Physical Properties of 3-Ethylsydnone and the Alkyl Substituents

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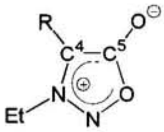
3-Ethyl-4-ethylsydnone was newly synthesized, and the physical properties of 3-ethylsydnone, 3-ethyl-4-methylsydnone and 3-ethyl-4-ethylsydnone at various temperatures were investigated. The highest dielectric constant was for 3-ethylsydnone. The alkyl substituent effect at the 4-position of the sydnone ring on the dielectric constant can be explained by the ^{13}C NMR spectra.

The sydnone compounds are well known as typical mesoionic compounds, which can not be satisfactorily represented by any one canonical structure.[1-3] They have a heterocyclic five-membered ring, which bears a fractional positive charge, balanced by a corresponding negative charge located on a covalently attached oxygen atom. These unique structures lead to a large dipole moment,[4-6] which increases the dielectric constant of some sydnones. 3-Alkylsydnones and 3,4-dialkylsydnones substituted by alkyl groups at the 3- and 4-positions of the sydnone ring have very high dielectric constants[7] compared with those of other polar solvents.[8] So far, there have been no detailed studies about the physical properties of 3-ethylsydnone(3-ESD) and its alkyl-substituted sydnones at the 4-position of the sydnone ring, such as 3-ethyl-4-methylsydnone(3-EMSD) and 3-ethyl-4-ethylsydnone(3-EESD). In this paper, the dielectric constant, refractive index, density and viscosity for 3-ESD, 3-EMSD and newly synthesized 3-EESD[9] are presented. The series of 3-ethylsydnone substituted by different alkyl groups at the 4-position of the sydnone ring also clearly shows the substitutive effect at the 4-position of the sydnone ring upon the physical properties.



3-ESD (R=H)
3-EMSD (R=Me)
3-EESD (R=Et)

The syntheses of alkylsydnones has been carried out essentially using the literature procedures,[10-13] that is, the N-nitroso derivatives of alkylamino acids are dehydrated with acetic anhydride to form a five-membered cyclic structure. The alkylamino acids are obtained via alkylamino esters starting from alkylamines and bromo-esters. The same route preparation is performed for 3-ESD, 3-EMSD and 3-EESD, although a slight modification is made for preparing the alkylamino esters intermediate. Every amino ester can be successively extracted from an aqueous solution of the reaction mixture containing ethylamine, excess bromo-ester and the triethylamine catalyst using diethylether.

Figure 1 shows the dielectric constant(ε) of 3-ESD, 3-EMSD and 3-EESD from 10 to 80 ℃. Very high dielectric constants for 3-ESD are revealed at these temperatures and exceed 100 at lower temperatures. These values are significantly higher than those of water and many polar organic solvents, for example, propylene carbonate(64.9 at 25℃) and ethylene carbonate(89.6 at 40℃).[8] Propylene carbonate and ethylene carbonate are now commonly used as polar organic solvents for lithium batteries[14] which are becoming important not only for the development of multimedia systems but also for application in electric vehicle batteries. The dielectric constants of 3-ESD, 3-EMSD and 3-EESD decrease slowly with increasing temperature, which should depend on the arrangement in the permanent dipole caused by the thermal motion of the molecule as previously described.[7] 3-EMSD and 3-EESD also exhibit higher values of 70.83 and 67.65, respectively at 25℃ than that of propylene carbonate. A remarkable tendency of a decreasing dielectric constant is observed as the alkyl group at the 4-position of the sydnone ring becomes longer. This result suggests that substitution of the alkyl group affects the polarity based on the positive charge associated with the sydnone ring system. It seems that the longer alkyl substituent increases the electron density of a sydnone ring system and the positive charge of the sydnone ring system is weakened. The electron-donor effect of the alkyl groups would bring about a decrease in the charge asymmetry of a sydnone ring system and the polarity of the molecule should be decreased. This interpretation can be illustrated by the ^{13}C-NMR spectra of 3-ESD, 3-EMSD, and 3-EESD. The C4 ring carbon resonance occurs at δ 95.01, 103.32 and 107.96 ppm, and the C5 one occurs at δ 169.69, 169.01 and 168.82 in 3-ESD, 3-EMSD and 3-EESD, respectively. Replacement of the 4-positioned alkyl group results in a

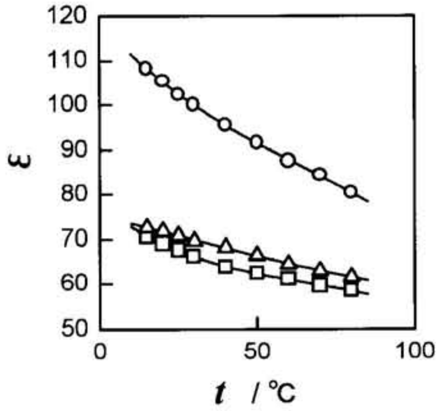


Figure 1. Temperature dependence of the dielectric constant(ε) of 3-ESD(○), 3-EMSD(△) and 3-EESD(□).

downfield shift of the C4 signal and very small upfield shift of the C5 signal. The upfield shift of the C5 atom shows that the C5 carbonyl carbon is due to the induced shielding effect on the basis of the electron-donating effect of an alkyl substituent group at the 4-position of the sydnone ring. In spite of the very small shift in the C5 atom, a difference in the electron density of the carbonyl carbon should significantly affects the polarity of the molecule. On the other hand, the downfield shift of the C4 atom can be explained by the increase in the deshielding effect[15] of the alkyl group on the C4 atom. The α and β effects are illustrated by the downfield shift of the C4 atom from 3-ESD to 3-EMSD and from 3-EMSD to 3-EESD, respectively.

Figure 2 shows the viscosity (η) of 3-ESD, 3-EMSD and 3-EESD from 10 to 80℃. Their viscosities have a strong exponential decrease with increasing temperature. It was shown that the viscosity became larger when the alkyl group was included in the 4-position of the sydnone ring. According to the high viscosity and dielectric constant, in spite of a small molecular weight, particularly in 3-ESD, it seems reasonable to assume that an associated compound (aggregate) is formed. The association of the sydnone compounds should be further investigated. Preparing mixed solutions with low viscosity solvents like ethers can compensate the large viscosity, which is a negative factor for the mobility of the electrolyte solution. Table 1 summarizes the dielectric constant, refractive index(n_D), density(ρ) and viscosity(η) of 3-ESD, 3-EMSD and 3-EESD at various temperatures. The refractive indexes of these sydnones are almost the same value. The density should depend on the molar volume.

3-ESD, 3-EMSD and 3-EESD are liquid at ambient temperature, and liquid alkylsydnones can be used as solvents for electrolytes. In this paper, we propose their availability as useful solvents for future electrolyte solutions. It is important to examine the syntheses and physical properties of several alkylsydnones in order to obtain useful solvents and study their electrochemical behavior and solvent ability.

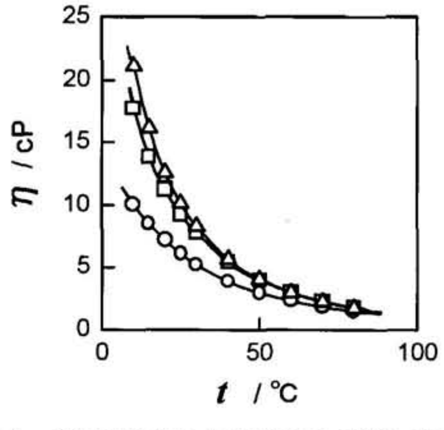


Figure 2. Temperature dependence of the viscosity(η) of 3-ESD(○), 3-EMSD(△) and 3-EESD(□).

Table 1. The dielectric constant(ε), refractive index(n_D), density(ρ) and viscosity(η) for 3-ethylsydnone(3-ESD), 3-ethyl-4-methylsydnone(3-EMSD) and 3-ethyl-4-ethylsydnone(3-EESD) at various temperatures

		3-ESD	3-EMSD	3-EESD
ε [a]	25℃	102.3	70.8	67.6
	40℃	95.6	68.3	63.8
	60℃	87.5	64.5	61.1
n_D [b]	25℃	1.506	1.506	1.500
	40℃	1.500	1.500	1.493
	60℃	1.494	1.491	1.485
ρ /g cm^{-3}	25℃	1.225	1.156	1.124
	40℃	1.212	1.143	1.112
	60℃	1.194	1.126	1.098
η /cP	25℃	6.6		
	40℃	3.9		
	60℃	2.3		

[a] Measured at a frequency of 1 MHz.
[b] Na D line (λ =589.3 nm).

References and Notes

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