This paper describes the isotopic dilution method for separation of intramolecular and intermolecular contributions to proton NMR-relaxation and applies it to several organic liquids. After separation of orientational and translational correlation times, microviscosity factors and deuteron quadrupole coupling constants could be derived. [The SCI® indicates that this paper has been cited in over 145 publications.]

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At the end of 1963 I finished my doctoral thesis under H.G. Hertz at the University of Münster. In that work I applied NMR relaxation-time measurements to study motions of water molecules in electrolyte solutions, which are influenced by hydration effects. Since I was allowed to continue NMR relaxation studies on systems of my own choice, I decided to turn to simpler liquids than electrolyte solutions. By chance I found the rather obscure paper by M. Eisner and R.W. Mitchell1 that proposed to dilute benzene \( \text{C}_6\text{H}_6 \) with its completely deuterated analogue \( \text{C}_6\text{D}_6 \) and to measure the proton relaxation as a function of composition. At the extrapolation point for vanishing \( \text{C}_6\text{H}_6 \) concentration, the remaining relaxation effect is essentially due only to intramolecular proton-proton magnetic dipolar interactions because the magnetic moment of the deuteron—in comparison to that of the proton—is so much smaller. This so-called isotopic dilution method fascinated me, and I wanted to do an extensive similar study with as many liquids as possible. The choice was limited by the availability of deuterated compounds, and the catalogues for such isotopic substances at that time were not at all comparable to what is now offered. In addition, the prices were terribly high, and funds were not easily available to me.

Initially I tried to prepare the samples myself, starting from the least expensive \( \text{CD}_3\text{O} \) for the synthesis. Methanol \( \text{CD}_3\text{OD} \) was prepared through electrolysis of \( \text{D}_2\text{O} \) to \( \text{D}_2 \) followed by reaction with \( \text{CO} \) under elevated pressure with a copper-zinc-chromium oxide catalyst. After much effort the methanol was obtained, but when the sample was stored in the refrigerator overnight, a colleague of mine spilled it and left me with the empty tube. Fortunately, a donation from the Fonds der Chemischen Industrie allowed me to give up these fruitless synthetic efforts and buy the compounds. So for the first time I could apply the isotopic dilution method to 10 different organic liquids. I was not aware until nearly the end of my work that two other research groups, those of J. Powles in Canterbury and of G. Bonera and A. Rigamonti in Pavia, performed similar experiments, although on just one or two systems. Thus, I had the advantage of covering a larger number of liquids.

After having separated intra- and intermolecular contributions to proton relaxation by this method I could extract quite a lot of useful and reliable information: rotational reorientation times, microviscosity factors, translational correlation times, and quadrupolar coupling constants for the deuteron. Such quantities were of much interest at that time, and I had a rewarding response when the paper was published.

The large number of citations to my paper is due, I think, to the fact that the isotopic dilution method has developed into a standard method2 used by people working on proton relaxation experiments.

   (Cited 250 times.)