NMR Evidence for Hydrogen Bonding in Ethyl Mercaptan

STURE FORSÉN

Research Group for NMR, Division of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden

Hydrogen bonding of the S—H... S type has for a long time been considered unlikely for mercaptans. Molecular weights determined by the method of freezing point depression have not revealed any tendency towards association [1]. Several investigators have failed to detect any dilution shifts in I.R. spectra of thiophenols and mercaptans [2,3]. Recently, however, Spurr and Byers [4] have studied the fundamental stretching region of the S—H group in some mercaptans and found two bands at about 2 580 cm^{-1} and 2 560 cm^{-1}, which they attribute to the monomer and dimer forms, respectively, of the mercaptans. They showed that the concentration dependent variations in the integrated adsorption coefficients for the two bands could be accounted for on the basis of a monomer-dimer equilibrium. As shown by a number of workers [5] the proton magnetic resonance (PMR) signal of the OH-proton in alcohols and phenols undergoes a shift towards higher fields as the compound is diluted in some inert solvent as CCl_4 or *cyclo*hexane. We have therefore looked for a corresponding dilution shift in the PMR-signal of the SH-group in ethyl mercaptan.

The measurements were carried out on a Varian V-4300 NMR-spectrometer operating at 40 Mc/s. All shifts were measured against an external water standard using coaxial glass cells [6] and correcting for the macroscopic susceptibility effects.

The shifts are discussed in terms of the dimensionless unit δ defined by the expression

$$\delta = 10^6 \cdot \frac{H_{sample} - H_{ext.water}}{H_{ext.water}}$$

The PMR spectrum of pure ethyl mercaptan is shown in Fig. 1 a. The SH-group gives rise to a triple-peak signal which partly covers the CH_3-group signal.

The ethyl mercaptan (Purum. FLUKA, freshly distilled) was diluted by CCl_4 (*pro analysi*, Merck, dried over P_2O_5) in steps down to $x = 0.01$ (mole fraction) and it was found that the SH-signal shifted totally $\Delta\delta_{SH} = 0.38 \pm 0.015$ towards higher fields. Within the accuracy of the measurements no shift of the CH_2- or CH_3-signals could be detected. We take the observed SH-dilution shift as evidence for a small but significant effect of hydrogen bonding. In Fig. 1 b the CH_3-region is shown at $x = 0.2$. The results are shown graphically in Fig. 2.

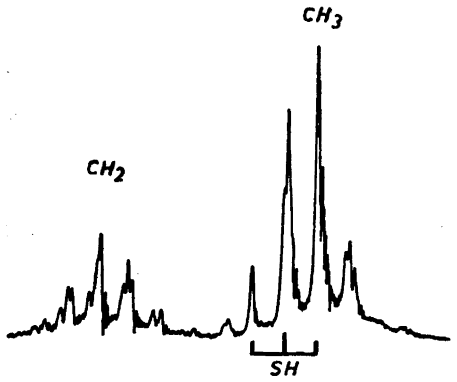

Fig. 1 a. The PMR spectrum of pure ethyl mercaptan. The position of the SH-group is indicated.

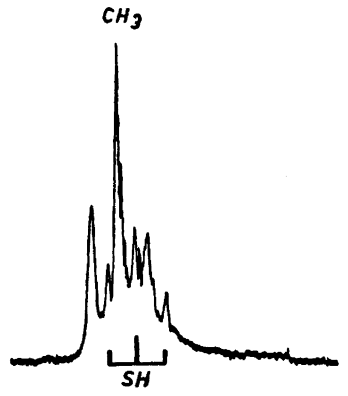

Fig. 1 b. The PMR spectrum of the CH_3-region in ethyl mercaptan diluted with carbon tetrachloride (mole fraction mercaptan = 0.2). The SH-signal has now moved to the right side of the CH_3-signal.

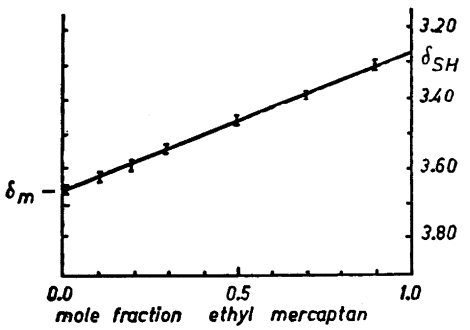

Fig. 2. The dilution shift in CCl_4-solution of the SH-proton resonance in terms of the dimensionless unit δ.

The SH-shift shows an almost linear dependence on the mole fraction mercaptan and this behaviour differs markedly from the one observed for alcohols [7]. The linear dependence and the smallness of the shift imply that the association constant in terms of mole fractions (K_x) should be small and that monomers and dimers dominate in the solution. Spurr and Byers give $K_c = 47$ mole/lit., which corresponds to $K_x = 0.22$. A rather crude approximation based on the formulas in Ref.[5a] is to set the slope of the δ_{SH} *vs.* x plot, $\left(\frac{d\delta}{dx}\right)$, equal to $2K_x\Delta_d$, and, somewhat arbitrarily, $\Delta_d = \delta_d - \delta_m$ to $\frac{1}{2} \cdot 0.38$ *. (See Ref.[5a] p. 1313). This gives $K_x = 0.38$ in reasonable agreement with the results of Spurr and Byers.

Acknowledgements. The author would like to thank the head of the NMR group Dr. Erik Forslind for his kind interest in this work. *Statens Råd för Atomforskning, Statens Naturvetenskapliga Forskningsråd* and *Statens Tekniska Forskningsråd* have provided financial support. The cost of the NMR apparatus has been defrayed by a generous grant from *Knut och Alice Wallenbergs Stiftelse.*

1. Lassettre, E. N. *Chem. Rev.*, **20** (1939) 259.
2. Gordy, W. and Stanford, S. C. *J. Am. Chem. Soc.* **62** (1940) 497.
3. Copley, M. J., Marvel, C. S. and Ginsberg, E. *J. Am. Chem. Soc.* **61** (1939) 3161.
4. Spurr, R. A. and Byers, H. F. *J. Phys. Chem.* **62** (1958) 425.
5a. Huggins, C. M., Pimentel, G. C. and Shoolery, J. N. *J. Phys. Chem.* **60** (1956) 1311.
b. Gutowsky, H. S. and Saika, A. *J. Chem. Phys.* **21** (1953) 1688.
6. Wilmad Glass Co., Landisville, New Jersey.
7. See *e. g.* Becker, E. D., Liddel, U. and Shoolery, J. N. *J. Mol. Spectr.* **2** (1958) 1.

Received September 4, 1959.

* δ_m is the shift of the monomer in relation to the reference ($H_2O_{ext.}$) and is given by δ_{SH} at $x = 0$. δ_d is the shift of the dimer and is not known exactly. It can not be taken as the value of δ_{SH} at $x = 1$.

Composition and Stability Constant of the Complex between Lead(II) and 4-(2-Pyridylazo)-resorcinol (PAR)

H. KRISTIANSEN and F. J. LANGMYHR

University of Oslo, Chemical Institute A, Blindern, Norway

For the EDTA-titration of lead(II) Weber [1] suggested PAR as metal indicator. Pollard, Hanson and Geary [2] recommended PAR as colorimetric reagent for cobalt, lead and uranium. The authors introduced [3] PAR as indicator by indirect EDTA-titration of macro and micro amounts of aluminium, the excess of EDTA being back-titrated with standard lead(II) solution.

In connection with the use of PAR as metal indicator, it is of interest to have information about the complex formed between the indicator and lead(II) ions. In this investigation the composition of the complex and its stability constant were determined spectrophotometrically.

Experimental. The sodium salt of PAR was synthesized according to a procedure given by Chichibabin [4]. The salt was purified by extractions with ether and transformed to the phenol by the passing of carbon dioxide. The phenol was extracted with ether, and again transformed to the sodium salt, which was recrystallized from alcohol. The product was finally dried *in vacuo* over phosphorus pentoxide. The