Physical Properties of 3-*s*-Butylsydnone

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Synopsis. The physical properties of 3-*s*-butylsydnone at various temperatures were investigated by dielectric constant, refractive index, density, and viscosity measurements. These physical constants were compared with those of other 3-alkylsydnones. Although the differences in the dielectric constant, refractive index and density between 3-butylsydnone and 3-*s*-butylsydnone were relatively small, the viscosity of 3-*s*-butylsydnone became particularly larger than that of 3-butylsydnone at lower temperatures.

The sydnones are well known as being typical mesoionic compounds, and have markedly large dipole moments and high dielectric constants[1—5] compared with those of other polar solvents. We have already reported on the physical properties of 3-propylsydnone[6] and 3-butylsydnone,[7] which are liquids at room temperature.[8] Though 3-*s*-butylsydnone is also liquid at room temperature, no detailed study concerning its physical properties has been reported.[8—10] It is worthwhile to clarify the physical properties of 3-*s*-butylsydnone and to investigate whether or not it may be a good solvent for electrolytes.

The purpose of the present paper is to elucidate the bulk physical properties, such as the dielectric constants, refractive indices, densities, and viscosities of 3-*s*-butylsydnone at various temperatures. In addition, a comparative study of 3-*s*-butylsydnone and some 3-alkylsydnones[4—7] for these physical properties was made.

Experimental

General. The apparatus and techniques for measuring the dielectric constant, refractive index, density, and viscosity were similar to those used previously.[7] The ^{1}H and ^{13}C NMR spectra were taken on the JEOL-90Q and -400WB NMR spectrometers.

Materials. The preparation and purification of 3-*s*-butylsydnone, starting with ethyl bromoacetate and *s*-butylamine, have been described elsewhere.[10] The purity and structure of 3-*s*-butylsydnone were confirmed by elemental analysis (Found: C, 50.73; H, 7.11; N, 19.95%. Calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71%), ^{1}H and ^{13}C NMR spectra. The purified 3-*s*-butylsydnone was dehydrated by purified molecular sieves(4A) before use. The water content of 3-*s*-butylsydnone, determined by Karl Fischer titration, was less than 50 ppm.

Results and Discussion

The dielectric constant (ε) of 3-*s*-butylsydnone gradually decreased with increasing temperature, as shown in Fig. 1, in a way similar to that of other 3-alkylsydnones. It is considered that, as described previously,[6,7] the decrease in ε with increasing temperature is dependent on the variation of the arrangement in the permanent dipole caused by the thermal motion of the molecule due to an increase in the temperature. The dielectric constant of 3-*s*-butylsydnone was 76.6 at 25 °C; this value was close to those of 3-butylsydnone (77.9)[7] and water (78.3),[11] a typical polar solvent with a high dielectric constant. However, the difference of ε between 3-butylsydnone and 3-*s*-butylsydnone at lower temperature became large. On the other hand, it was found that the refractive index (n_D) of 3-*s*-butylsydnone was also very close to that of 3-butylsydnone in the temperature range of 10 to 80 °C.

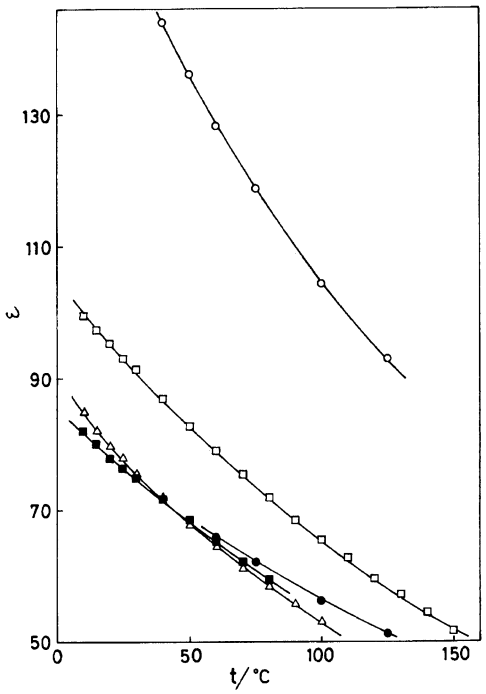

Fig. 1. Temperature dependence on the dielectric constant (ε) measured by 1 MHz of 3-alkylsydnones. (○) : 3-methylsydnone, (□) : 3-propylsydnone, (●) : 3-isopropylsydnone, (△) : 3-butylsydnone, (■) : 3-*s*-butylsydnone. The data of 3-methylsydnone and 3-isopropylsydnone were quoted from Ref. 4.

Figure 2 shows the temperature dependence on the density (ρ) of 3-alkylsydnones. The density of 3-*s*-butylsydnone decreased lineary with increasing temperature, similarly to those of other 3-alkylsydnones. In addition, the difference of density in the 10 to 80 °C temperature range between 3-butylsydnone and 3-*s*-butylsydnone is considerably small. It is therefore assumed that a size of 3-*s*-butylsydnone is nearly equal to that of 3-butylsydnone. By using the density and dielectric

Table 1. Physical Properties of 3-Alkylsydnons

		3-Methylsydnone[a]	3-Propylsydnone[b]	3-Isopropylsydnone[a]	3-Butylsydnone[b]	3-*s*-Butylsydnone
	25 °C		93.0		77.9	76.6
	40 °C	144.0	87.1		71.6	71.5
(1 MHz)	60 °C	128.3	79.2	66.0	64.5	65.1
	25 °C		1.499_8		1.493_8	1.494_0
n_D	40 °C	1.515_0	1.493_8		1.487_8	1.487_1
	60 °C	1.508_0	1.484_8	1.485_2	1.479_8	1.478_9
	25 °C		1.161_6		1.115_2	1.119_0
$\rho/10^3$kg m^{-3}	40 °C	1.3085	1.148_9		1.103_4	1.106_9
	60 °C	1.2896	1.132_3	1.1324	1.088_3	1.090_8
	25 °C		10.3		11.3	16.1
η/cP	40 °C	5.501	6.2		6.3	8.0
	60 °C	3.546	3.5	3.864	3.3	3.7
E_η/kJ mol^{-1}		16.5	26.2	17.5	29.3	34.7

a) Ref. 4. b) Ref. 7. Activation energies (E_η) for 3-methylsydnone and 3-isopropylsydnone were calculated with Ref. 4.

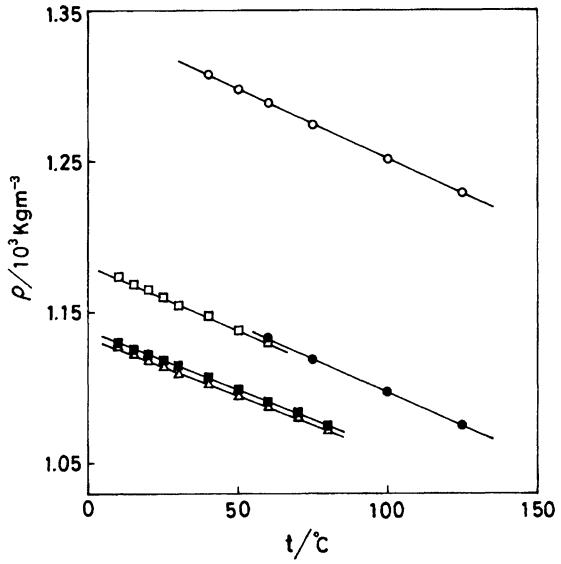

Fig. 2. Temperature dependence on the density (ρ) of 3-alkylsydnones. (○) : 3-methylsydnone, (□) : 3-propylsydnone, (●) : 3-isopropylsydnone, (△) : 3-butylsydnone, (■) : 3-*s*-butylsydnone. The data of 3-methylsydnone and 3-isopropylsydnone were quoted from Ref. 4.

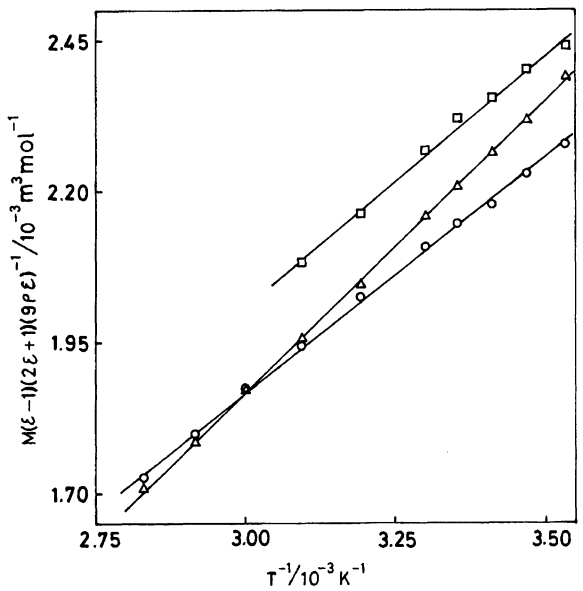

Fig. 3. Plot of $M(\varepsilon-1)(2\varepsilon+1)/9\rho\varepsilon$ vs. $1/T$. M denotes the molecular weight of each 3-alkylsydnones. (□) : 3-propylsydnone, (△) : 3-butylsydnone, (○) : 3-*s*-butylsydnone.

constant data, it was considered whether the Kirkwood equation[12—16] holds or not for 3-*s*-butylsydnone. Figure 3 shows plots of $M(\varepsilon-1)(2\varepsilon+1)/(9\rho\varepsilon)$ vs. $1/T$, where M denotes the molecular weight of each 3-alkylsydnone. In Fig. 3, 3-*s*-butylsydnone, such as 3-propylsydnone and 3-butylsydnone, satisfied the Kirkwood equation, because the plot for 3-*s*-butylsydnone is linear. In general, the correlation factor (g) must be known in order to estimate the dipole moment by using the Kirkwood equation. The g factor gives an indication of the type for arrangements of molecular dipoles in polar liquids. The g factors for 3-alkylsydnones, except for 3-methylsydnone and 3-isopropylsydnone, have not yet been determined. The g factors for 3-methylsydnone (1.03)[4] and 3-isopropylsydnone (0.91)[4] are nearly equal to unity. A liquid with a g factor near to unity suggests that the arrangement of the dipole in the liquid is not completely parallel or antiparallel, but is random. If the arrangement of the dipole in 3-*s*-butylsydnone is random, that is, the g factor is close to unity, the dipole moment of 3-*s*-butylsydnone can be estimated from the slope of the straight line in Fig. 3. The dipole moment obtained was about 3.78×10^{-29} C m (11.3 D). This value is very high compared with those of many polar organic solvents. However, this value is smaller than

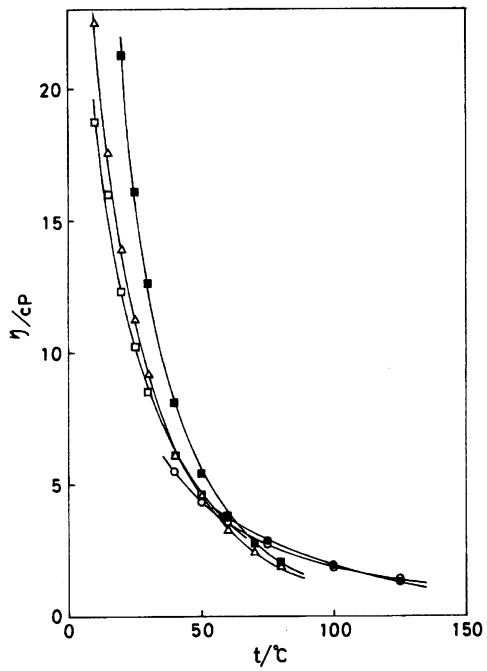

Fig. 4. Temperature dependence on the viscosity (η) of 3-alkylsydnones. (○) : 3-methylsydnone, (□) : 3-propylsydnone, (●) : 3-isopropylsydnone, (△) : 3-butylsydnone, (■) : 3-*s*-butylsydnone. The data of 3-methylsydnone and 3-isopropylsydnone were quoted from Ref. 4.

those of 3-propylsydnone (11.7 D)[6] and 3-butylsydnone (12.6 D)[7] obtained based on a similar assumption.

The viscosity (η) obtained by using the density data in Fig. 2 for 3-alkylsydnones are shown in Fig. 4. It seems reasonable to assume that an associated compound (aggregate) is formed in each 3-alkylsydnone, since the 3-alkylsydnones have high dielectric constants and viscosities, in spite of lower molecular weight. The viscosity of 3-*s*-butylsydnone is higher than other 3-alkylsydnones at 25 and 40 °C. The viscosity of 3-*s*-butylsydnone decreased markedly with increasing temperature in Fig. 4, similarly to that of 3-propylsydnone and 3-butylsydnone. Furthermore, it appears that the difference in the viscosities for five kinds of 3-alkylsydnones becomes small at higher temperature. On the other hand, a plot of $\log\eta$ vs. $1/T$ (Arrhenius equation) in the range of 10 to 80 °C yielded a straight line. From the slope of the line, the activation energy (E_η) for the viscosity of 3-*s*-butylsydnone was found to be 34.7 $kJ\,mol^{-1}$. The E_η of 3-*s*-butylsydnone is higher than those of 3-propylsydnone and 3-butylsydnone (Table 1).

In Table 1, the differences of n_D and ρ between 3-propylsydnone and 3-isopropylsydnone, and 3-butylsydnone and 3-*s*-butylsydnone are very small. This fact shows that the difference in these small alkyl groups on the 3-position of the sydnone ring hardly effects n_D and ρ. However, the differences in their viscosities are large, especially at low temperature. For example, the viscosity of 3-*s*-butylsydnone at 25 °C became larger by about 43% compared with that of 3-butylsydnone. Accordingly, it is assumed that the extent of association in 3-*s*-butylsydnone is higher than that in 3-butylsydnone. In addition, it was found that 3-*s*-butylsydnone is stable for several months if it is kept in a brown desiccator.

In conclusion, 3-*s*-butylsydnone can be expected to be a good solvent for many electrolytes because of its very high dielectric constant (near to that of water), large dipole moment, moderate viscosity and stable compound. However, the solubilities of various electrolytes in 3-*s*-butylsydnone should be further investigated.

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