

The Dielectric Polarization of Formic Acid Vapor

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The Dielectric Polarization of Formic Acid Vapor

Some time ago, C. T. Zahn¹ studied the dielectric polarization of formic acid vapor between 71°C and 150°C. We have re-investigated this, with an improved apparatus,² and, in view of the recent interest in the separate properties of the monomer and dimer of this acid,³ we think it timely to give a preliminary report of our observations, which are not in agreement with those of Zahn.

Dielectric polarization as a function of pressure was measured between 37.5°C and 127°C. Measurements at 37.5°, 53.9°, 64.4° and 74.2° were over a sufficiently broad pressure range to permit the determination of the polarizations of the monomer and dimer, P_1 and P_2 , from the relation $P = P_1 f_1 + P_2 f_2$. P is the apparent polarization at the mole fractions f_1 , f_2 , which are calculated from the vapor density data of Coolidge.⁷ The "least squares" results and probable errors are:—

t°C	P_1	P_2
37.5	42.1 ± 0.9	32.0 ± 0.5
53.9	44.2 ± 0.2	31.7 ± 0.2
64.4	45.2 ± 0.3	31.8 ± 0.3
74.2	44.7 ± 0.3	33.3 ± 0.6

The figure for the temperature 64.4° shows a typical series of results. Those at 95° and 127° do not permit of such an extrapolation, but by assuming $P_2 = 32.0$ cc one obtains for P_1 , 43.6 and 42.0, respectively. (The measurements at these temperatures are so close to the $f_2 = 0$ axis, that the values of P_1 are not very sensitive to the value assumed for

P_2 .) There is some indication from the 95° results that P_2 has risen to 36–38 cc, but this is not very certain.

The polarization of the monomer appears first to rise with temperature and then to diminish, the maximum being at about 70°. This behavior suggests that in the temperature range studied, there is a transition from one state to another of higher energy and higher dipole moment.⁴ The transition is perhaps from a low energy state in which the "hydroxyl" hydrogen atom is locked *cis* to the "carbonyl" oxygen, owing to resonance and hydrogen bonding forces to a high energy state in which either the hydrogen atom is fixed *trans* to the "carbonyl" oxygen⁵ or is free to rotate around the "hydroxyl" oxygen. This latter case is somewhat analogous to that of ethylene dichloride.⁶

If one of these interpretations is correct, it is to be expected that:—

- The infra-red spectrum of formic acid monomer at 40°C would be different from that at 140°C.³
- Depending upon the relation between the energy difference for the two postulated structures, and the amount of zero point energy in each, the polarization temperature behavior of monomeric "half-heavy" formic acid HCO_2D might well be different from that for the ordinary monomer.

The polarization of the dimer is either constant or increases with temperature. We therefore disagree with Zahn who concluded tentatively that the dimer has a permanent dipole moment. The difference of 15.5 cc between the total polarization and the electron polarization is probably atom polarization, since it has recently been demonstrated that in such molecules as this, where large moments are opposed and may readily be changed with respect to one another, large values for the atom polarization are to be expected.²

We hope, in the near future, to modify our apparatus to measure larger changes of dielectric constant from vacuum, so that more precise information may be obtained as to the polarization of the dimer at high temperatures.

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November 4, 1938.

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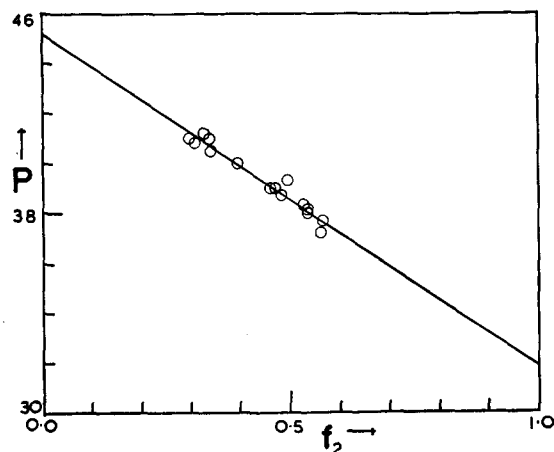


FIG. 1.

¹ Zahn, Phys. Rev. 37, 1516 (1931).

² Coop and Sutton, J. Chem. Soc. 1269 (1938).

³ Bonner and Hofstadter, J. Chem. Phys. 6, 531 (1938). Hofstadter, J. Chem. Phys. 6, 540 (1938).

⁴ Zahn, Phys. Rev. 35, 1056 (1930).

⁵ Marsden and Sutton, J. Chem. Soc. 1383 (1936).

⁶ Lennard-Jones and Pike, Trans. Faraday Soc. 30, 830 (1934).

⁷ Coolidge, J. Am. Chem. Soc. 50, 2166 (1928).