

## DIELECTRIC STUDY OF SOLUTIONS OF 2-METHYLOBUTANOL-2

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Dielectric polarization and its variation in an electric field are measured in solutions of 2-methylbutanol-2 in the solvents: *n*-hexane, cyclohexane, carbon tetrachloride, *p*-xylene, benzene, 1,1,1-trichloroethane and triethyloamine. From the experimental results, correlation factors for polarization,  $R^{(p)}$ , and correlation factors for dielectric saturation,  $R^{(s)}$ , are calculated.

### 1. Introduction

Dielectric investigation is a source of abundant data concerning the structure of associates and complexes, as well as inter and intra-molecular interactions [1].

The present study dealt with dielectric polarization, and its variations under the influence of an externally applied electric field (dielectric saturation effect), in solutions of 2-methylbutanol-2 (tertiary isomer of amylic alcohol) in neutral, polar and active solvents: *n*-hexane, cyclohexane<sup>1</sup>, carbon tetrachloride, *p*-xylene, benzene, 1,1,1-trichloroethane, and triethyloamine. Experiment showed solutions of the alcohol to exhibit various dielectric properties, according to the solvent.

### 2. Methods of measurement

In order to determine numerically the dielectric polarization and molar constant of dielectric saturation of a medium, one has to know its dielectric permittivity  $\epsilon$  and variation in permittivity  $\Delta\epsilon$  under the effect of an external electric field  $E$ , as well as its density  $d$  and light refractive index  $n$ . In measuring  $\epsilon$  and  $\Delta\epsilon$ , use was made of the beat circuit described in detail in Refs [2, 3]. Electric permittivity was determined by measuring the difference in capacitance of a condenser when field with the solution and when empty.

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<sup>1</sup> The dielectric properties of 2-methylbutanol-2 in cyclohexane had already been determined by Mrs Danielewicz-Ferchmin [4].

Variations of the dielectric permittivity of the solution with a strong electric field  $E$  applied to the condenser were defined as:

$$\Delta\varepsilon = \varepsilon^E - \varepsilon$$

with  $\varepsilon^E$  — the permittivity measured with field  $E$  applied and  $\varepsilon$  — at  $E = 0$ . The absolute value of the variation in permittivity is proportional to the square of  $E$ :

$$|\Delta\varepsilon| = \text{const. } E^2.$$

Hence,  $\frac{\Delta\varepsilon}{E^2} = \text{const.}$  provides a measure of the nonlinear properties of the medium (in a quadratic approximation) and defines the so-called dielectric saturation effect.

The determination of  $\frac{\Delta\varepsilon}{E^2}$  consists in measuring variations ( $\Delta C$ ) in capacitance of a condenser containing the solution under investigation on applying an electric field  $E$  to the condenser (since  $\Delta\varepsilon = \frac{\Delta C}{C_0}$ ) and in measurements of the capacitance  $C_0$  of the empty condenser as well as of the electric field strength  $E$ .

The field was applied to the condenser by the pulse method, at a pulse duration of order  $10^{-3}$ s [5]. The pulse method was necessary because of the high electric conductivity  $\sigma$  of the solutions attaining values of  $10^{-9} \Omega^{-1} \text{cm}^{-1}$ . Applied pulsewise, the field acts on the solution during a considerably shorter time; this greatly reduces heating, a source of undesirable changes in permittivity which superimpose themselves on the effect under investigation. The density of the solutions was determined with a picnometer. The dielectric measurements covered the entire range of concentrations of the alcohol, and were performed at  $20^\circ\text{C}$ .

### 3. Error of measurement

Dielectric permittivity  $\varepsilon$  and density  $d$  were measured to within 0.5 and 0.03%, respectively. Temperature variations when measuring  $\varepsilon$  and  $d$  did not exceed  $\pm 0.1^\circ\text{C}$ . In dielectric saturation determinations, temperature was constant to within  $\pm 1^\circ\text{C}$ . Error of saturation measurements was assessed at about 10%, chiefly as due to error in determining changes in capacitance  $\Delta C$ , voltage  $U$  and interelectrode distance in the liquid condenser. The short electric field pulse applied eliminated changes in permittivity by heating. Changes in  $\varepsilon$  due to electrostriction [6] were negligible. Error in determining concentration amounted to 0.05%.

### 4. Purification of the liquids

As criterion of purity, we took the electric conductivity and, in some cases, IR absorption spectra of the substances.

Reagents of *pro analysi* and spectroscopic purity were used subsequent to further

purification by drying and distillation. In drying,  $P_2O_5$  was applied for cyclohexane, 1,1,1-trichloroethane and carbon tetrachloride, KOH for triethyloamine, metallic sodium for benzene, and anhydrous magnesium sulfate for *p*-xylene.

### 5. Experimental results

Fig. 1 shows the dielectric permittivity  $\epsilon$  vs concentration for 2-methylbutanol-2 in *n*-hexane, cyclohexane,  $CCl_4$ , *p*-xylene, benzene, triethyloamine, and 1,1,1-trichloroethane. The permittivity is found to increase with the concentration of the alcohol in solution. In the case of 1,1,1-trichloroethane, a solvent with a rather large dipole moment

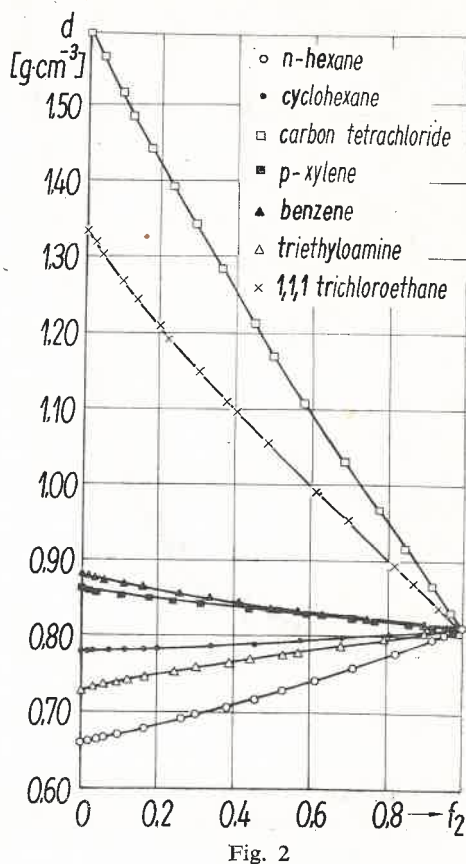
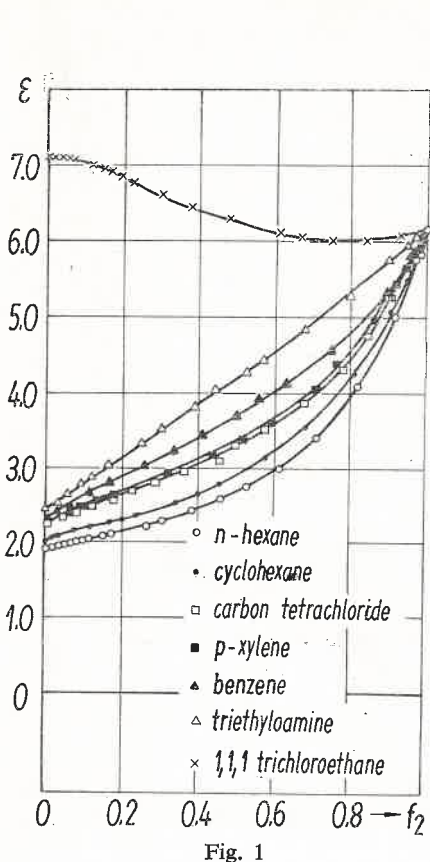


Fig. 1. Dielectric permittivity  $\epsilon$  in function of the concentration of 2-methylbutanol-2 in the solvents: *n*-hexane, cyclohexane, carbon tetrachloride, *p*-xylene, benzene, triethyloamine, and 1,1,1-trichloroethane

Fig. 2. Density vs concentration for solutions of 2-methylbutanol-2 in the solvents noted in Fig. 1

( $\mu = 1.5 D$ ) and a permittivity of  $\epsilon = 7.092$ , however, the curve of  $\epsilon = \epsilon(f_2)$  exhibits a minimum at a concentration of about 0.8.

Fig. 2. shows the density vs concentration for solutions of 2-methylbutanol-2 in the preceding 7 solvents.

Figs 3a and 3b represent the dependence of  $\Delta\epsilon/E^2$  in c. g. s. units on the concentration of 2-methylbutanol-2 in the same solvents. On applying an electric field  $E$  to the condenser containing the solution, a rise in permittivity is observed in proportion to the alcohol concentration. In the case of 1,1,1-trichloroethane solvent, which has a non-zero dipole

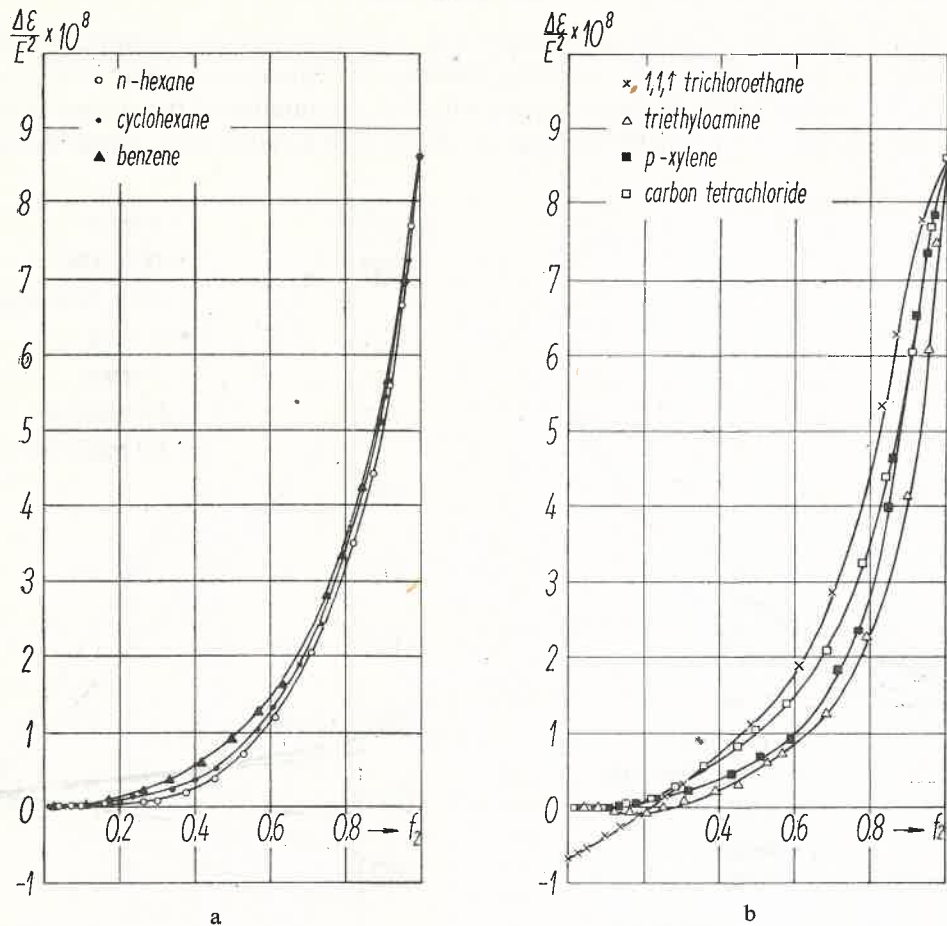


Fig. 3. Dielectric saturation  $\Delta\epsilon/E^2$  in function of the concentration of 2-methylbutanol-2 in *n*-hexane, cyclohexane, and benzene (a) as well as in carbon tetrachloride, *p*-xylene, triethylamine, and 1,1,1-trichloroethane (b)

moment, the permittivity decreases on applying an external electric field  $E$  as a result of the usual process of molecular reorientation in the field. With increasing alcohol concentrations, the electric permittivity increases under the influence of the field  $E$ ; at an alcohol concentration of  $f_2 = 0.21$ , the effect, from negative, becomes positive.

Table I contains data for some properties of 2-methylbutanol-2 as well as of the solvents. Values for  $\epsilon$ ,  $d$  and  $\Delta\epsilon/E^2$  were obtained experimentally. The remaining data were taken from the Landolt-Börnstein Tables [7].

TABLE I

Substance	$\epsilon$	$d$	$\frac{\Delta\epsilon}{E^2} \times 10^8$	$n_D^{20}$	molecular mass	$\mu(D)$
2-methylbutanol-2 $C_5H_{12}O$	6.165	0.8109	8.62	1.4052	88.14	1.60
cyclohexane $C_6H_{12}$	2.023	0.7783	0	1.4262	84.15	0
<i>n</i> -hexane $C_6H_{14}$	1.8893	0.6594	0	1.3750	86.17	0
carbon tetrachloride $CCl_4$	2.232	1.5952	0	1.4604	153.84	0
<i>p</i> -xylene $C_8H_{10}$	2.273	0.8613	0	1.4961	106.16	0
benzene $C_6H_6$	2.2828	0.8789	0	1.5012	78.11	0
1,1,1-trichloroethane $CH_3CCl_3$	7.092	1.3342	-0.68	1.4383	133.42	1.5
triethylamine $(C_2H_5)_3N$	2.450	0.7278	0	1.4010	101.19	0.79

### 6. Discussion of the results

The experimentally measured values of the dielectric permittivity  $\epsilon$ , electric field-induced changes in permittivity  $\Delta\epsilon/E^2$ , density  $d$ , light refractive index  $n$  and concentration  $f$  of the solutions can serve for calculating quantities describing 1 mole of molecules of 2-methylbutanol-2. In calculating the molar constant of dipole polarization, we applied Eq. (6.1), derived on the assumption of Onsager's model [8] generalized to solutions associating with dipolar and active solvents [9]:

$$P = (f_1 - x)(P_1^n + g_1 P_1^{\text{dip}})g_1 + xP_1^n g_2 + f_2(P_2^n + g_2 P_2^{\text{dip}})g_2. \quad (6.1)$$

The indices "1" and "2" refer to the solvent and solute, respectively; quantities describing the solution are noted without index.  $P_i^n$  and  $P_i^{\text{dip}}$  stand for molar distortional polarizabilities and molar dipolar polarizabilities, respectively. The symbol  $x$  denotes the concentration of solvent molecules inbuilt into complexes.

$P_2^{\text{dip}}$  can be determined from Eq. (6.1) on assuming  $x = 0$ . The resulting error in  $P_2^{\text{dip}}$  is insignificant, since  $P_1^{\text{dip}}$  is close to zero for all the solvents applied, except 1,1,1-trichloroethane, where the error due to assuming  $x = 0$  is at present difficult to evaluate, and depends on  $x$ . We obtain:

$$P_2^{\text{dip}} = [P - P_1^n f_1 g_1 - P_2^n f_2 g_2] \frac{1}{f_2 g_2} \quad (6.2)$$

where:

$$P = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} V, \quad P_1^n = \frac{n_1^2 - 1}{n_1^2 + 2} V_1,$$

$$P_2^n = \frac{n_2^2 - 1}{n_2^2 + 2} V_2, \quad g_i = \frac{(2\epsilon + 1)(n_i^2 + 2)}{3(2\epsilon + n_i^2)}$$

$V$  is the molar volume, and  $n$  the refractive index extrapolated to infinite wavelength of light.

In non-associating substances,  $P_2^{\text{dip}}$  is proportional to the value of  $\mu_2^2$  of the molecules under investigation, whereas for associating ones  $P_2^{\text{dip}}$  is given by the relation:

$$P_2^{\text{dip}} = \frac{4\pi N}{9kT} \bar{\mu}_2^2,$$

where  $k$  is Boltzmann's constant,  $T$  the absolute temperature,  $N$  Avogadro's number, and  $\bar{\mu}_2^2$  the mean squared dipole moments of the associates present in the solution [10].

The following correlation factor of polarization  $R^{(p)}$  is introduced, defined as:

$$R^{(p)} = \frac{P_2^{\text{dip}}}{P_2^{\text{dip}}{}_{\text{gas}}} = \frac{9kTP_2^{\text{dip}}}{4\pi N\mu_2^2} = \frac{\bar{\mu}_2^2}{\mu_2^2}, \quad (6.4)$$

with  $\mu_2$  — the dipole moment of the molecule investigated, when in the gaseous state.

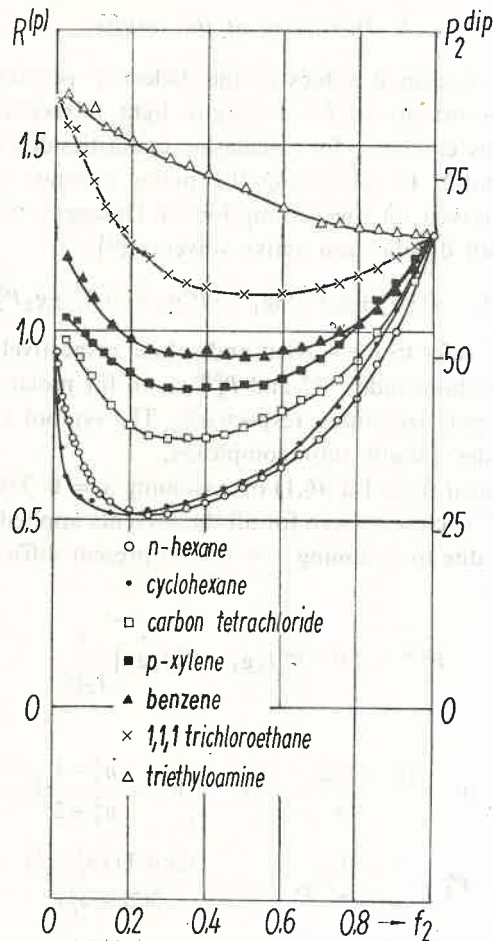


Fig. 4.  $R^{(p)}$  in function of the concentration of 2-methylbutanol-2 in *n*-hexane, cyclohexane, carbon tetrachloride, *p*-xylene, benzene, 1,1,1-trichloroethane, and triethyloamine

For determining  ${}_{\text{gas}}P_2^{\text{dip}}$ , a value of  $\mu_2 = 1.6 D$  was assumed, yielding  ${}_{\text{gas}}P_2^{\text{dip}} = 53.89 \text{ cm}^3$ .

Fig. 4 shows  $R^{(p)}$  vs the concentration of 2-methylbutanol-2 for all the solvents. The ordinates, beside  $R^{(p)}$ , give values of  $P_2^{\text{dip}}$ . The solvent is seen to affect the shape of  $R^{(p)} = R^{(p)}(f_2)$  markedly. In neutral solvents,  $R^{(p)}(f_2)$  presents a well-defined minimum and values less than unity. This can be attributed to the existence of associates of cyclic structure. In the more strongly active solvents, the rise in polarization is due to the presence of complexes with open structure and a large dipole moment.

The amount of dielectric saturation  $\Delta\epsilon/E^2$  — an effect pointing to nonlinear dielectric properties of the medium — is also accessible to expression by means of a molar quantity, the molar constant of dielectric saturation  $S_2^m$ . The quantity was introduced by Piekara in 1950 [1] and is defined for the dielectric medium as a whole. Małeckı [9], in calculating  $S_2^m$ , considers the contributions from dipolar and active solvents. The molar constant of dielectric saturation  $S_2^m$  is defined as the derivative of  $P_2^{\text{dip}}$  with respect to the squared internal field component ( $F$ ) parallel to the externally applied electric field  $E$ :

$$S_2^m = \frac{\partial P_2^{\text{dip}}}{\partial(F^2)} \quad (6.5)$$

where

$$F = \frac{\epsilon(n^2+2)}{2\epsilon+n^2} E \quad \text{on the assumption of Onsager's model.}$$

For free molecules with dipole moment  $\mu_2$  given by Eq. (6.5), we obtain:

$${}_{\text{gas}}S_2^m = \frac{-4\pi N\mu_2^4}{45k^3T^3} \quad (6.6)$$

By analogy to the correlation factor for polarization, a correlation factor of dielectric saturation  $R^{(s)}$  can be introduced. This factor is defined as follows:

$$R^{(s)} = \frac{S_2^m}{{}_{\text{gas}}S_2^m} \quad (6.7)$$

On insertion herein of the value for  ${}_{\text{gas}}S_2^m$ , we obtain:

$$R^{(s)} = \frac{-45k^3T^3S_2^m}{4\pi N\mu_2^4} \quad (6.8)$$

Considerations by Małeckı [9] led to the following relations for dipolar and active solvents:

$$S_2^m = \frac{S^m}{f_2} - \frac{f_1-x}{f_2} \gamma_1^2 S_1^m \quad (6.9)$$

where:

$$S^m = \frac{(2\epsilon^2+n^4)(2\epsilon+n^2)^2}{\epsilon^4(n^2+2)^2(n^2+2)^2} V \frac{\Delta\epsilon}{E^2} \quad (6.10)$$

$$S_1^m = \frac{(2\epsilon_1^2 + n_1^4)(2\epsilon + n^2)^2}{\epsilon^2 \epsilon_1^2 (n_1^2 + 2)^2 (n^2 + 2)^2} V_1 \frac{\Delta \epsilon_1}{E^2} \quad (6.11)$$

$$\gamma_1 = \frac{(n_1^2 + 2)(2\epsilon + n_2^2)}{(n_2^2 + 2)(2\epsilon + n_1^2)} \quad (6.12)$$

Non-dipolar liquids maintain a constant polarization when subjected to a strong electric field  $E$ , whence  $S_1^m = 0$ .

For dipolar liquids, provided the value of  $P_1^{\text{dip}}$  is close to zero, the assumption  $x = 0$  can be made too. The error thus incurred in calculations of  $S_2^m$  is small.

Figs 5a and 5b represent  $R^{(s)}$  vs. the concentration of 2-methylbutanol-2 in *n*-hexane, cyclohexane and benzene (a) as well as in carbon tetrachloride, *p*-xylene, triethyloamine and 1,1,1-trichloroethane (b). Except in one case,  $R^{(s)}$  is found to present negative and

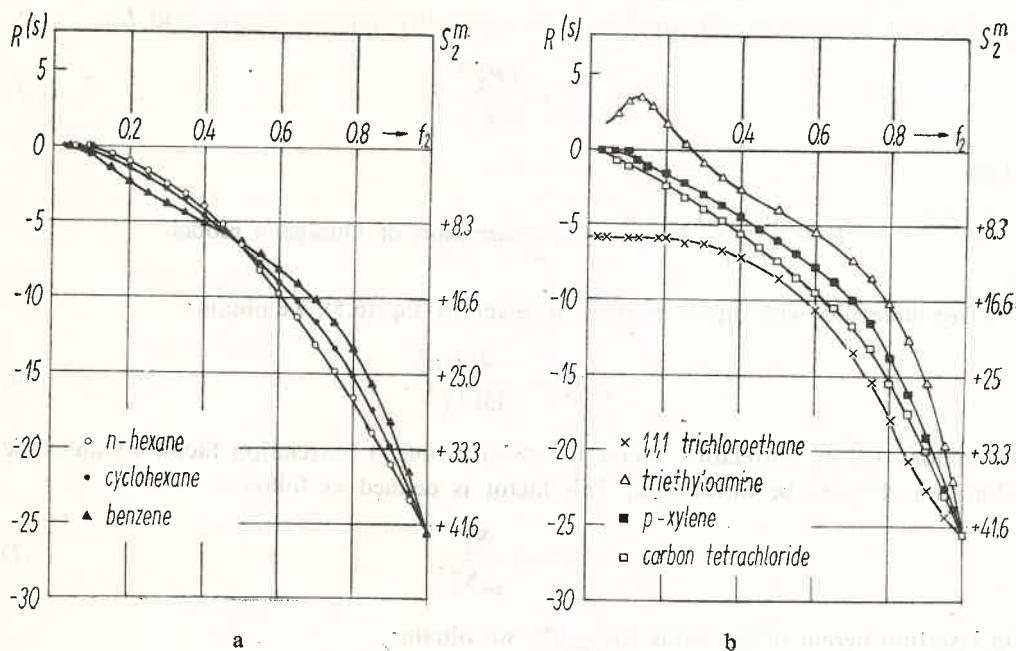


Fig. 5.  $R^{(s)}$  in function of the concentration of 2-methylbutanol-2 in *n*-hexane, cyclohexane, and benzene (a) as well as in carbon tetrachloride, *p*-xylene, triethyloamine, and 1,1,1-trichloroethane (b)

decreasing values throughout the entire range of concentrations. This means that  $S_2^m$  is positive. The negative values of  $R^{(s)}$  can be explained on the basis of the model of Refs [11] and [12]. The increase in  $R^{(s)}$  in triethyloamine can be due to the formation of complexes with the latter [9].

The present results permit the conclusion that, in the systems investigated, the values of  $P_2^{\text{dip}}$  and  $S^m$  depend essentially on intermolecular interaction by way of hydrogen bonding.

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