

Dielectric Properties of Odd-Numbered Alcohol Esters of C₁₄, C₁₆ and C₁₈ Acids

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ABSTRACT

The dielectric properties of pentadecyl and heptadecyl tetradecanoate, pentadecyl hexadecanoate, pentadecyl and heptadecyl octadecanoate were investigated over a frequency range of 0.1 kHz to 100

kHz and a temperature range of -30 C to +25 C. The thermodynamic parameters for the dielectric process were calculated and related to the X-ray long spacings of the esters.

INTRODUCTION

In a previous publication (1), the dielectric properties of a homologous series of esters were reported. The series included all combinations of C₁₄, C₁₆ and C₁₈ normal alcohols and acids. The data were discussed in relationship to chain length, crystal form, and relative position of the polar group along the molecular chain. Meakins (2) extended the study to include esters of docosanoic acid. These results were combined to determine the relationship between the enthalpy of dipole activation, ΔH_e^\ddagger , and the molecular chain length, n . The data to be presented here are an extension of the previous studies by including odd-numbered n -alkyl esters prepared from C₁₄, C₁₆ and C₁₈ normal acids.

EXPERIMENTAL PROCEDURES

The esters were purchased from Lachat Chemicals, Inc. Each compound was passed through a 100 g column of 80% silica acid (precipitated, analytical grade, from Mallinckrodt Chemical Works) and 20% flow gel (Hyflo Super-Cel filter aid) using a solvent of redistilled Skellysolve F with 1% ether. The thin layer chromatographs of these treated samples gave no indication of free alcohol or acid. The melting points and X-ray data were given elsewhere (3).

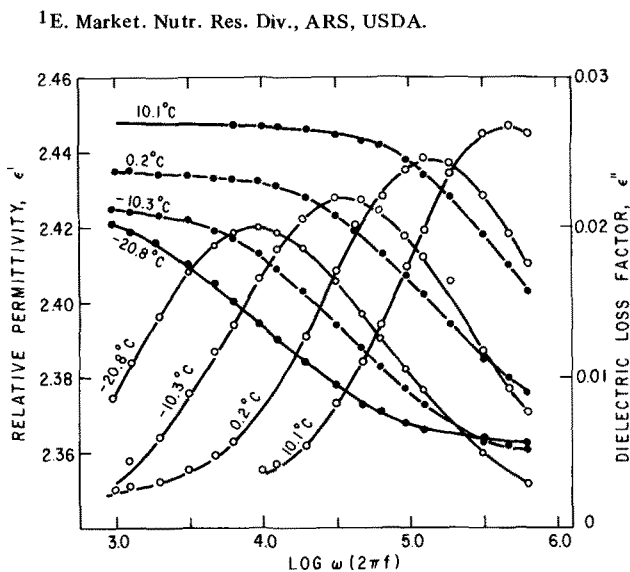


FIG. 1. Temperature dependence of the dielectric dispersion for pentadecyl tetradecanoate. ●, ϵ' ; ○, ϵ'' .

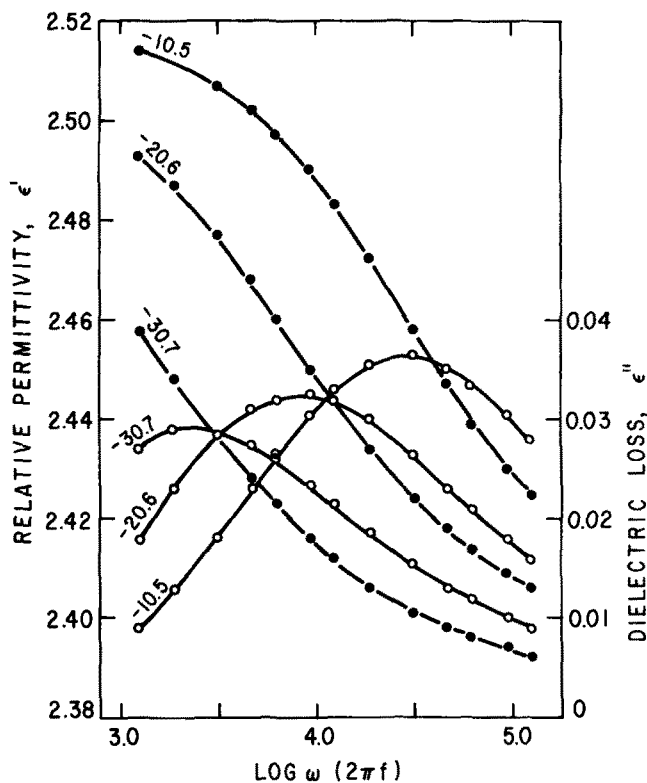


FIG. 2. Temperature dependence of the dielectric dispersion for heptadecyl tetradecanoate. ●, ϵ' ; ○, ϵ'' .

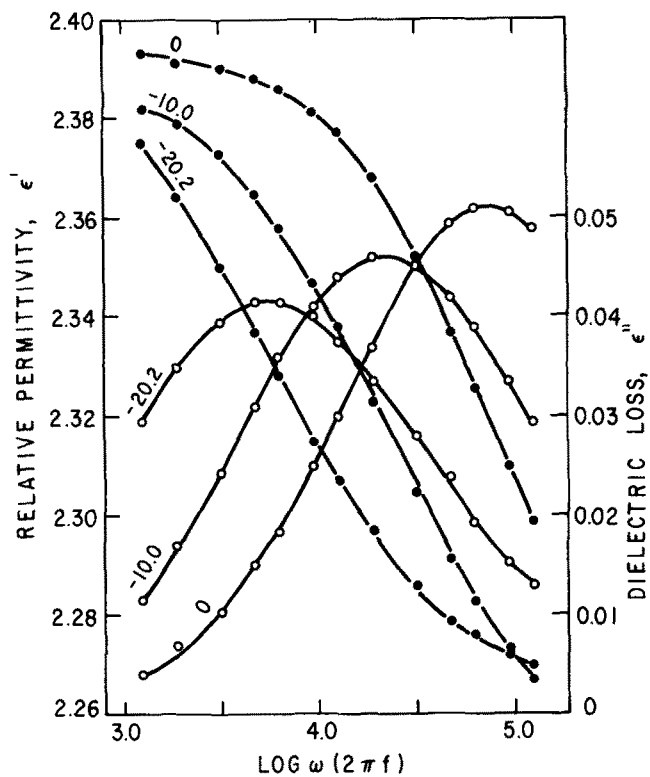


FIG. 3. Temperature dependence of the dielectric dispersion for pentadecyl hexadecanoate. ●, ϵ' ; ○, ϵ'' .

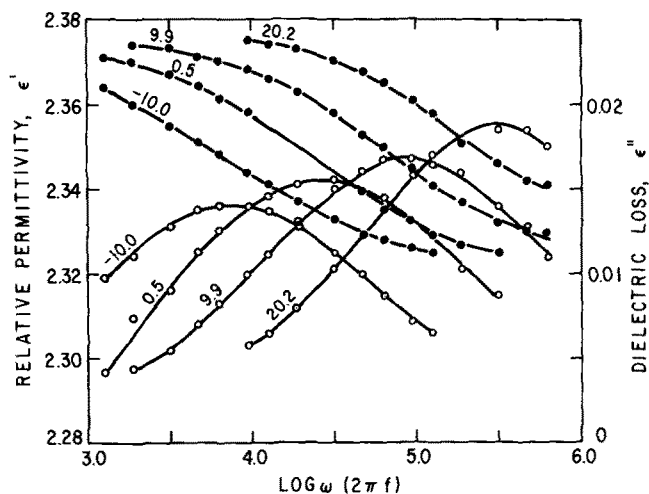


FIG. 4. Temperature dependence of the dielectric dispersion for pentadecyl octadecanoate. ●, ϵ' ; ○, ϵ'' .

The capacitances and conductances were measured with a General Radio bridge, type 1615-A, energized by a General Radio oscillator, type 1310-A, and the bridge balance detected by a General Radio amplifier and null detector, type 1232-A.

A modified Balsbaugh Laboratories guarded cell, type MC-50, was used as the sample holder. The modification consisted of a Teflon cylinder concentric with the guarded electrode and a spring concentric to the Teflon cylinder. The modification was needed to insure contact of the guarded electrode with the sample over the temperature range investigated.

The sample cell was placed in a Delta design test chamber, model MK2300. Liquid nitrogen was used as the coolant which had a two-fold purpose: (a) it permitted a wide temperature range, +25 C to -30 C, to be covered; and (b) presented a nitrogen atmosphere inside the test chamber which eliminated the formation of water condensate. The temperature inside the cell was monitored by a copper-constantan thermocouple.

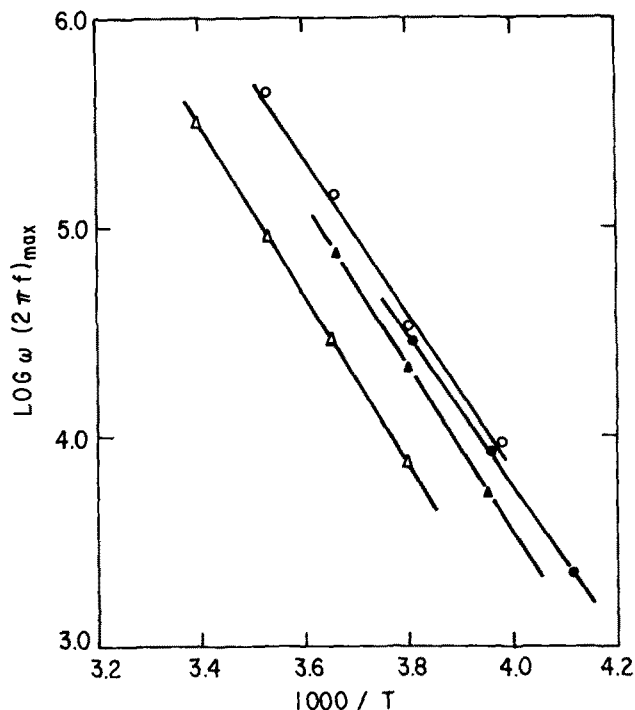


FIG. 5. Temperature dependence of $\log \omega_{\max}$ for: pentadecyl tetradecanoate (○); heptadecyl tetradecanoate (●); pentadecyl hexadecanoate (▲); pentadecyl octadecanoate (△).

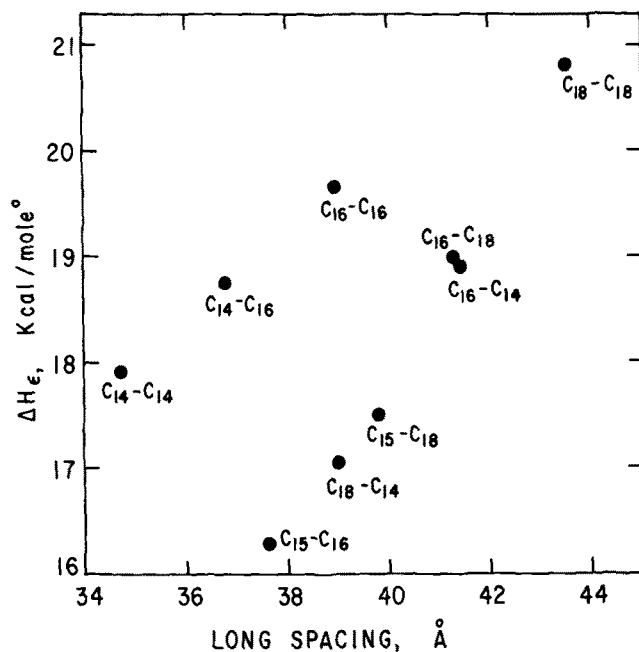


FIG. 6. Plot of $\Delta H_{\epsilon}^{\dagger}$ vs. X-ray long spacings.

The discs used in the dielectric measurement were formed from the melt within the sample holder. The discs were carefully removed from the cell after the measurements were completed and their thickness determined by a micrometer.

RESULTS AND DISCUSSION

Figures 1-4 show the frequency dependence of the relative dielectric permittivity, ϵ' , and dielectric loss, ϵ'' , each at several temperatures. There are two features that should be noted about these curves: (a) that the frequency at which the dielectric loss curves is a maximum; and (b) the magnitude of the dielectric absorption.

The dielectric absorption in long chain compounds has been attributed to the rotation of the molecules about the long axis from one position of equilibrium to another. Kauzmann (4) and Smyth (5) has shown that the dielectric dispersion can be treated as a rate process, and that the process of molecular rotation requires an activation energy to overcome the energy barrier separating these equilibrium

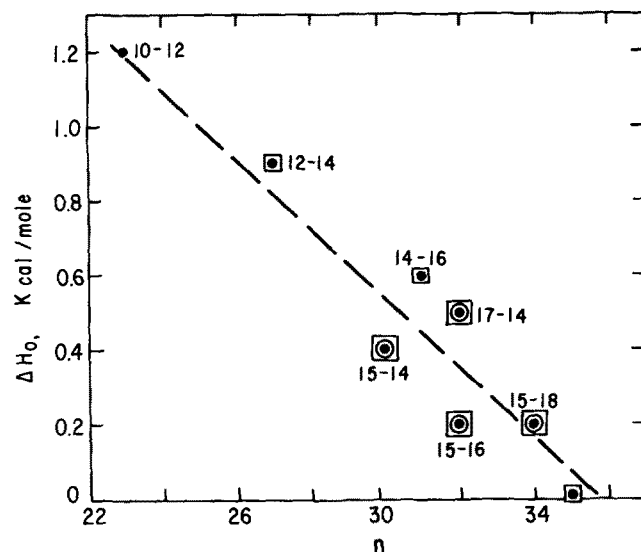


FIG. 7. Relationship between ΔH_0 and chain length, n ; ●, Meakins (2); ○, this study; □, Lutz et al. (3).

TABLE I

Thermodynamic Parameters for Dipole Orientation

Compound	n^a	$\Delta H_\epsilon^\ddagger$ kcal/mole	$\Delta S_\epsilon^\ddagger$ cal/mole °	ΔH_0 kcal/mole
Pentadecyl tetradecanoate	30	16.7	26.2	0.4
Heptadecyl tetradecanoate	32	16.4	25.5	0.5
Pentadecyl hexadecanoate	32	16.4	24.1	0.2
Pentadecyl octadecanoate	34	17.5	26.3	0.2
Heptadecyl octadecanoate	36	---	---	---

^a n = Number of atoms in the ester chain.

positions. Thus the number of times per second such a rotation will occur is given by:

$$f_{\max} = kT/h \exp(-\Delta F_\epsilon^\ddagger/RT) \quad [1]$$

where f_{\max} is the frequency at which the dielectric loss is at a maximum, k is the Boltzmann constant, h is the Planck constant, R is the gas constant, and T is the absolute temperature. From thermodynamic considerations, $\Delta F = \Delta H - T\Delta S$, and Equation 1 can be rewritten as:

$$f_{\max} = (kT/h) \exp(-\Delta H_\epsilon^\ddagger/RT) \exp(\Delta S_\epsilon^\ddagger/R). \quad [2]$$

Differentiation of Equation 2 and rearranging gives

$$-\Delta H_\epsilon^\ddagger = R \frac{d \ln f_{\max}}{d(1/T)} \cdot RT.$$

The approximate linearity of the plot of $\log f_{\max}$ versus T^{-1} has been well established. Figure 5 shows the relationship between $\log f_{\max}$ and T^{-1} for the four esters. Table I presents the calculated enthalpy, $\Delta H_\epsilon^\ddagger$, and entropy, $\Delta S_\epsilon^\ddagger$, for dipole activation.

There seems to be no clear relationship between enthalpy of activation and X-ray long spacings, as shown in Figure 6, for these compounds and others previously studied. Meakins (2) correlated enthalpy and chain length, and concluded that the enthalpy of activation would reach a constant value above a certain chain length. This conclusion, however, is based on what appears to be a rather arbitrary division of experimental points.

One further parameter that can be obtained from these measurements is the magnitude of the dielectric absorption. This can be used to measure the difference in energy values, ΔH_0 , of the equilibrium positions of the dipoles in the

dielectric process (6). The equation used for this calculation is:

$$\epsilon''_{\max} = (1/2)(\epsilon'_0 - \epsilon'_\infty) = (C/T)[1 - \cosh(\Delta H_0/RT)]^{-1} \quad [3]$$

where ϵ''_{\max} is the maximum for the dielectric loss, ϵ'_0 is the relative dielectric permittivity at frequencies below the absorption, ϵ'_∞ is the relative permittivity above the absorption, and C is a constant. Since there is a distribution of relaxation times, as noted by the changes in the width of the dielectric loss curves, it is more convenient to use the $(\epsilon_0 - \epsilon_\infty)$, the magnitude of the dielectric absorption. ΔH_0 values were calculated and are listed in column 5 of Table I. Figure 7 shows that values of ΔH_0 can be correlated with those calculated by Meakins (2) for compounds known to crystallize in the same form (3) as those studied. These results agree with Meakins' observation that ΔH_0 values decrease as the chain length increases. This seems to indicate that a chain twisting mechanism is involved in the dielectric dispersion of long chain compounds.

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