Physical Properties of 3-Propylsydnone

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The physical properties of 3-propylsydnone at various temperatures were investigated by dielectric constant, refractive index, density and viscosity measurements. The dielectric constant (ε) of 3-propylsydnone is very high compared to those of many organic solvents. For example, this value was found to be 95.0 at 25 °C. The dielectric constant of 3-propylsydnone is approximately expressed by a cubic equation of the temperature. The Kirkwood equation holds over the range from 10 to 150 °C. The refractive index (n_D) and density (ρ) data for 3-propylsydnone are described as linear equations of the temperature with maximum deviations of 0.008 and 0.005%, respectively. The viscosity (η) of 3-propylsydnone at 25 °C is 8.45 cP (1 cP=10^{-3} N s m^{-2}). This value is larger than those of many organic solvents, but smaller than those of sulfolane and 1,2-ethanediol. A plot of log η vs. $1/T$ for 3-propylsydnone yields a straight line. The activation energy of the viscosity for 3-propylsydnone was found to be 25.0 kJ mol^{-1}.

The molecule, 3-phenylsydnone is well known as being the first mesoionic compound synthesized by Earl and Mackney.[1] The structure, reactions, and various physicochemical properties of sydnone compounds have already been reviewed by Baker, Ollis,[2] Stewart,[3] Ohta and Kato.[4] However, no detailed study concerning the physical properties of sydnone compounds, except for some alkylsydnones,[5–7] has been reported. Sydnone compounds were shown to be fairly soluble in most organic solvents and have remarkably large dipole moments[8] compared to those of other polar solvents. Though most sydnone compounds have relatively high melting points, 3-propylsydnone is a liquid at or near room temperature.[3] Considering the large dipole moment and low melting point of 3-propylsydnone, it can be expected to be used as a good solvent for many electrolytes.

The purpose of the present paper is to elucidate such bulk physical properties as the dielectric constants, refractive indices, densities, and viscosities of 3-propylsydnone at various temperatures. A comparative study of 3-propylsydnone and some 3-alkylsydnones[6,7] for these physical properties was made.

Experimental

General. The apparatus and techniques for measurements of the dielectric constant, density, and viscosity are similar to those used previously.[9] The refractive index was measured on an Abbe model 2_T refractometer equipped with jackets through which water from a constant-temperature bath was circulated. The ^1H and ^{13}C NMR spectra were taken on a JEOL-90Q spectrometer.

Materials. The preparation and purification of 3-propylsydnone (Fig. 1), starting with ethyl bromoacetate and propylamine, have been described elsewhere.[10] The purity and structure of 3-propylsydnone were confirmed by elemental analysis (Found: C, 46.49; H, 6.53; N, 21.48%. Calcd for $C_5H_{10}O_3N_2$: C, 46.87; H, 6.29; N, 21.89%), ^1H (Fig. 2) and ^{13}C NMR spectra (Fig. 3). The preparation and

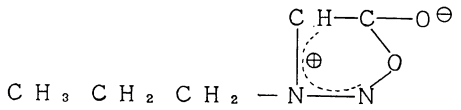

Fig. 1. Structure of 3-propylsydnone.

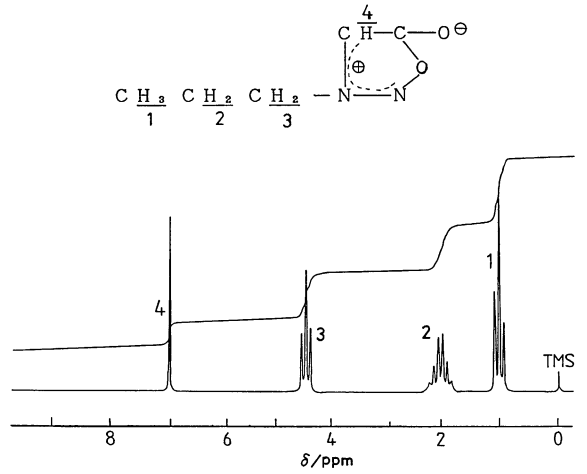

Fig. 2. ^1H NMR spectrum of 3-propylsydnone in $CDCl_3$ with 1% TMS. The numbers in spectrum were assigned to those of protons in 3-propylsydnone.

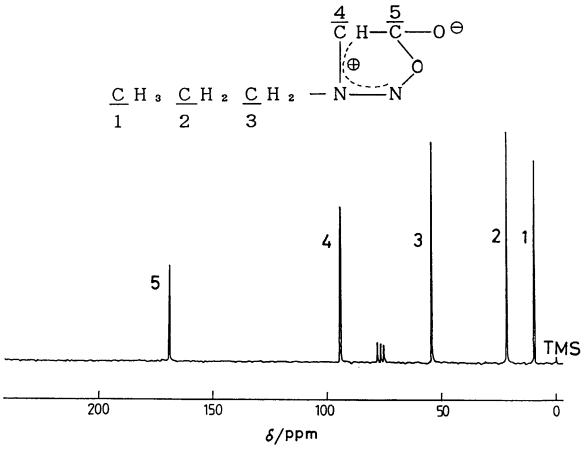

Fig. 3. ^{13}C NMR spectrum of 3-propylsydnone in $CDCl_3$ with 1% TMS. The numbers in spectrum were assigned to those of carbons in 3-propylsydnone. The confirmation on carbons of number 4 and 5 was carried out with selective decoupling method.

purification of *N,N*-dimethylformamide (DMF), propylene carbonate (PC) and hexamethylphosphoric triamide (HMPA) have been described elsewhere.[11,12]

Results and Discussion

The dielectric constant (ε) of 3-propylsydnone decreases slowly with increasing temperature, as shown in Fig. 4, in a way similar to those of 3-methylsydnone and 3-isopropylsydnone. This means that the arrangement of the permanent dipole is prevented by thermal motion of the molecule due to the increase in temperature. The decomposition of 3-propylsydnone seems to begin at more than 150 °C, since it is difficult to obtain a reproducible value of ε beyond 150 °C. The dielectric constant data for 3-propylsydnone can be described as a function of temperature as follows. By employing

$$\varepsilon = 105.76 - 4.74 \times 10^{-1}t + 8.24 \times 10^{-4}t^2 - 3.96 \times 10^{-9}t^3,$$

it is possible to calculate the dielectric constant of 3-propylsydnone at any temperature. The maximum deviation between the experimental and calculated values was found to be <0.6% in the range from 10 to 150 °C. The dielectric constant of 3-propylsydnone for each temperature is larger than those of 3-isopropylsydnone[6] and many organic solvents, but smaller than that of 3-methylsydnone,[6] as shown in Fig. 4.

Figure 5 shows the change in the refractive index (n_D) of 3-propylsydnone near room temperature. The refractive index of 3-propylsydnone decreases linearly with temperature. The refractive index data for 3-propylsydnone were well fitted to the following equation with a maximum deviation of 0.008%:

$$n_D = -3.997_3 \times 10^{-4}t + 1.507_3.$$

The density (ρ) data for 3-alkylsydnones are shown in Fig. 6. The density for each 3-alkylsydnone is described as a linear equation of the temperature. The equation for 3-propylsydnone,

$$\rho = -7.960 \times 10^{-4}t + 1.177,$$

has a maximum deviation of 0.005%. By use of the density and dielectric constant data, it was considered whether the Kirkwood equation[13-17] holds or not for 3-propylsydnone. Figure 7 shows a plot of $M(\varepsilon-1)(2\varepsilon+1)(9\rho\varepsilon)^{-1}$ vs. $1/T$, where M denotes the molecular weight of 3-propylsydnone. In Fig. 7, it can be seen that the plot is linear. This means that 3-propylsydnone satisfies the Kirkwood equation. Accordingly, the dipole moment of 3-propylsydnone can be obtained from the slope of the straight line in

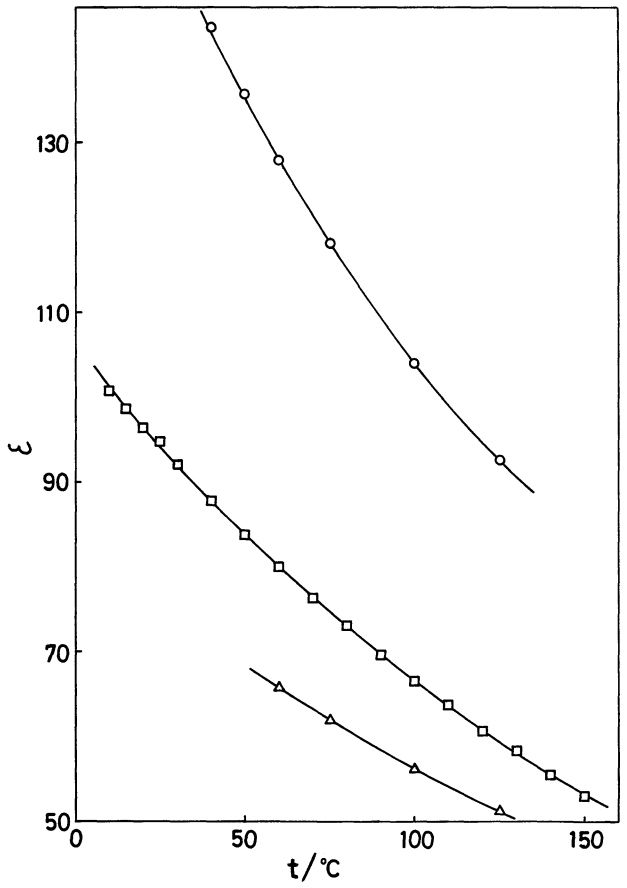

Fig. 4. Temperature dependence on the dielectric constant (ε) of 3-alkylsydnones. (○): 3-methylsydnone, (□): 3-propylsydnone, (△): 3-isopropylsydnone. The data of 3-methylsydnone and 3-isopropylsydnone were quoted from Ref. 6.

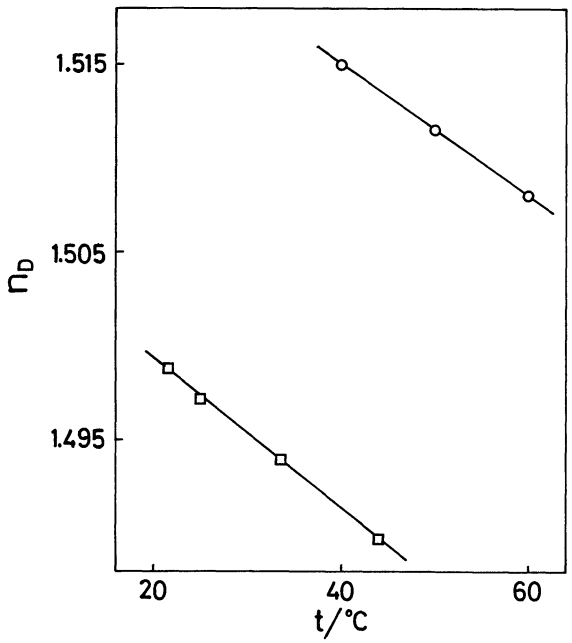

Fig. 5. Temperature dependence on the refractive index (n_D) of 3-methylsydnone and 3-propylsydnone. (○): 3-methylsydnone, (□): 3-propylsydnone. The data of 3-methylsydnone were quoted from Ref. 6.

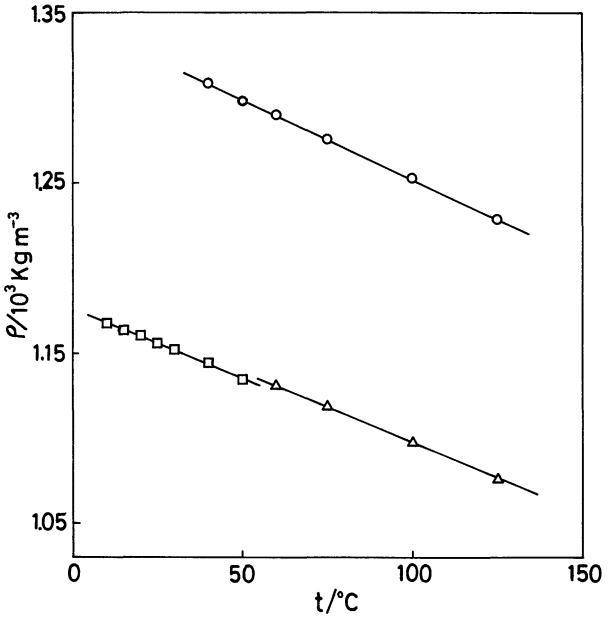

Fig. 6. Temperature dependence on the density (ρ) of 3-alkylsydnones. (○): 3-methylsydnone, (□): 3-propylsydnone, (△): 3-isopropylsydnone. The data of 3-methylsydnone and 3-isopropylsydnone were quoted from Ref. 6.

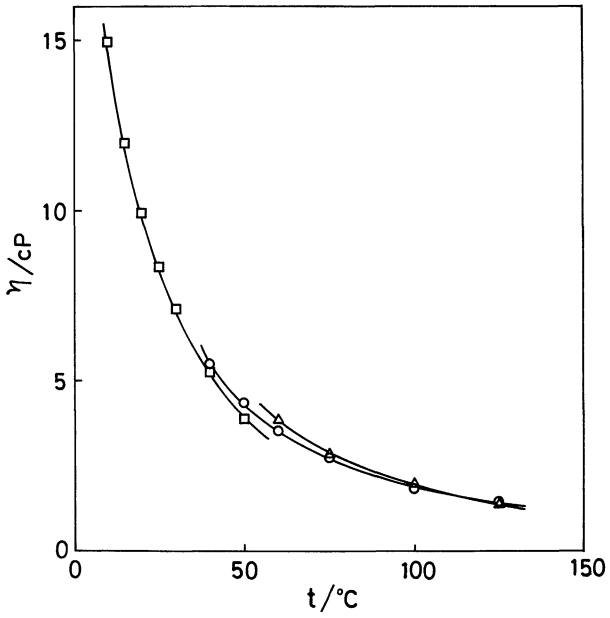

Fig. 8. Temperature dependence on the viscosity (η) of 3-alkylsydnones. (○): 3-methylsydnone, (□): 3-propylsydnone, (△): 3-isopropylsydnone. The data of 3-methylsydnone and 3-isopropylsydnone were quoted from Ref. 6.

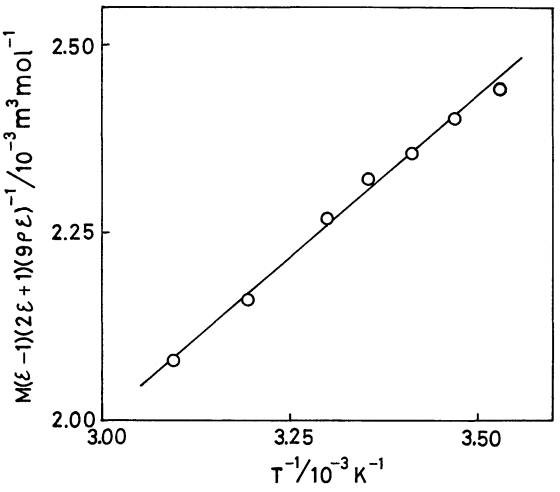

Fig. 7. Plot of $M(\varepsilon-1)(2\varepsilon+1)/9\rho\varepsilon$ vs. $1/T$. M denotes the molecular weight of 3-propylsydnone.

Fig. 7 if the correlation factor, g, of 3-propylsydnone is close to unity, such as 3-methylsydnone and 3-isopropylsydnone.[6] The dipole moment obtained in this way was about 3.91×10^{-29} Cm (11.7 D). This value is very high compared to those of other 3-alkylsydnones[6] and polar organic solvents. However, the exact dipole moment of 3-propylsydnone should be further considered from the correlation factor, g. Figure 8 shows the temperature dependence of the viscosity (η) of 3-alkylsydnones. The viscosity of 3-propylsydnone decreases markedly as the temperature is raised, as shown in Fig. 8. In addition, it seems that the viscosity of three kinds of 3-alkylsydnone becomes equal at higher temperature. The variation of the viscosity of a liquid with temperature is best expressed by means of a logarithmic equation,[18]

$$\log \eta = \frac{E_\eta}{2.303RT} + \log A,$$

where $E\eta$ and A are the activation energy and a constant for a given liquid, respectively. The plot of $\log \eta$ vs. $1/T$ for 3-propylsydnone yields a straight line, as shown in Fig. 9. From the slope of the straight line, the value of the activation energy of the viscosity for 3-propylsydnone was found to be 25.0 kJ mol^{-1}. The activation energies of four typical nonaqueous solvents (DMSO, HMPA, PC, and DMF) were also calculated with the viscosity data in Fig. 10. In Fig. 10, the data of DMSO are quoted from the literature.[19]

In Table 1, these experimental data at 25 °C of 3-propylsydnone are summarized in order to compare it with those of other 3-alkylsydnones and typical nonaqueous solvents. The dielectric constants for 3-alkylsydnones decrease markedly as the alkyl group on the 3-position of the sydnone ring becomes larger. The dielectric constant (88.2) of 3-propylsydnone at 40 °C is nearly equal to that (89.78)[12] of ethylene carbonate. This implies that 3-propylsydnone has the possibility to be available as a good solvent for the electrolyte. The refractive indices for 3-alkylsydnones decrease slightly with an increase in the size of the

Table 1. Physical Properties for 3-Alkylsydnones and Typical Nonaqueous Solvents at 25 °C

Solvent	ε	n_D	$\rho/10^3$ kg m^{-3}	η/cP	E_η/kJ mol^{-1}
3-Methylsydnone (40 °C)[a,b]	144.0	1.5150	1.3085	5.501	16.5
3-Prpylsydnone	95.0	1.4972	1.1575	8.459	25.0
3-Isopropylsydnone (60 °C)[a]	66.0	1.4852	1.1324	3.864	17.5
3-Butylsydnone[a]	52.8	1.487	1.097	21.4	
PC[c]	64.92	1.4199	1.1951	2.530	15.1
DMF[c]	36.71	1.4282	0.9439	0.802	8.9
DMSO[c]	46.45	1.4775	1.0954	1.991	14.2
HMPA[c]	29.6	1.4570	1.0202	3.10	16.0

a) Ref. 6. b) Ref. 7. c) Ref. 12. Activation energies for 3-methylsydnone, 3-isopropylsydnone, and DMSO were calculated with Ref. 6 and 19, respectively.

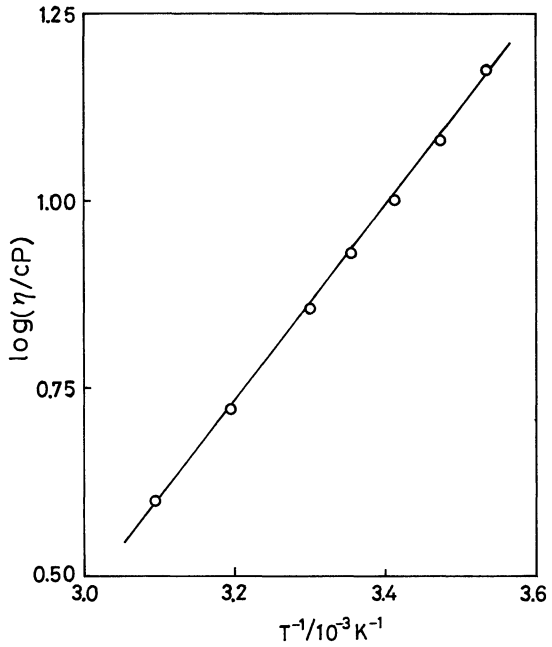

Fig. 9. Plot of the logarithm of viscosity vs. $1/T$ for 3-propylsydnone.

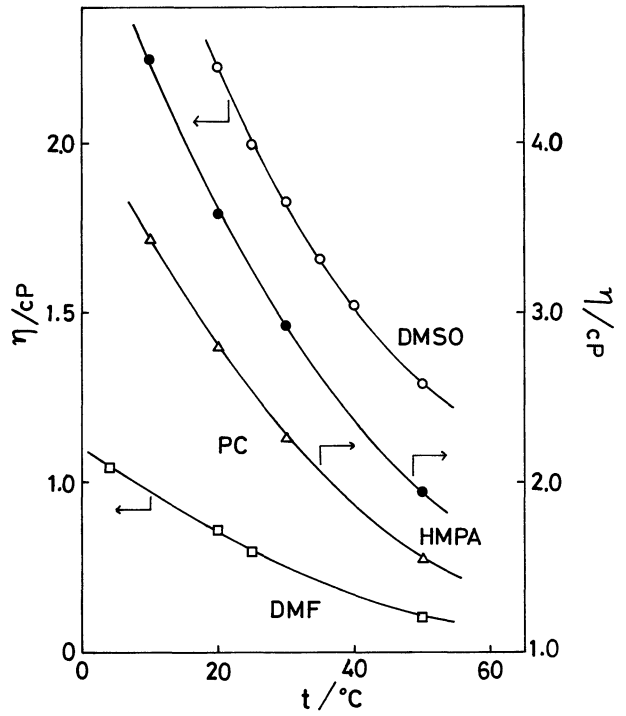

Fig. 10. Temperature dependence on the viscosity (η) of the typical nonaqueous solvents. The data of DMSO were quoted from Ref. 19.

alkyl group. The densities for 3-alkylsydnones, as might be expected, show a large decrease with an increase in the size of the alkyl group. The viscosities for 3-alkylsydnones, on the contrary, increase as the alkyl group becomes larger. In addition, the viscosity of 3-propylsydnone is larger than those for PC and HMPA but smaller than those for sulfolane and 1,2-ethanediol (ethylene glycol). The activation energy of 3-propylsydnone is very large compared to those of 3-methylsysnone and 3-isopropylsydnone. The activation energy of 3-alkylsydnones does not necessarily depend on the viscosity. However, it was found that the higher the viscosity of the typical nonaqueous solvents, the larger the activation energy of these solvents (Table 1).

In conclusion, 3-propylsydnone can be expected to be a good solvent for many electrolytes because of the very high dielectric constant, large dipole moment, moderate viscosity and convenient liquid range.

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