

phase surface tension to low temperatures is uncertain. Accordingly, the present authors are proceeding to make critical supersaturation measurements at low temperatures on low freezing substances, e.g., ethyl alcohol, the propyl alcohols, etc. Such data, in conjunction with bulk phase surface tension measurements at low temperatures, may permit quantitative evaluation of the change in surface tension of liquid droplets due to decrease in size.

A major assumption in this approach to the problem is that the free energy of the droplet is essentially the same as that of a portion of liquid of the same volume and shape existing in a large amount of the liquid, except for the contribution due to surface tension. This assumption, together with various criticisms of the method, will be discussed in a future publication.

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Chemical Effects on Nuclear Induction Signals from Organic Compounds*

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THE influence of the chemical compound upon the nuclear magnetic resonance frequency of a nucleus has been previously reported. Large chemical shifts have been observed¹ for some of the heavier elements, and a line structure has been seen in complex molecules containing the observed nuclei in regions of different magnetic shielding. Small shifts have been measured between several hydrogen compounds,² and there has been an indication of a fine structure in some organic liquids.³

The development of a nuclear induction apparatus with a resolution better than 1 part in 10^7 has enabled us to measure many such chemical shifts for hydrogen in gases and in organic liquids and to measure a fine structure in the lines of a large number of organic compounds.

The apparatus includes an electromagnet operating at 7600 gauss which has 12-inch diameter pole pieces and a gap of 1.75 inches. The magnetic field is stabilized by voltage, current, and proton controlled regulators. The rf field for both the proton control and the main nuclear induction apparatus is supplied by the same crystal controlled oscillator operating at 32.4 mc. The sharp lines are achieved by a carefully shimmed magnet and a small cylindrical sample which has a diameter of 2 mm and a length of 1 cm. The magnetic field over the region of the sample is changed linearly by a pair of small coils at a sweep rate the order of 0.05 gauss per second. This slow sweep either satisfies the conditions for steady-state behavior of the signal or is slow enough so that all transient effects are over before the next peak is reached. The steady-state or near steady-state behavior of the nuclear induction signal gives line shapes which can be described by a simple solution of Bloch's nuclear induction equations.⁴ The nuclear induction signal is amplified by rf and direct-coupled amplifiers, and the amplitude is plotted on an oscillograph screen as a function of the magnetic field. Figure 1 shows the fine structure in ethyl alcohol and is typical of the signals which we observe. The trace is 75 milligauss wide and is traversed in 2 seconds. A measurement of the ratios of the areas of the lines yields the ratios of the number of hydrogen atoms associated with each line. In ethyl alcohol the ratios are nearly 1-2-3. In most cases it is

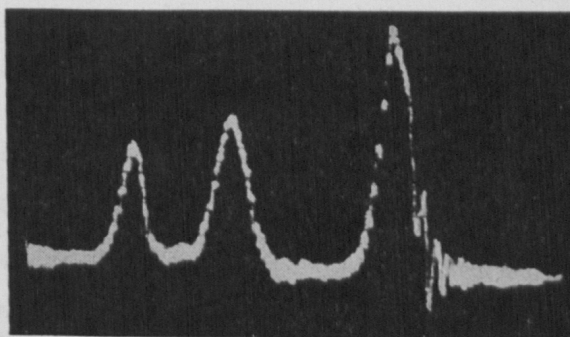


FIG. 1. Oscillograph trace of the nuclear induction signal from ethyl alcohol. The total trace is 75 milligauss wide and was traversed in 2 seconds. The peaks from left to right represent OH, CH₂, CH₃.

necessary to consider the areas under the lines because the line widths are not the same for the different peaks.

Table I gives data for the first five primary alcohols. The peaks have been labeled on the basis of their relative areas to correspond with groups in the alcohols. The OH peak, which comes at the lowest applied field, has been taken to have unity area, and

TABLE I.

Name of normal alcohol	Groups	Group characteristics			Remarks
		Ratio of areas of lines ($\pm 10\%$)	Peak separation in milligauss from OH	Line widths in milligauss (± 0.05)	
Methyl	OH	1		1.6	
	CH ₃	2.7	13 \pm 2	1.9	
Ethyl	OH	1		2.4	
	CH ₂	2.1	16 \pm 3	3.2	
	CH ₃	3	37 \pm 5	2.2	
Propyl	OH	1		2.5	
	CH ₂	1.8	18 \pm 4	2.5	
	CH ₂ CH ₂	5	38 \pm 5	2.9	
Butyl	OH	1		2.5	
	CH ₂	1.9	15 \pm 3	2.2	
	CH ₂ (CH ₂) ₂	7.1	36 \pm 5	4.2	There seem to be two peaks overlapping
Amyl	OH	1		2.2	
	CH ₂	1.7	15 \pm 3	2.9	
	CH ₂ (CH ₂) ₃	9.2	37 \pm 5	4.2	Two peaks overlapping as in butyl

all shifts have been measured relative to its position. The listed half-line width values are measured values and include the magnet line width of about one milligauss. The third peak in the alcohols higher than ethyl contains both CH₂ and CH₃ groups which are not resolved because the natural line widths are greater than their separation.

The iso- and tertiary-alcohols show a fine structure which is different from that of the primary alcohols but is compatible with the known structural formulas.

The greatest shift which we have observed in a single molecule is in the organic acids and is about 75 milligauss between the COOH and the other groups.

It seems to us that there may be certain chemical problems besides analysis, such as the study of chemical reactions and equilibria, which can be investigated by this method. We are continuing our measurements upon related series of organic liquids and upon the question of the different transverse relaxation times.

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