

DIELECTRIC ANOMALIES AND MOLECULAR PHENOMENA IN THE  
SOLIDIFICATION OF *n*-CETYL ALCOHOL AND ITS SOLUTIONS

BY B. PIEKARA\*

Research Physics Laboratory, Technical School TME, Gdańsk

*(Received March 2, 1971)*

The temperature dependence of electric permittivity  $\epsilon$  and electric conductivity  $\sigma$  were investigated for *n*-cetyl alcohol and its solutions in benzene and hexane around their freezing points. Two temperatures of freezing were found: at the first one the liquid, while solidifying, passes into gel phase in which  $\epsilon$  and  $\sigma$  increase suddenly; at the second one a solid phase arises from the gel phase, and the  $\epsilon$  and  $\sigma$  drop rapidly to values lower than those for the liquid. Basing on the theory of Debye-Onsager-Kirkwood as well as on the theory of A. Piekara which concerns the role of hydrogen bonding in polarization of alcohols, the author proposed explanations of the anomalies  $\epsilon(t)$  and  $\sigma(t)$ , indicating some molecular phenomena which may be responsible for the behaviour of the two quantities  $\epsilon$  and  $\sigma$ . They are: orientational polarization of hydrogen bonds in the gel phase (sudden increase in  $\epsilon$  and  $\sigma$  at the temperature of the first freezing point), polarization reversal effect of the OH-chains in the gel phase caused by the transition of protons through the potential barrier in the bridge O—H...O, and a probable structural change of the hydrogen bonds chain from open to cyclic form at the temperature of the second freezing point (sudden drop of  $\epsilon$  and  $\sigma$ ).

*1. Introduction*

*n*-cetyl alcohol belongs to substances associating strongly by the hydrogen bonding. The existence of the type O—H...O interaction presumably allows us to explain the phenomenon of anomaly of electric permittivity in *n*-cetyl alcohol, found also in other compounds by Smyth and co-workers [1, 2], and also studied by the author in pure alcohol and its solutions in benzene and hexane.

The anomaly of electric permittivity  $\epsilon$ , observed during the solidification, consists in a sudden and a very great increase in  $\epsilon$  at the freezing point (Fig. 1c); by further cooling down the substance, the electric permittivity remains high until the temperature at which  $\epsilon$  drops rapidly to values lower than  $\epsilon_{\text{liquid}}$  (the temperature of the second freezing point). However — in most of the dipole liquids a sudden drop of the electric permittivity may already be observed at the first freezing temperature (Fig. 1a), caused by stiffening of the dipoles in the crystal lattice, and at the same time the system receives the characteristics of

---

\* Address: Zakład Fizyki, Wyższa Szkoła Nauczycielska, Siedlce, Poland.

non-polar substance ( $\epsilon \cong n^2$ ). On the other hand, in some substances such as camphor and its derivatives [3], or in solutions of the palmitic acid in hexane [4] for any temperature above and below the freezing point there is a monotonic increase in electric permittivity (Fig. 1b). This proves that reorientation of dipoles can occur in the liquid phase as well as in the solid one (that concerns mainly the spherical or cylindrically shaped molecules).

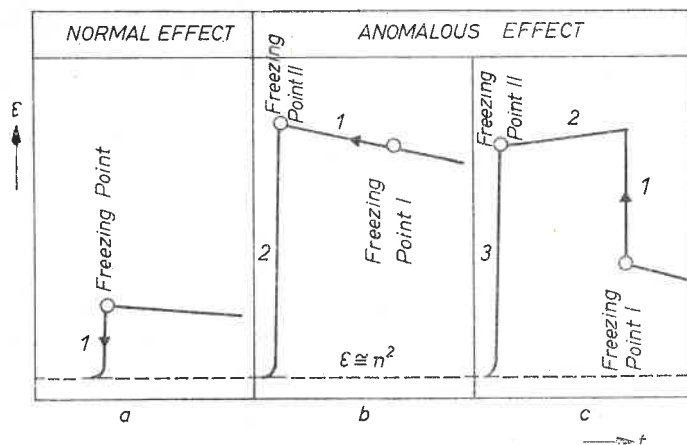


Fig. 1. Three types of the dependence of  $\epsilon(t)$  in the solid state of substances (schematic). (a) Normal effect of freezing: the electric permittivity  $\epsilon$  drops rapidly to the values  $\epsilon \cong n^2$ ; (b) and (c) Anomalous effect of freezing: (b) monotonic increase in  $\epsilon$ , (c) sudden and very great increase in  $\epsilon$  at the freezing point for many long-chain compounds

The measurements of electrical conductivity  $\sigma$  taken for *n*-cetyl alcohol and its solutions have shown the existence of a similar anomaly, just like the one which occurs in the dependence  $\epsilon(t)$ . Tests have been undertaken in order to explain non-typical curves  $\epsilon(t)$  and  $\sigma(t)$ , assuming the proton mechanism of electric conductivity, in which the existence of two energy states of the hydrogen bridge is postulated [5].

In the present paper, the dielectric and electric properties of *n*-cetyl alcohol and its solutions in benzene and hexane are reported for the temperature range around the freezing point. This paper is also an attempt to determine the structure of the systems of associated molecules in both phases formed during solidification.

## 2. Experimental

The measurements of electric permittivity were performed by a beat method with oscillographic registration (Fig. 2). The condenser filled with the liquid to be investigated was connected to one of the two RF generators ( $\approx 10^6$ Hz) which, together with an RF mixer, constituted a heterodyne circuit. Capacity changes of the condenser were compensated by a calibrated, rotating-scale Philipps' condenser with an accuracy of 0.02 pF. The conducted current was measured with a microammeter. In order to remove the air evolving during the solidification of pure alcohol, the measurements were performed in a special condenser adapted for investigations under vacuum and immersed in oil bath, in a thermostat.

The measuring condenser (Fig. 3) consisted of a cylindrical shield (*a*) acting simultaneously as electrode and of an inner electrode (*b*) fixed to a kalite insulator (*k*), both electrodes of stainless steel. The distance between the electrodes was  $d = 0.05$  cm and radius of the inner electrode  $r = 1.00$  cm. The internal electrode was pressed to the base (*a*) by threaded

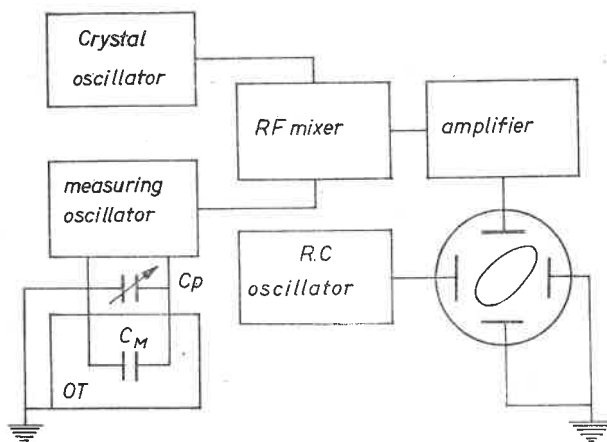


Fig. 2. Block diagram of the electronic arrangement for the measurement of small changes in capacity  $C_M$ .  $C_M$ —measuring condenser, *OT*—oil-thermostat,  $C_P$ —Philipp's condenser

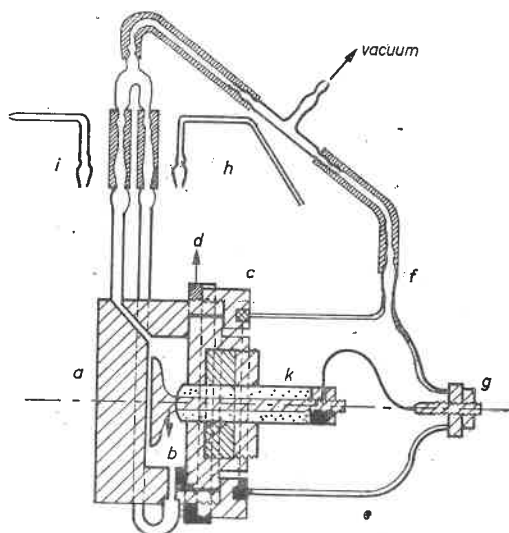


Fig. 3. The liquid condenser for measuring in vacuum

metal ring (*c*) whose lower edge was caulked with rubber disc (*d*); to the upper edge was fastened by araldit a little bell-glass (*e*) with tube (*f*) onto the vacuum and metallic ending (*g*) from the internal electrode. The liquid was introduced into the condenser through the inflow tube (*h*). This condenser was calibrated with benzene which was distilled and then dehydrated by means of metallic sodium.

### 3. Results and discussion

#### 3.1. *n*-cetyl alcohol

Fig. 4. presents the results of the measurements; the curve of  $\epsilon(t)$  and  $\sigma(t)$  shows the anomaly of electric permittivity and electric conductivity as well as the hysteresis loop obtained in the temperature interval between the first freezing (48.3°C) and the second freezing point (24°C). Earlier investigations [6] have shown that similar hysteresis curves

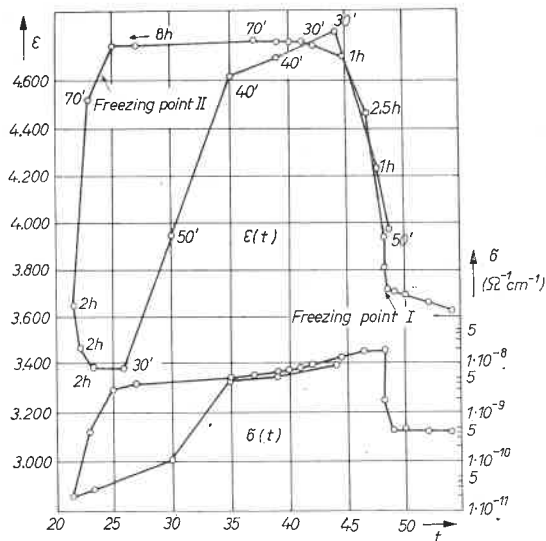


Fig. 4. Anomalous effect of freezing in *n*-cetyl alcohol. Next to the measuring points in the diagram of  $\epsilon(t)$  are given the freezing times at the constant temperature

are obtained for gelling solutions, and that may justify the name “gel” phase given here to the intermediate phase of solidified alcohol being formed between the first and the second freezing point, during which a soft, gradually hardening geleous mass is formed. The phase which is formed below the second freezing point has been called the solid phase<sup>1</sup>.

##### 3.1.1. Electric permittivity investigation

The variation of  $\epsilon$  and  $\sigma$  as a function of temperature at the boundary between the liquid and the gel phase as well as between the gel and solid phase suggests the existence of certain molecular phenomena responsible for the observed anomaly. The study of these phenomena would shed some light on the matter of structural form of the hydrogen bond chain in multimers which form the solid as well as the gel phase of alcohol.

The orientational polarization of multimers may be mentioned as the first phenomenon. In liquid phase the orientation of multimers is disturbed by thermal motion, whereas at the threshold of the gel phase the multimers pass, as it may be assumed, from a random space distribution of molecules to a much more orderly one, with greater ease of reorientation

<sup>1</sup> Smyth and his co-workers designate the gel phase as  $\alpha$  and the solid phase as  $\beta$  [7].

and that seems to justify the considerable increase in permittivity  $\epsilon$ , because  $\epsilon = 1 + 4\pi \frac{\partial P}{\partial E}$ , where  $P$  and  $E$  are dipole polarization and external field respectively.

The second phenomenon which may play a great role in explaining the facilitated reorientation, responsible for great values of  $\epsilon$  in the gel phase of alcohol, is the polarization reversal effect of the chains of hydrogen bonds in multimers (Fig. 5). According to A. Pie-

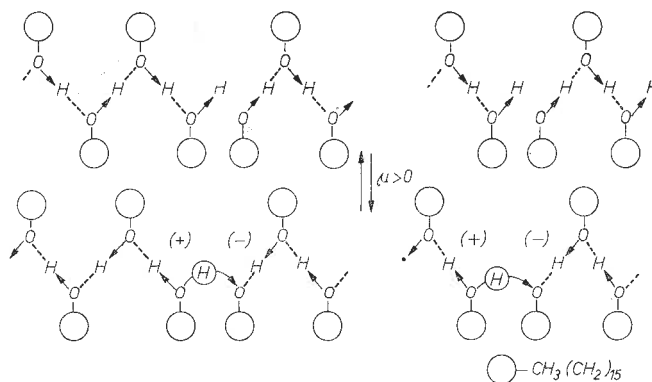


Fig. 5. Polarization reversal of the chains of hydrogen bonds (simulates rotation of multimers). Collective proton shift to the potential cavity with greater energy causes the reversal of electric moments of the OH groups, with simultaneous splitting off of hydrogen from the last chain link

kara [5] it consists in the apparent reorientation of electric moments of the hydroxyl groups, and is caused by collective proton shift along the whole chain of bonds from the potential cavity 1 with smaller energy (Fig. 6) to the cavity 2 with greater energy, and that corresponds

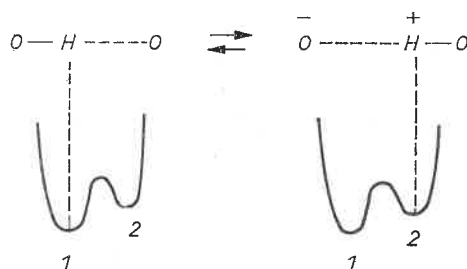


Fig. 6. The process of proton migration in the hydrogen bridge: two energy states of the bridge (1) and (2) correspond with the two positions of the proton

with two extreme positions of hydrogen in the bridge  $O-H...O$ . The polarization reversal effect may be, in principle, considered as a process of reorientation of multimers, which should be understood not as free rotation of systems of molecules but as a phenomenon of rotation simulated by the inversion of the electric moments [8].

The third phenomenon is connected with the sudden drop of the  $\epsilon$ , during transition of the gel phase into solid phase, until the value which is characteristic for non-polar compounds ( $\epsilon \approx n^2; \mu = 0$ ). This property of the nascent solid phase suggests that the new

phenomenon changing the dielectric properties of the polar gel phase into those of the non-polar solid phase is perhaps the change in hydrogen bonds structure in multimers, consisting in the transition from open structure (in gel phase) to the closed structure (in solid phase). It may be expected that the most probable closed form could be the cyclic tetramers, which are also subject to polarization reversal effect (Fig. 7). It seems that the mechanism of

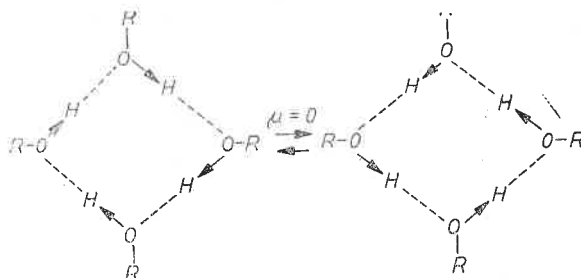


Fig. 7. The process of polarization reversal of cyclic tetramers presumably formed in the solid phase (below the temperatures of the second freezing). The potential energies of the two forms and their electrical moments are the same ( $\mu = 0$ )

polarization reversal effect of the hydrogen bridges O—H...O is common for all structures of alcohol, assuming that the potential barrier separating the two cavities is not too high. In the case of the cyclic tetramers both conformations have the same potential energy and the same electric moment  $\mu = 0$ ; this may explain the fact that no dielectric saturation in the solid phase was found by the present author.

### 3.1.2. Investigation of electric conductivity

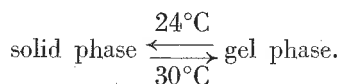
The great increase in electric conductivity (and also permittivity) observed during the first freezing process (Fig. 4) may be explained, assuming that: 1° — transport of the electrical charge occurs through the process of migration of proton in the hydrogen bridge, 2° — in the gel phase the long-chain hydrogen bonds have a tendency to be aligned with their axes parallel to each other.

The hypothesis of polarization reversal effect of the chains also seems to explain the fact of the occurrence of large  $\sigma$  values in the whole region of the gel phase. In the process of polarization reversal the jumps of proton through the potential barrier in hydrogen bridges, constituting the chain links of hydrogen bonds, lead to a situation in which proton splits off from the last OH group and becomes attached with the beginning of the neighbouring chain, thus assuring the transport of electric charge between the chains (Fig. 5). It ensues from the mechanism of this process that intensity of the conducted current depends upon the degree of orientation of multimers and that is corroborated by the measurements: in the gel phase of *n*-cetyl alcohol the value of electric conductivity is greater by almost two orders of magnitude than in the liquid phase. The possible appearance of closed structures in the solid phase at the temperature  $t = 24^\circ\text{C}$ , seems to justify the decrease in the conductivity of alcohol by two orders of magnitude (namely from the value of  $3 \cdot 10^{-9}$  down to  $2 \cdot 10^{-11} \text{ om}^{-1}\text{cm}^{-1}$ ), because the cyclic structure of the multimers does not create a situa-

tion which renders possible the splitting off of the proton. Similar influence of the structural forms of hydrogen bridges on the electric conductivity has been observed in benzoic acid [9] (dimers closed,  $\sigma = 5 \cdot 10^{-20}$ ), in *p*-nitrophenol [10] (chains open,  $\sigma = 1 \cdot 10^{-16}$ ) and in other substances.

### 3.1.3. Hysteresis curves $\varepsilon(t)$ and $\sigma(t)$

The analogy between the dependences of  $\varepsilon(t)$  and  $\sigma(t)$  applies not only to cooling curves, but also concerns the hysteresis curves (Fig. 4). A comparison of cooling and heating curves permits us to observe that the differences between cooling and heating processes consists in a transition delay of the solid phase into gel phase:



This delay may be caused by the differences in the activation energy for both directions of transitions from open forms of chain multimers into closed ring forms and *vice versa*.

### 3.1.4. Theoretical calculations

The long-chain molecules of *n*-cetyl alcohol form in the gel phase a two-layers structure which is the consequence of the mechanism of the above described molecular phenomena; in those layers the molecules are arranged almost parallel to one another ( $\uparrow\uparrow$ ). Since the multimers in the gel phase have the freedom of reorientation caused by the exchange of electrical moment of the OH groups for the reverse (polarization reversal effect), the multimers of alcohol form a system whose properties are similar to those of liquids. This fact justifies the possibility of applying the Onsager formula for molar polarizability of dipolar liquids for *n*-cetyl alcohol in gel phase

$$\frac{4\pi N_A}{9kT} (\mu \cdot \sin \psi)^2 = \frac{(\varepsilon - n_\infty)^2 (2\varepsilon + n_\infty)^2}{\varepsilon (n_\infty^2 + 2)^2} \cdot \frac{M}{d} \quad (1)$$

where  $\psi$  is the angle formed by the direction of electric moment with the longitudinal axis of the molecule;  $\frac{M}{d}$  is the molar volume. The value of refraction index for yellow light has been taken as the value  $n_\infty$ .

The Onsager formula is valid for non-associating liquids, but as it follows from Cole's diagram [11] as well as from the small value of  $\varepsilon$  for *n*-cetyl alcohol, it can be applied with good approximation for the tested alcohol. Kirkwood [12] has generalized that formula by introducing correlation factor  $g$  on the lefthand of the Onsager formula:

$$g = 1 + z \overline{\cos \gamma} \quad (2)$$

where  $\gamma$  is the angle between a given dipole and its neighbour,  $\overline{\cos \gamma}$  is an average value over all orientations of both dipoles, and  $z$  is the number of nearest neighbours of a given molecule. In the absence of orientation the factor  $g$  has the value of 1; with parallel orientation of molecules ( $\uparrow\uparrow$ ) as in the case of *n*-cetyl alcohol, the value of  $g = 2$  (if  $z = 1$ ). The Kirkwood-Onsager formula allows us to calculate the electric permittivity  $\varepsilon$  in the gel phase by substi-

tuting the following values:  $\mu = 1.66 \cdot 10^{-18}$ ,  $T = 299^\circ\text{K}$ ,  $n^2 \simeq 2.1$ ,  $d_{26^\circ} = 0.85$ , hence for  $g = 2$  we receive  $\epsilon_{26^\circ} = 4.74$ . Comparing this value with that measured  $\epsilon_{26^\circ}^{\text{meas}} = 4.74$  (see Fig. 4) we receive excellent agreement, and thus the model of the system of molecules arranged in parallel in gel phase can be regarded as realistic. By comparing the Kirkwood-Onsager formula with the expression for molar orientational polarizability

$$P^{\text{dip}} = \frac{4\pi N_A}{9kT} \cdot \bar{\mu}^2 \quad (3)$$

where  $\bar{\mu}^2$  is the average square value of dipole moments of the multimers present in alcohol, we obtain

$$\bar{\mu}^2 = \mu^2 \cdot g \quad (4)$$

therefrom for the temperature  $t = 26^\circ\text{C}$   $(\bar{\mu}^2)_{\text{calc.}} = 5.5D^2$ . However the value  $(\bar{\mu}^2)_{\text{meas}}$  for the temperature  $t = 50^\circ\text{C}$  obtained by the present author [13] by measuring the electric permittivity and density amounts to  $(\bar{\mu}^2)_{\text{meas}} = 4.04D^2$ . Substituting this value into the relation (4) we obtain the correlation factor with a value of  $g = 1.4$ , thus indicating a great degree of dipole-dipole interaction for molecules of liquid alcohol ( $50^\circ\text{C}$ ). One may remark that the Kirkwood correlation parameter  $g$  is identical with the A. Piekara correlation factor of polarizability  $R_p$  (see [14] and [15]).

### 3.2. Solutions of *n*-cetyl alcohol in benzene and hexane

The results of measurements of electric permittivity  $\epsilon$  as a function of the temperature and concentration are presented in Fig. 8. It can be seen that for the concentrations between  $0.316 \leq f \leq 1$  there is always the same temperature of the second freezing point ( $24^\circ\text{C}$ )

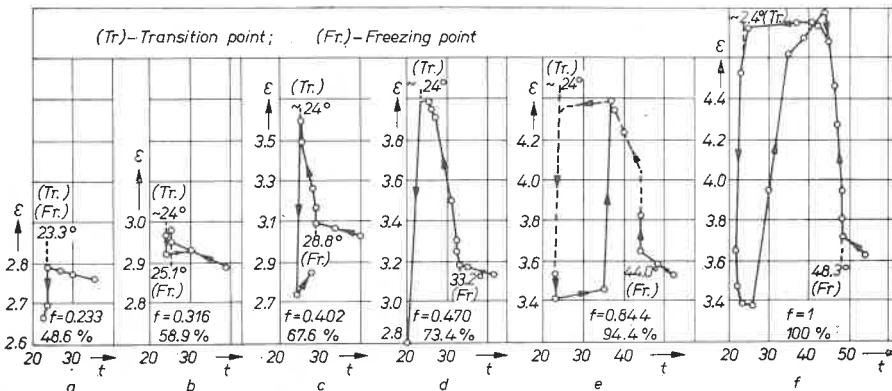


Fig. 8. In the diagrams of  $\epsilon(t)$  with the gel phase (b, c, d, e, f) we observe the same temperature of the second freezing point ( $24^\circ\text{C}$ ) for various concentrations of *n*-cetyl alcohol in benzene

which is identical with the temperature of the second freezing point for pure *n*-cetyl alcohol. This temperature has also been observed in solutions in hexane. The fact of its occurrence indicates that the multimers of alcohol presumably play a dominant role in these solutions. They are probably responsible for the anomaly of permittivity  $\epsilon$  in solidified solutions (Fig. 8b, c, d, e) as well as for the hysteresis curves (Fig. 8c, e).



The process of the decreasing difference  $\epsilon_{\text{gel}} - \epsilon_{\text{liquid}}$  manifests the influence of complexes consisting of molecules of alcohol and of a molecule of solvent. Their presence in a solution may probably diminish the degree of the orientational polarization of all the systems of molecules during the solidification process. The measurement of dipolar polarizability in liquid solutions made by the author [13] corroborates this opinion. It is found that, when the concentration of the solutions decreases, the average square of the dipole moment of the systems of molecules present in the solution, and calculated from the formula (3), also decreases.

Fig. 9 presents the curves of electric permittivity  $\epsilon(t)$  for solutions with various concentrations of alcohol in benzene (measurement points marked with circles) and in hexane (measurement points marked with triangles) in the region of the temperature of the first

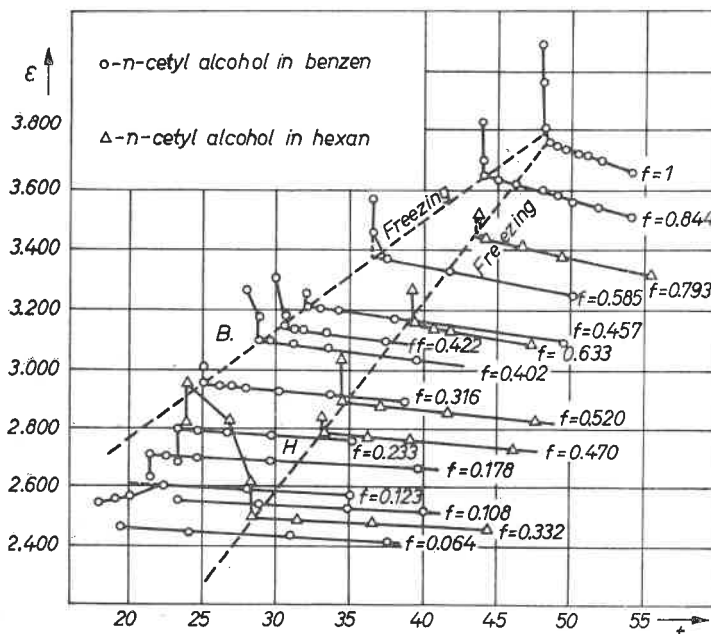


Fig. 9. Comparison of the electric permittivity values at the temperature of the first freezing point for solutions  $n$ -cetyl alcohol in benzene and in hexane. The linear distribution of values  $\epsilon$  is characteristic for the gel phase of solutions in benzene (B) and in hexane (H)

freezing point. For the solutions with concentrations greater than  $f = 0.332$  in hexane and greater than  $f = 0.316$  in benzene one observes linear distribution of the value  $\epsilon$ , corresponding to the various temperatures of first freezing. Whereas for the solutions in benzene with concentrations smaller than  $f = 0.316$ , in which the gel phase is not formed, the values of  $\epsilon$  measured during the solidification of the solutions do not lie on the straight line of freezing. The slopes of the lines for solutions in benzene and hexane are different thus indicating various degrees of activity of the solvents.

The gel phase which was formed at the first freezing point, seems to be for all concentrations a mixture of multimers with open structure of hydrogen bonds, and of complexes

and molecules of pure solvent. In the solid phase of the solutions obtained from gel phase there presumably develops a predominance of tetramers with the cyclic structure, whereas in the solid phase of the diluted solutions freezing below the temperature of 24°C, there appears a predominance of the complexes; these, probably, are not subject to simulated rotation (the polarization reversal effect), because in complexes at the end of the chain of hydrogen bonds they find a molecule of solvent. In both cases the electric conductivity of solid phase is much smaller than that of the liquid solutions.

The author is much indebted to Professor A. Piekara and his co-workers for valuable discussions throughout this work.

#### REFERENCES

- [1] Ch. P. Smyth, W. O. Baker, *J. Amer. Chem. Soc.*, **60**, 1229 (1938).
- [2] R. W. Crowe, J. D. Hoffman, Ch. P. Smyth, *J. Chem. Phys.*, **20**, 550 (1952).
- [3] M. Davies, *Some Electrical and Optical Aspects of Molecular Behaviour*, Warszawa 1968, Oxford 1965.
- [4] B. Piekara, *Phys. Z.*, **37**, 264 (1936); *Acta Phys. Polon.*, **4**, 301 (1935).
- [5] A. Piekara, *J. Chem. Phys.*, **36**, 2145 (1962).
- [6] A. Piekara, B. Piekara, *CR, Acad. Sci. (France)*, **198**, 803 (1934); *Koll. Z.*, **73**, 273 (1935).
- [7] J. D. Hoffman, Ch. P. Smyth, *J. Amer. Chem. Soc.*, **71**, 431 (1949).
- [8] R. J. Meakins, R. A. Sack, *Nature*, **164**, 798 (1949).
- [9] C. C. Gravatt, P. M. Cross, *J. Chem. Phys.*, **46**, 413 (1967).
- [10] H. Chojnacki, *Thesis*, Wroclaw 1964.
- [11] A. Hippel, *Dielectrics and Waves*, Warszawa 1963, New York 1959.
- [12] J. C. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).
- [13] B. Piekara, to be published.
- [14] A. Piekara, *Proc. Roy. Soc.*, **A172**, 360 (1939).
- [15] A. Piekara, S. Kielich, *J. Phys. Rad.*, **13**, 490 (1957).