $10^{-12} \Omega^{-1} \text{cm}^{-1}$ .

For measuring dielectric saturation, the device described previously [4] was used. High voltage was applied to the measuring condenser plates from a ZWO-02 type high voltage supply. The electric field strength ranged from 10 to 40 kV/cm.







The cylindrical brass measuring condenser had a capacity of 15.3 pF.

All measurements are for  $20^\circ \pm 1^\circ\text{C}$ .

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TABLE I

Compound	Chemical formula	Molecular mass	Density $\rho_{20^\circ} \left[ \frac{\text{g}}{\text{cm}^3} \right]$	Dipole moment $\mu$ [D]	Dielectric permittivity $\epsilon_{20^\circ}$
nitrobenzene		123.108	1.203	3.99	35.68
benzene		78.108	0.878	0	2.284
cyclohexane		84.156	0.778	0	2.023
carbon tetrachlorid	CCl <sub>4</sub>	153.838	1.594	0	2.238
toluene		92.134	0.867	0.37	2.379 <sub>25°C</sub>
chlorobenzene		112.557	1.106	1.56	5.67 <sub>25°C</sub>
<i>o</i> -dichlorobenzene		147.006	1.309	2.27	9.93 <sub>25°C</sub>

### Results

The dielectric saturation  $\frac{\Delta\epsilon}{E^2}$  as a function of the nitrobenzene concentration  $f_2$ , expressed in molar fraction is plotted in Fig. 1 for the various solvents.

The curves of Fig. 1 are essentially, similar in shape: in all cases, there is inversion of the sign of saturation from negative to positive, as first observed for nitrobenzene in benzene by Piekara and Piekara [5]. The explanation of this shape of the saturation curve in solutions of nitrobenzene in benzene, as proposed by Piekara [6, 7] is as follows: In pure nitrobenzene, the mean intermolecular distance is small, and interactions leading to antiparallel pair formation are large. The externally applied electric field causes an increase in the mean resultant moment of the pairs of dipoles, leading to an increase in the electric susceptibility and to a positive sign of the saturation phenomena. With increasing dilution, the mean intermolecular distances augment, the interactions weaken, and normal Debye saturation with  $\frac{\Delta\epsilon}{E^2} < 0$  becomes predominant. Thus, in pure nitrobenzene the changes in electric susceptibility in an electric field are positive and relatively large, but decrease steeply and change their sign to negative with proceeding dilution. Finally, the dielectric exhibits properties resembling those of a gas.

This paper is aimed at establishing the influence of dipolar and nondipolar solvents on the concentrational dependence of dielectric saturation of nitrobenzene in the entire range of concentration.

The curves of Fig. 1 allow to state that in the case of solutions of nitrobenzene in dipolar solvents (chlorobenzene, *o*-dichlorobenzene) inversion of the sign of saturation from negative to positive occurs at a lower concentration than in nondipolar solvent (carbon tetrachloride,

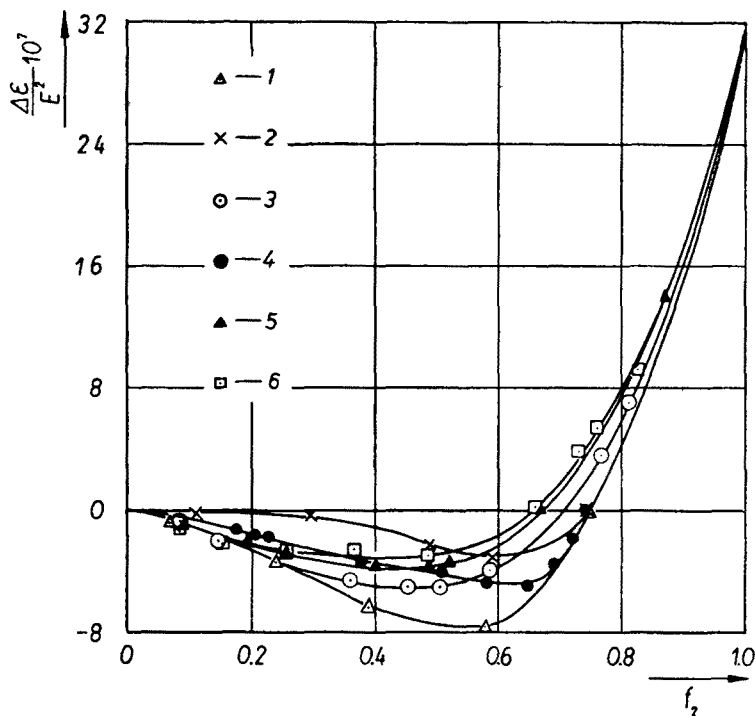


Fig. 1. Dielectric saturation  $\frac{\Delta\epsilon}{E^2}$  versus the concentration  $f_2$  of nitrobenzene in the following solvents: 1 - benzene, 2 - cyclohexane, 3 - carbon tetrachloride, 4 - toluene, 5 - chlorobenzene, 6 - *o*-dichlorobenzene

cyclohexane) and shifts towards lower concentrations with increasing polarity of the solvent molecules. The most markedly neutral behaviour is exhibited by carbon tetrachloride, where the intermolecular interactions appear to be the weakest. In toluene, some influence of interactions is apparent already at low nitrobenzene concentrations. In benzene the interactions appear to be stronger, and increase still more markedly as one goes over to solutions in chlorobenzene and *o*-dichlorobenzene. The interaction of the nitrobenzene molecules with one another and with the molecules of the various dipolar solvents employed seem to be of the same nature [4-8]. This leads to variations of  $\frac{\Delta\epsilon}{E^2}$  in the direction of positive values for each of the solvents, as compared to carbon tetrachloride. These variations increase with the polarity of the solvent molecules, *i. e.* with increasing interaction energy.

The shape of the saturation curve for solutions of nitrobenzene in cyclohexane is somewhat different, pointing to strong interactions between the nitrobenzene molecules already in the range of low concentrations. Plausibly, the situation here is similar to that observed in a system exhibiting critical solubility properties as *e. g.*, solutions of nitrobenzene in hexane [9, 10, 11].

The only general conclusion to be drawn from the present experiment is that dielectric saturation in solutions of nitrobenzene depends on the kind of solvent used and, in particular, on the degree of polarity of its molecules. More detailed information as to what kind of interaction intervenes and why well-apparent differences in dielectric saturation of nitrobenzene occur even in the case of nondipolar solvents can be awaited from future further, reaching investigations of relevant dielectric properties (determinations of the dipolar polarization and molar constants of the solutions in question). Work upon these lines is now in progress, and the results will be published separately.

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