

## QUADRATIC CHANGES IN ELECTRIC PERMITTIVITY OF CHLOROBENZENE

BY J. ZIOŁO

Institute of Physics, Silesian University, Katowice\*

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The results of the quadratic changes in electric permittivity  $\frac{\Delta\epsilon}{E^2}$  measurements in carbon tetrachloride solution of chlorobenzene. The data indicate the intermolecular interactions in chlorobenzene, which cause antiparallel orientation of nearest dipoles.

### 1. Introduction

The present study was undertaken to investigate the intermolecular interactions in chlorobenzene by the quadratic changes in electric permittivity method. Previously, frequently cited works reporting the results obtained by Kautzsch [1-3], indicated that there were no distinct intermolecular interactions in chlorobenzene. However, such effects are easily noticeable when other methods, such as NMR [4], are applied. Due to this reason it was decided to repeat the  $\frac{\Delta\epsilon}{E^2}$  measurements in chlorobenzene and carbon tetrachloride.

### 2. Experimental

The quadratic changes in electric permittivity method consists in determining changes in the dielectric permittivity of solution contained in a condenser if a strong electric field  $E$  is applied

$$\Delta\epsilon = \epsilon^E - \epsilon.$$

These changes are proportional to  $E^2$  and can be depicted by the formula

$$\Delta\epsilon = f(T, \mu, \epsilon) R_s \cdot E^2,$$

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\* Address: Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland.

where  $R_s$  is the correlation factor  $R_s = S/S_1$ , and  $S$  is the molar constant defined [5] as:

$$S = \frac{\partial P^{\text{dip}}}{\partial(F^2)},$$

where  $P^{\text{dip}}$  is the molar dipole polarization and  $F$  is the local field component,

$$S_1 = -\frac{4\pi N\mu_0^4}{45k^3T^3}.$$

Here  $N$  is Avogadro's number,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature and  $\mu_0$  is the dipole moment of a free molecule.  $R_s$  is a measure of the intermolecular interactions. Applying the Onsager local field model  $R_s$  can be depicted by the formula [5]:

$$R_s = \frac{(2\varepsilon^2 + n^4)(2\varepsilon + n^2)^2}{\varepsilon^4(n^2 + 2)^4} \frac{V}{S_1} \frac{\Delta\varepsilon}{E^2},$$

where  $n$  is the refractive index and  $V$  is the molar volume.  $\frac{\Delta\varepsilon}{E^2}$  measurements have been performed using apparatus with phase detection capabilities [6] and that developed by Małeckı [7]. The results obtained on both devices for pure chlorobenzene were consistent to an accuracy better than 2%.

### 3. Results

The measurements were performed on chlorobenzene — supplied by Polskie Odczynniki Chemiczne, Gliwice — after twice distilling and drying on molecular sieves. obtained results for various chlorobenzene concentrations in carbon tetrachloride, are shown in Fig. 1. All the values are given in the cgs system. The  $\frac{\Delta\varepsilon}{E^2}$  values are comparable to the electrocaloric  $\frac{\Delta\varepsilon_a}{E^2}$ , and electrostriction  $\frac{\Delta\varepsilon_e}{E^2}$  effects. According to [2] these values for chlorobenzene they are

$$\frac{\Delta\varepsilon_a}{E^2} = -4.2 \cdot 10^{-10}, \quad \frac{\Delta\varepsilon_e}{E^2} = 2.1 \cdot 10^{-10}$$

Providing that magnitude of these effects in the solution is proportional to the chlorobenzene concentration, the straight line 2 in Fig. 1 should be considered as the concentration dependence of  $\frac{\Delta\varepsilon_a + \Delta\varepsilon_e}{E^2}$ . Line 3 in this figure represents the quadratic changes in electric permittivity participation of carbon tetrachloride. The resultant course of  $\frac{\Delta\varepsilon}{E^2}$  for chlorobenzene is shown by line 4 in Fig. 1.

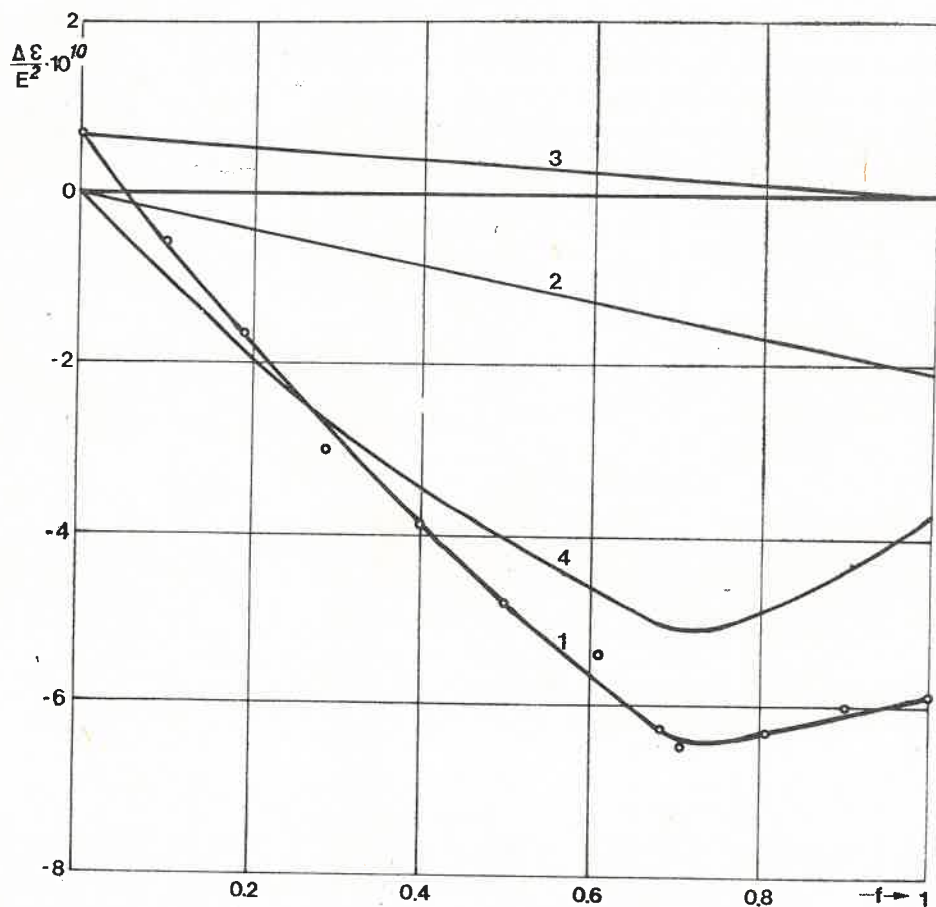


Fig. 1. The concentration dependence of  $\frac{\Delta \epsilon}{E^2}$  for the solution of chlorobenzene in carbon tetrachloride:

1 — the experimental values of  $\frac{\Delta \epsilon}{E^2}$  for the solutions, 2 — the dependence  $\frac{\Delta \epsilon_a + \Delta \epsilon_e}{E^2}$  vs concentration, 3 — the effect attributed to  $\text{CCl}_4$ , 4 — the resultant effect attributed to  $\text{C}_6\text{H}_5\text{Cl}$

#### 4. Discussion

The dependence of  $\frac{\Delta \epsilon}{E^2}$  on concentration for chlorobenzene (Fig. 1) resembles that for nitrobenzene [2]. Fig. 2 shows the dependences of  $R_s$  and  $R_p$ , where  $R_p$  is the correlation factor defined as  $R_p = \frac{\bar{\mu}^2}{\mu_0^2}$  with  $\bar{\mu}^2$  being the mean dipole moment of a molecule in the solution. For this plot the value  $\mu_0 = 1.69$  D was accepted. According to Piekara [8] such a form of the concentration dependence of  $\frac{\Delta \epsilon}{E^2}$  as well as the value of  $R_s < 1$ , may

be attributed to short range intermolecular interactions which make the neighbouring dipoles arrange themselves, so they form an obtuse angle. The investigations of the chemical shift of protons [4] indicate that the mean value of this angle is about  $150^\circ$ .

The interpretation of experimental results presented here takes into account only the dipole interactions. The theory developed by Kielich [9, 10] takes also into consideration

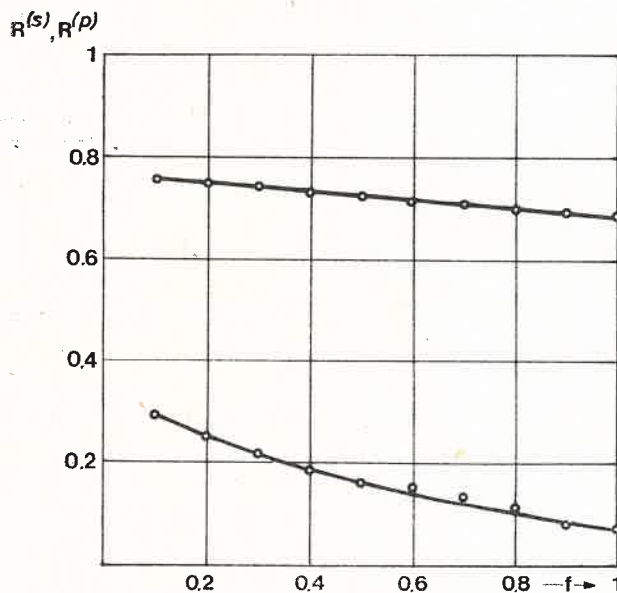


Fig. 2. Plots of  $R_s$  and  $R_p$  (upper curve) on concentration for the solutions of  $C_6H_5Cl$  in  $CCl_4$

other mechanisms, i.e. the radial angular correlations and statistical — fluctuation effects. They has been checked for some non-dipolar substances and yields results in approximate agreement with the experiment [10].

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#### REFERENCES

- [1] F. Kautzsch, *Phys. Z.* **29**, 105 (1928).
- [2] A. Piekara, A. Chełkowski, S. Kielich, *Z. Phys. Chem.* **206**, 375 (1957).
- [3] S. Kielich, in *Dielectric and Related Molecular Processes*, Ed. M. Davies, Chem. Soc., London 1972.
- [4] E. Kluk, H. Kluk, G. Skawińska, IFJ Kraków Report 819, 1973.
- [5] S. Kielich, *Acta Phys. Pol.* **17**, 239 (1958).
- [6] L. Tomawski, J. Ziolo, *Acta Phys. Pol.* **A40**, 91 (1971).
- [7] J. Małecki, *J. Chem. Soc. Faraday Trans. II*, **72**, 1214 (1976).
- [8] A. Piekara, *Acta Phys. Pol.* **10**, 37, 107 (1950).
- [9] S. Kielich, *Chem. Phys. Lett.* **7**, 347 (1970).
- [10] B. Kasprowicz-Kielich, S. Kielich, *Acta Phys. Pol.* **A50**, 215 (1976).