^{14}N NMR Relaxation Study of 3-Alkylsydnone

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The spin-spin relaxation times T_2 of ^{14}N on the 3-position in the sydnone ring for 3-propylsydnone and 3-butylsydnone were measured in the temperature range of 10–60 °C. Both were observed as the functions of temperature. The increase of T_2 with increasing temperature corresponds well to the decrease of viscosity for these two sydnones. The plots of $\log(1/T_2)$ vs $1/T$ yield the straight lines. The activation energies of molecular motion for 3-propylsydnone and 3-butylsydnone calculated from the slopes of these straight lines were in fairly accordance with those from viscosity measurements.

Sydnones are well known as mesoionic compounds with significant large dipole moment and as organic ones miscible with many solvents [1–4]. The bulk physical properties such as dielectric constant, refractive index, density and viscosity of these two sydnones had been reported at various temperatures [5,6]. 3-propylsydnone and 3-butylsydnone are liquids with very high dielectric constants at or near room temperature. Thus they are expected to be as good solvents for many electrolytes.

The structure of sydnones has been studied with both ^{14}N and ^{15}N NMR [7,8]. Since ^{14}N has I (spin quantum number)=1, the relaxation process is usually dominated by the quadrupolar mechanism. Stefaniak [7] reported the ^{14}N NMR spectra of some sydnones showing a broad peak with about 450Hz half-height width for nitrogen on 2-position and a sharp peak about 120Hz half-height width for nitrogen on the 3-position of the sydnone ring with chemical shift in the range about $-(79 \sim 108)$ ppm referred to neat nitromethane as external standard.

In low viscosity liquids the extreme narrowing conditions as shown in Eq(1) [9,10] are usually obeyed,

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$$(2\pi\nu_o\tau_c) \ll 1 \quad (1)$$

where ν_o is resonance frequency of nucleus and τ_c is the correlation time. Thus the quadrupolar relaxation time $T_2 = T_Q$ is given by ^[11]

$$1/T_2 = 1/T_Q = (3\pi^2(2I+3)/10I^2(2I-1))\chi^2(1+\eta^{*2}/3)\tau_c \quad (2)$$

where η^* is an asymmetry parameter that represents the distortion of the electric field from axial symmetry ^[9,10] and the nuclear quadrupole coupling constant, χ , in frequency unit between the quadrupole moment, e_Q , and the electric field gradient at the nucleus, e_q , is given by

$$\chi = e_q \cdot e_Q/h \quad (3)$$

For ^{14}N of $I=1$ there is ^[9,10,12,13]

$$1/T_2 = (3/2)(\pi\chi)^2(1+\eta^{*2}/3)\tau_c \quad (4)$$

Therefore the measurement of T_2 for ^{14}N may give an important information about molecular motion characterized by τ_c which depends on temperature and is proportional to the viscosity, η , of liquid.

Fig.1 The spectrum of ^{14}N for 3-propylsydnone at 25 °C

Fig.2 T_2 of ^{14}N for sydnones vs temperature

1: 3-propylsydnone,
2: 3-butylsydnone

Experimental

The preparation and confirmation of 3-propylsydnone and 3-butylsydnone have been described elsewhere ^[3,5,6,14]. The measurements of T_2 for ^{14}N were carried out on a JEOL-400 WB NMR Spectrometer equipped with a temperature controlled unit by CPMG pulse

sequence at resonance frequency of 28.75 MHz with accumulation of 16-64 times. The 90° pulse was 28 μs. The 10mm NMR tube including CDCl₃ - CH₃NO₂ mixture (volume ratio 1:1) as a lock solvent and an external standard outside a 8mm NMR tube containing sample was used for recording of spectra. The temperature was controlled to an accuracy of 0.1 °C. T_2 reported was an average of 2 or 3 measurements with an error ±5%.

Results and Discussion

The spectrum of ¹⁴N on the 3-position in sydnone ring for 3-propylsydnone is shown in Fig.1. The peak of nitrogen on 3-position of -97ppm referred to nitromethan as external standard is in fairly agreement with that of literature[7]. The peak for 2-position is too broad to be observed. The T_2 of ¹⁴N on 3-position for both 3-propylsydnone and 3-butylsydnone increases with temperature as shown in Fig.2. It means that molecular motion becomes faster by decrease of viscosity of sydnones with a rise in temperature. T_2 of 3-propylsydnone is longer than that of 3-butylsydnone. It seems that the increase of T_2 with temperature corresponds well to the decrease of viscosity for these sydnones described in previous papers [5,6].

Fig.3 $\log(1/T_2)$ vs $1/T$
1: 3-propylsydnone,
2: 3-butylsydnone

Although the viscosity of both 3-propylsydnone and 3-butylsydnone is about 10 times larger than that of common liquid near room temperatures, the τ_c of many liquids is about a few ps [13]. Therefore it is considered that the extreme narrowing conditions in Eq.1 are satisfied for these sydnones. Often the asymmetry parameter η^* is sufficiently small so that $(1 + \eta^{*2}/3)$ may equal to unity [13]. In general it is reasonable to assume that the electric field gradient in a neat liquid

is hardly changed in a narrow temperature range. Therefore it is considered that the nuclear quadrupole coupling constant is a constant. Consequently it is thought that in Eq. (4) the T_2 for ¹⁴N in neat liquids mainly depends on the correlation time τ_c . Thus the variation of T_2 for ¹⁴N of 3-propylsydnone and 3-butylsydnone gives the information about whole molecular motion in these neat liquids characterized by τ_c , which is proportional to the viscosity η of liquid accordingly to an extension of Debye theory [15]. On the other hand the variation of viscosity of liquids with temperature, T , is expressed as a logarithmic equation [16,5,6]

$$\log \eta = E_a / 2.303RT + A \quad (5)$$

where E_a is the activation energy of molecular motion and A is a constant. A combination

of Eqs. (4) (5) and the extension of Debye theory gives Eq.(6)

$$\log(1/T_2) = E_a/2.303RT + B \quad (6)$$

where B is another constant. The plots of $\log(1/T_2)$ vs $1/T$ for 3-propylsydnone and 3-butylsydnone yield the straight lines shown in Fig.3. The activation energies for 3-propylsydnone and 3-butylsydnone were calculated from the slopes of the lines according to Eq.(6) and listed in table 1 together with data from previous paper [5,6]. The activation energies from T_2 measurements are in fairly accordance with those from viscosity measurements. In conclusion it is considered that the spin-spin relaxation time T_2 for ^{14}N in 3-propylsydnone and 3-butylsydnone is dominated by molecular motion characterized by correlation time proportional to viscosity of liquid.

Table 1 Activation energy e_a for 3-propylsydnone and 3-butylsydnone

	$E_a/(\text{kJ}\cdot\text{mol}^{-1})$	
	3-propylsydnone	3-butylsydnone
T_2 measurement	22.4	25.4
Viscosity measurement	26.2 ^a (25.0) ^b	29.3 ^b

a, Ref. [6]; b, Ref. [5].

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^{14}N NMR 弛豫法研究 3- 烷基斯德酮

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摘要 常温下 3- 丙基斯德酮和 3- 丁基斯德酮为具有很高介电常数的液体, 与许多溶剂混溶, 预期可以作为许多电解质的优良溶剂. 斯德酮环 3 位上的氮原子给出尖锐的 ^{14}N NMR 峰. ^{14}N 的四极矩弛豫时间 $T_Q=T_2$. 利用变温下 ^{14}N NMR T_2 测量, 得出这两个化合物成液态时分子运动活化能. 结果与粘度测量法所得的吻合.

关键词: 斯德酮, ^{14}N NMR, 弛豫时间, 相关时间, 活化能

简 讯

国际电化学 (ISE) 第 46 届年会将于 1995 年 8 月 27 日至 9 月 1 日在中国厦门召开. 本届大会由中国厦门大学主办, 中国科学院院士、厦门大学田昭武教授任大会主席. 会议主题为: (1) 物理电化学; (2) 电化学研究原位技术; (3) 电化学传感器和电分析化学; (4) 生物电化学和有机电化学; (5) 电化学能源技术; (6) 电化学新材料; (7) 腐蚀电化学、电沉积及表面技术; (8) 工业电化学与化学工程.

中国第八届电化学学术会议由复旦大学主办, 亦将于其时在厦门召开. 此外, 会议期间还将举办国际电化学新仪器, 新技术, 新产品展览会, 届时将有众多国内外电化学专家和厂商参展. 热烈欢迎广大电化学家和有关厂商出席会议, 踊跃参展.

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