The Dielectric Properties of Some Alkyl Thiol

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As has already been studied by some authors, molecular crystals with a spherical molecular shape sometimes possess a small entropy of fusion, and such physical properties as nuclear magnetic resonance, dielectric properties, and X-ray diffraction can be well explained by the assumption of molecular rotation on the crystalline lattice site.

2-Methyl-2-propanethiol and 2-methyl-2-butanethiol also have small entropies of fusion,[1] 2.16 cal./deg. mol. and 0.86 cal./deg. mol. respectively, and the X-ray diffraction study of the plastic phase IV (the highest temperature solid phase) of 2-methyl-2-propanethiol shows a random orientation of molecules on the face-centered-cubic crystal lattice sites.[2] These facts lead us to the assumption that molecules on the lattice sites would make rotational motion as a whole, in spite of the possibility of interactions between thiol groups revealed by infrared spectroscopy of other compounds in liquid states.[3] It is of interest to compare the properties of such compounds with those of 2-methyl-2-propanol, which forms a stronger intermolecular hydrogen bond between hydroxyl groups than do thiols and which is not a plastic crystal.

Similarly, it is also interesting to compare the properties of cyclohexanethiol with those of cyclohexanol, which shows many properties characteristic of plastic crystals[2] in spite of the existence of a hydrogen bond between molecules. It is questionable whether or not cyclohexanethiol, which is supposed to have a weaker intermolecular interaction between thiol groups, is a plastic crystal. The dielectric study of these compounds has, therefore, been carried out, in both liquid and solid states, in respect to the dipole interaction of these molecules in condensed states, as one of the series of dielectric investigations of plastic crystals.

Experimental

Sample Preparation and Measuring Apparatus. —2-Methyl-2-propanethiol and 2-methyl-2-butanethiol were supplied in vacuum-sealed glass ampules with breakable joints by the U. S. Bureau of Mines, through the courtesy of Dr. J. P. McCullough. These were vacuum-sublimed, dried with magnesium perchlorate, and then placed in glass dielectric cells with platinum electrodes. All these procedures were carried out in the same vacuum system without any exposure to air. The melting points of these materials after repurification are equal to those obtained by McCullough and others[1] within the range of experimental error. Cyclohexanethiol was synthesized in this laboratory from cyclohexanol and purified by the same method. However, the purity of this sample was not as high as that of the others, as may be seen in the curve near the melting point in Fig. 3, partly because of the difficulty in drying.

The measuring circuit used in this study is a low-frequency bridge with a frequency range from 10^2 to 10^4 c. p. s. It has been described elsewhere.[4] The dielectric constant was determined by a comparison of the electric capacity with purified organic liquids, such as benzene, ethyl ether and acetone, with accurate dielectric constant values.

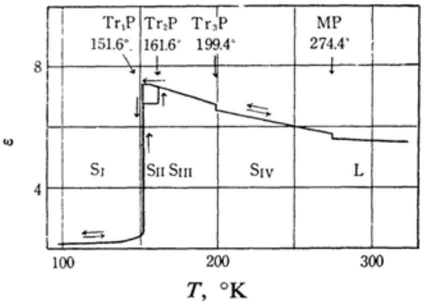

Fig. 1. The dielectric constant versus temperature curve of 2-methyl-2-propanethiol.

Results and Discussion

2-Methyl-2-propanethiol.—The variation in the dielectric constant of this material with the temperature is illustrated schematically in Fig. 1. The value of the dielectric loss, tan δ, was less than 10^{-3}. This value, together with that of the dielectric constant, showed no detectable frequency effect within our temperature range. The dipole moment, μ, of

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[1] J. P. McCullough, D. W. Scoff, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerpy and G. Waddington, *J. Am. Chem. Soc.*, **75**, 1818 (1953).

[2] S. Kondo, *Memoirs of Osaka Gakugei University*, **B**, **6**, 25 (1957).

[3] R. A. Spurr and H. F. Byer, *J. Phys. Chem.*, **62**, 425 (1958). M. O. Bulanin, G. S. Denisov and R. A. Pushkina, *Optics and Spectroscopy*, **VI**, 491 (1959).

[4] S. Kondo and T. Oda, This Bulletin, **27**, 567 (1954).

this molecule in the liquid state at 20° C can be calculated by using the Onsager equation[5] for pure polar liquid,

$$\frac{(\varepsilon-n^2)(2\varepsilon+n^2)M}{\varepsilon(n^2+2)^2 d}=\frac{4\pi N}{3}\,\frac{3kT}{\mu^2}$$

With $T=293°$ K, dielectric constant $\varepsilon=5.55$, density $d=0.8002$ g./cm^3,[6] and refractive index $n=1.4232$, the value of μ is calculated to be 1.67 D. This is almost equal to that of ethanethiol, 1.56 D, in the gas phase,[7] suggesting that the molecular association through the intermolecular hydrogenbond is very small.

The dipole moment of the plastic Phase IV, as calculated in the same manner, is 1.6 D, equal to that of the liquid. This suggests that the degree of molecular dipole rotation in the plastic phase is almost the same as that in the liquid state, as has been seen in other plastic crystals studied elsewhere.[2] The high symmetry of this crystal phase (face-centered-cubic structure) as shown by X-ray diffraction work,[2] compared with the low molecular symmetry of this compound, can be explained by the molecular rotation.

The same order of magnitude of the dielectric constant in phases III and II indicates the existence of some kind of molecular rotation in these phases. A thermal hysteresis of phase change was observed in phase II, as may be seen in Fig. 1. Careful thermal treatment shows that this is a sort of supercooling phenomenon probably accompanied by the molecular rearrangement process in this temperature region. The dielectric constant of phase I is nearly equal to the square of the refractive index of this material, suggesting the absence of the rotation of the molecular dipole in this phase.

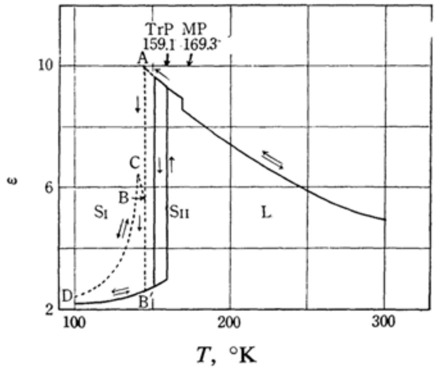

Fig. 2. The dielectric constant versus temperature curve of 2-methyl-2-butanethiol.

2-Methyl-2-butanethiol.—The dielectric constant versus the temperature relation is shown in Fig. 2. No anomalous dispersion has been observed in the present frequency and temperature range. As the application of the Onsager equation to the liquid and crystalline phase II of this material in the same manner as was done with 2-methyl-2-propanethiol gives, in both states, the value of 1.6 D as the dipole moment, this seems to be reasonable in comparison with those of other aliphatic thiols. This fact, and the very low entropy of fusion of this material, indicate the existence of molecular rotation in phase II. As may be seen in Fig. 2, this material shows a large thermal hysteresis on the phase transition from phase II to phase I; this hysteresis depends upon the cooling velocity. With a cooling rate smaller than 0.2 deg./min., the phase change occurs in accordance with the full line in Fig. 2. More rapid cooling gives rise to complicated behavior such is shown by the dotted line "A-B-C-D". Heating this sample from point "D" leads to the change "D-C-B-B′," and from point "B′" the system follows the full line. These facts seem to indicate the existence of a supercooled crystalline phase. McCullough and others observed a very small λ-type heat capacity anomaly at about 145°K which is likely to coincide with our point "C" in Fig. 2. The small value of the dielectric constant in phase I suggests the cessation of the rotation of the molecular dipole in this phase.

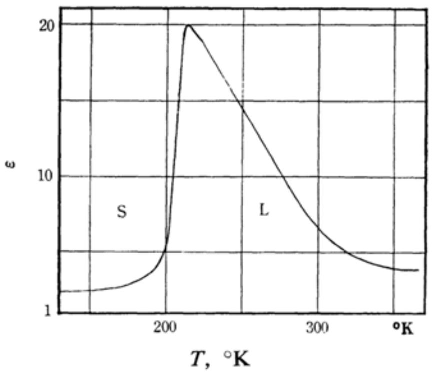

Fig. 3. The dielectric constant versus temperature curve of cyclohexanethiol.

Cyclohexanethiol.—In Fig. 3, the dielectric constant of this material decreases to about 2 in the solid phase upon being frozen, and no further marked change in the dielectric constant which indicates the phase change, has been observed within the present temperature and frequency range.

The curve of Fig. 3 near the melting point is somewhat ambiguous, as has been described

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[5] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
[6] J. P. McCullough, *Private communication.*
[7] M. Kubo, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 122 (1936).

in the section on sample preparation, because of the low purity of the sample. Therefore, no more detailed discussion will be made on this material beyond the suggestion that this material is not a plastic crystal.

The infrared absorption spectroscopy of this material by Kozima and Koda[8] shows the existence of a weak hydrogen bond in both the liquid and solid phases. They also concluded on the basis of an analysis of SH group vibration frequencies in these two states, that the molecule assumes both "a" and "e" forms in liquid phase but only "a" form in the solid phase. These properties of cyclohexanethiol are in marked contrast to those of cyclohexanol, which is a plastic crystal.

Summary

It has been concluded that both 2-methyl-2-propanethiol and 2-methyl-2-butanethiol are plastic crystals and that, in their highest temperature crystalline phases, molecules perform a rotational motion on the lattice sites. The intermolecular S-H···S hydrogen-bond, which might possibly exist in these phases, seems to be too weak to hinder the molecular rotation. Cyclohexanethiol does not seem to be a plastic crystal, probably because of its low molecular symmetry in the solid phase and its intermolecular hydrogen bond.

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[8] K. Kozima and Y. Kada, Presented at the 12th Annual Meeting of the Chemical Society of Japan, 1959.