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Dielectric Behavior of *N*-Methylacetamide

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Synopsis. The dielectric constants and losses of liquid *N*-methylacetamide were measured in the frequency range 0.356—2.10 GHz at 31.4 °C. The result provides a definitive evidence for the validity of the simple Debye equation for the dielectric relaxation process of liquid *N*-methylacetamide.

The molecular structure of *N*-methylacetamide has been intensively studied by various physical methods. Infrared and Raman spectra,[1,2] dipole moment,[3] and electron diffraction[4] have been measured and discussed. Bass *et al.*[5] studied dielectric relaxation, but not in a sufficiently wide frequency range. They employed only the VHF range of 1—250 MHz. The present note provides complementary dielectric data for liquid *N*-methylacetamide in view of its great importance as a model compound of biological materials.

Experimental

Commercial *N*-methylacetamide was purified by vacuum distillation prior to use. The purity was examined by measurements of the infrared spectra.

Dielectric constants, ε', and losses, ε'', were measured at 31.4°C at the UHF frequencies of 0.356, 0.516, 0.698, 1.00, 1.50, and 2.10 GHz with an equipment reported in previous papers.[6,10] The errors of the measurement are of the order of a few per cent.

Relaxation time, τ, and the limiting low- and high-frequency dielectric constants, ε_0 and ε_∞, respectively, were calculated by the Debye equation:

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \qquad (1)$$

where ω is the angular frequency. An iterative method by an electric computer was used for the calculation.

Results and Discussion

The ε' and ε'' values observed at 31.4 °C are summarized in Table 1. Figure 1 shows the Cole-Cole diagram (dashed line) constructed from the UHF data obtained by the present writers and the VHF data provided by Bass *et al.*[5] We see that all the measured points lie in a semi-circle with its center in the ε' axis.

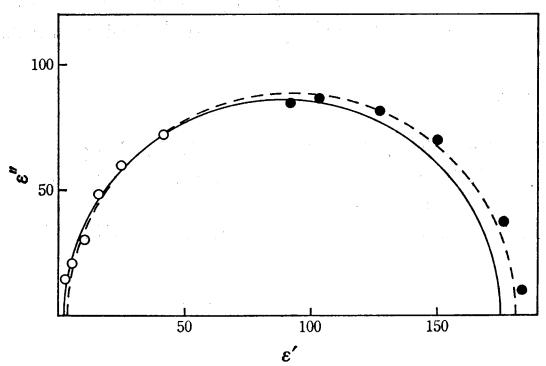

Fig. 1. Cole-Cole plots for liquid *N*-methylacetamide at 31.4 °C: open circles, results of the present investigation; closed circles, literature values from S. J. Bass *et al.*[5] The solid line corresponds to the values of ε_0, ε_∞, and τ of 175.5, 2.37, and 808 ps, respectively, and the dashed line to the values of 181.5, 3.44, and 769 ps, respectively.

TABLE 1. THE OBSERVED AND CALCULATED ε' AND ε'' VALUES OF LIQUID *N*-METHYLACETAMIDE AT 31.4 °C

Frequency (GHz)	ε'		ε''	
	Obsd	Calcd	Obsd	Calcd
2.10	2.43	3.87	14.4	16.0
1.50	5.28	5.31	21.0	22.4
1.00	10.4	8.80	30.3	32.8
0.698	15.7	15.1	48.3	45.3
0.516	25.0	24.4	59.9	57.7
0.356	41.8	42.9	71.9	73.3

The values of the parameters, ε_0, ε_∞ and τ, calculated by Eq. (1) and ε'_{obsd} and ε''_{obsd} in Table 1 are 175.5, 2.37, and 808 ps, respectively. The semi-circle (solid line, Fig. 1) is drawn with the use of this set of parameters. The values of ε'_{calcd} and ε''_{calcd} (Table 1) are those calculated by using the same values of the parameters. If the VHF values of ε' and ε'' reported by Bass *et al.*[5] are included in the calculation, the values of ε_0, ε_∞, and τ become 181.5, 3.44, and 769 ps, respectively—this set of parameters gives the semi-circle (dashed line, Fig. 1).

The experimental values were examined also by the use of the Cole-Cole equation:

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} \qquad (2)$$

The distribution parameter, $\alpha=0$, was also obtained, confirming that the dielectric dispersion of liquid *N*-methylacetamide is of the Debye type.

The static dielectric constant of *N*-methylacetamide was reported to be 177.0 at 31.4 °C[5] which lies between 175.5 and 181.5 obtained in this work. The refractive index, n_D, of *N*-methylacetamide is reported to be 1.4185.[5] The fact that ε_∞ is larger than n_D^2 only by 15% suggests that the second and third dielectric relaxations in a higher frequency region, if they exist at all, would have very small values of dielectric absorption.

The results seem to show that all the data for *N*-methylacetamide can be represented by the simple Debye equation. As in the case of the principal dispersion of alcohols, the dielectric relaxation of this substance is governed by the simple exponential decay process. All the existing theories explaining the simple Debye dis-

persion[7,8] assume no interaction between orientating dipoles, which is not suitable for the system of strongly hydrogen-bonded liquids such as alcohols and *N*-substituted amides. The switch-over[9] and cluster[10] mechanisms have been tentatively proposed for the explanation of the dielectric relaxation of alcohols. For liquid *N*-methylacetamide, which is considered to be composed of the linear chains of the hydrogen-bonded molecules, the mechanism might be simpler than that of alcohols.

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