Physical and Donor–Acceptor Properties of 3-Propyl-4-ethylsydnone

Minoru Handa,* Mayumi Kataoka, Makoto Wakaumi, and Yukio Sasaki

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics,
1583 Iiyama, Atsugi, Kanagawa 243-02

(Received July 17, 1996)

The physical properties of 3-propyl-4-ethylsydnone at various temperatures were investigated by dielectric constant (ε), refractive index (n_D), density (ρ), and viscosity (η) measurements. The dielectric constant of 3-propyl-4-ethylsydnone was very high compared with those of many organic solvents. For example, it was found to be 64.6 at 25 °C, close to that of propylene carbonate (64.9), a typical nonaqueous polar solvent with a high dielectric constant. The refractive index and density for 3-propyl-4-ethylsydnone decreased linearly with increasing temperature. The viscosity of 3-propyl-4-ethylsydnone at 25 °C was 11.2 cP ($1 \text{ cP} = 10^{-3} \text{ N s m}^{-2}$). This was larger than those of many organic solvents and close to that of phenol (11.6 cP at 20 °C). From a line for $\log \eta$ vs. $1/T$, the activation energy (E_η) for the viscosity of 3-propyl-4-ethylsydnone was found to be 29.7 kJ mol^{-1}. The estimation of donor (DN) and acceptor (AN) numbers for 3-propyl-4-ethylsydnone were also done from ^{29}Si and ^{13}C NMR spectroscopies, respectively. Donor number of 3-propyl-4-ethylsydnone was about 25, and its acceptor number was approximately about 20. Both numbers were large in many organic solvents. Both physical and donor–acceptor properties were influenced by alkyl substituent groups in the 3-, 4-positions of the sydnone ring.

The sydnone compounds are well known as typical mesoionic compounds. The structure, reactions, and limited physicochemical properties of sydnone compounds have already been reviewed by Baker, Ollins,[1] Stewart,[2] Ohta, and Kato.[3] However, no detailed study concerning the physical properties of sydnone compounds, except for some alkylsydnones,[4—6] has been reported. In previous papers we reported on the physical properties of some 3-alkylsydnones, such as 3-propylsydnone,[7] 3-butylsydnone,[8] and 3-s-butylsydnone.[9] They were liquids at room temperature and had large dipole moments, and very high dielectric constants compared with those of other polar solvents. Furthermore, we have already reported[10] that the binary mixtures of 3-propylsydnone–tetrahydrofuran and 1,2-dimethoxyethane with low viscosity were preferable as good solvents for the electrolytes. In addition, these binary mixtures were applied to the electrolytes for lithium batteries.[11] We described how sydnone compounds and their mixed solvents with ethers were superior to propylene carbonate, which generally has been used as a good solvent for the lithium batteries. Accordingly, studies of the physical properties for various sydnone compounds are very important to obtain useful solvents for the electrolytes. No studies about donor–acceptor properties for sydnone compounds have so far been done. These properties are very important in order to study the electrochemical behavior and solvent ability for the electrolytes. Consequently, it is valuable to estimate the donor and acceptor numbers for sydnone compounds. Our interest focuses on the substitutive effect in the 3-, 4-positions of the sydnone ring upon physical properties.

In this paper, first, we elucidate the bulk physical proper-

ties such as the dielectric constant, refractive index, density, and viscosity of 3-propyl-4-ethylsydnone in a group of 3, 4-dialkylsydnones and compare these data with those of 3-propylsydnones. Second, we show the donor and acceptor numbers of sydnone compounds. It is of interest to know the Lewis basicity and acidity of sydnone compounds containing different alkyl substituent groups in the 3-, 4-positions of the sydnone ring.

Experimental

General. The apparatus and techniques for measurements of the dielectric constant, refractive index, density, and viscosity at various temperatures were similar to those previously used.[8] The frequency was 1 MHz for measurement of the dielectric constant. The C–H COSY, ^{29}Si, and ^{13}C NMR spectra were taken on a JEOL JNM-EX400WB FT NMR system. The ^{29}Si and ^{13}C NMR spectra for estimation of donor and acceptor numbers were measured at 25 °C, referred to tetramethylsilane (TMS) as an external reference in the manner of literature.[12—15] Dilute solutions, mol ratio of trimethylsilanol : solvent = 1 : 20, were used for ^{29}Si NMR measurement. The chemical shift values did not need to be corrected for volume susceptibility differences, since a large concentration dependence of ^{29}Si resonances was not shown and a good correlation between the chemical shift values and donor numbers was obtained. The solutions, mol ratio of acetone : solvent = 1 : 10, which were more dilute than that in the literature (1 : 6),[13] were used for ^{13}C NMR measurement. ^{13}C chemical shift values agreed with which obtained by extrapolation to infinite dilution within the range of 0.5 ppm.

Materials. 3-Propyl-4-ethylsydnone (Fig. 1) was prepared and purified as described in the literature,[16,17] starting from ethyl 2-bromobutyrate and propylamine. It was a high boiling liquid, b.p. 155 °C at 3 mm, and more inflammable than 3-propylsydnone. The purity and structure of 3-propyl-4-ethylsydnone were
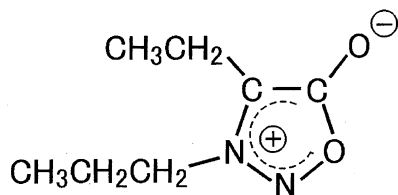
Fig. 1.   Structure of 3-propyl-4-ethylsydnone.

confirmed by elemental analysis (Found: C, 54.11; H, 8.05; N, 17.54%. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94%) and C–H COSY NMR spectrum (Fig. 2). The water content of 3-propyl-4-ethylsydnone was less than 50 ppm, measured by Karl Fischer titration. 3-Propylsydnone and 3-butylsydnone were prepared and purified as described in the literature.[16,17] Benzene, dioxane, acetone, ethyl acetate, methanol, tetrahydrofuran, N,N-dimethylformamide, and acetonitrile were obtained as high purity solvents for high pressure liquid chromatography. Acetic anhydride, propylene carbonate, diethyl carbonate, diethyl ether, ethanol, acetic acid, N-methylpyrrolidinone, N,N-dimethylacetamide, 1-butanol, pyridine, hexamethylphosphoric triamide, hexane, dimethyl sulfoxide, and chloroform were special grade quality. All of the solvents were dehydrated by purified molecular sieves (4A) before use.

Results and Discussion

The dielectric constant (ε) of 3-propyl-4-ethylsydnone decreases with increasing temperature as a function of the third order like many organic and inorganic solvents, as shown in Fig. 3. The decrease in ε, as described previously,[7—9] should be depend on the arrangement in the permanent dipole caused by the thermal motion of the molecule due to an increase in temperature. The dielectric constant of 3-propyl-4-ethylsydnone is 64.6 at 25 °C, which is close to that of propylene carbonate (64.9 at 25 °C).[18] Propylene carbonate has been
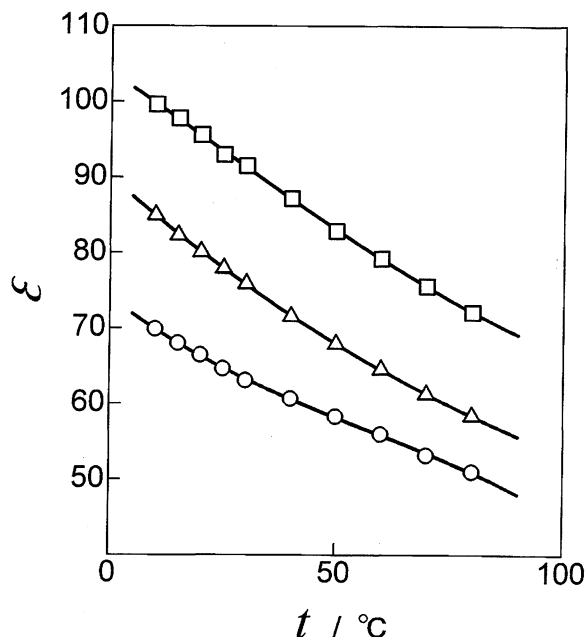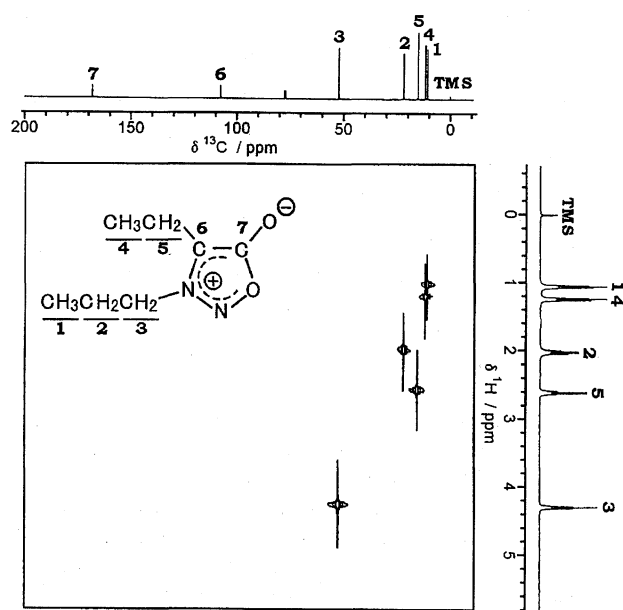

Fig. 2.   C–H COSY NMR spectrum of 3-propyl-4-ethyl-sydnone in $CDCl_3$ with 1% TMS. The numbers in spectrum were assigned to those of protons and carbons in 3-propyl-4-ethylsydnone.

Fig. 3.   Temperature dependence on the dielectric constant (ε) of ($\bigcirc$) 3-propyl-4-ethylsydnone, ($\triangle$) 3-propylsydnone, and ($\square$) 3-butylsydnone.

used as a typical good solvent in the binary mixtures for the electrolytes of lithium batteries. 3-Propyl-4-ethylsydnone would be expected to be good enough to use for the electrolytes as an alternative to propylene carbonate, with a high dielectric constant. A remarkable trend, that is, the dielectric constants for 3-alkylsydnones decrease as the alkyl group in the 3-position of the sydnone ring becomes larger, was discovered previously.[7] This tendency can be applied to the alkyl group in the 4-position of the sydnone ring, since the dielectric constant of 3-propyl-4-ethylsydnone is smaller than that of 3-propylsydnone.

Figure 4 shows changes in the refractive index (n_D) of 3-propyl-4-ethylsydnone. The refractive index of 3-propyl-4-ethylsydnone decreases linearly with temperature similarly to other 3-alkylsydnones without an alkyl group in the 4-position, and the value is somewhat smaller than that of 3-alkylsydnones. The density (ρ) of 3-propyl-4-ethylsydnone depends linearly on the temperature, as shown in Fig. 5, and the slope is almost the same as those of other 3-alkylsydnones. The value should be expected to decrease with an increase in the size of the alkyl groups of the sydnone ring, not only in the 3-position but also in the 4-position. These values of n_D and ρ of sydnone compounds should almost depend on their difference size of the alkyl group. By use of the density and dielectric constant data, it is considered whether the Kirkwood equation[19—23] holds or not for 3-propyl-4-ethylsydnone. Figure 6 shows plots of $M(\varepsilon - 1)(2\varepsilon + 1)/(9\rho\varepsilon)$ vs. $1/T$, where M denotes the molecular weight of each sydnone compound. 3-Propyl-4-ethylsydnone satisfies the Kirkwood equation because of the linear relationship as well as those of 3-alkylsydnones. According to the slope of the straight line, the dipole moment of 3-propyl-4-ethylsydnone can be obtained if its correlation factor (g) is known. If

M. Handa et al.
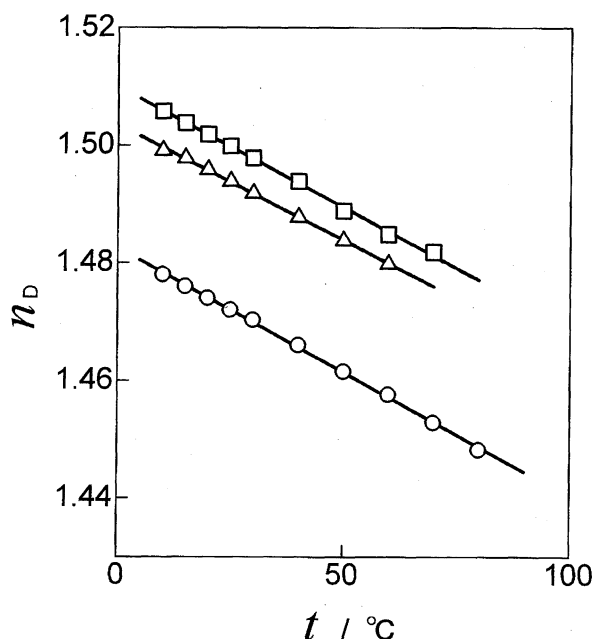
Bull. Chem. Soc. Jpn., 70, No. 2 (1997)   317

Fig. 4.   Temperature dependence on the refractive index (n_D) of (○) 3-propyl-4-ethylsydnone, (△) 3-propylsydnone, and (□) 3-butylsydnone.
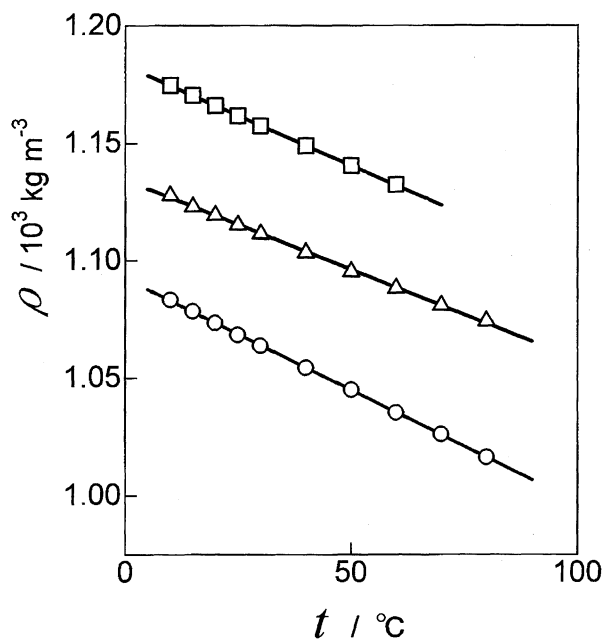

Fig. 6.   Plot of $M(\varepsilon - 1)(2\ \varepsilon + 1)/(9\ \rho\ \varepsilon)$ vs. $1/T$. M denotes the molecular weight of each sydnone compounds. (○) 3-propyl-4-ethylsydnone, (△) 3-propylsydnone, and (□) 3-butylsydnone.

carbonate. Therefore, it is expected that 3-propyl-4-ethylsydnone will be used as a good solvent for the electrolytes.

The viscosity of 3-propyl-4-ethylsydnone is 11.2 cP at 25 °C; this value is close to that of phenol (11.6 cP at 20 °C).[18] The viscosity (η) of 3-propyl-4-ethylsydnone has a strong exponential decrease with increasing temperature, as shown in Fig. 7. The value of 3-propyl-4-ethylsydnone is very close to that of 3-butylsydnone and larger than that of 3-propyl-

Fig. 5.   Temperature dependence on the density (ρ) of (○) 3-propyl-4-ethylsydnone, (△) 3-propylsydnone, and (□) 3-butylsydnone.
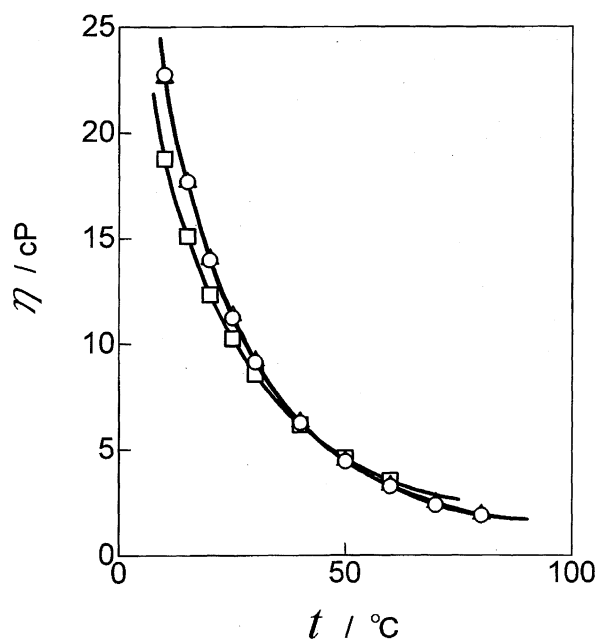
Fig. 7.   Temperature dependence on the viscosity (η) of (○) 3-propyl-4-ethylsydnone, (△) 3-propylsydnone, and (□) 3-butylsydnone.

the g factor of 3-propyl-4-ethylsydnone is nearly equal to unity, similarly to those of 3-methylsydnone (1.03)[3] and 3-isopropylsydnone (0.91),[3] the dipole moment of 3-propyl-4-ethylsydnone would be about 3.56×10^{-29} C m (10.7 D) in Fig. 6. The value is very high, like that of 3-propylsydnone (11.7 D)[7] and 3-butylsydnone (12.5 D),[8] compared with those of many polar organic solvents. The dipole moment of 3-propyl-4-ethylsydnone is larger than that of propylene
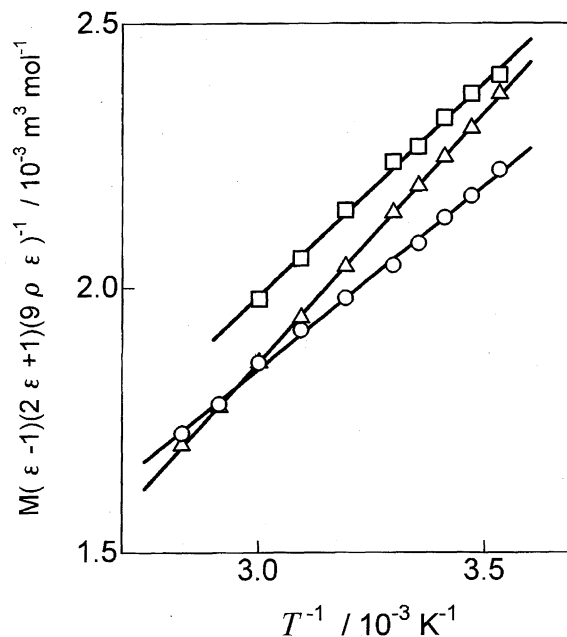
sydnone. The variation of the viscosity of a liquid with temperature is best expressed by the Arrhenius equation.[24] An Arrhenius plot of log η vs. $1/T$ for 3-propyl-4-ethylsydnone yields a straight line, as shown in Fig. 8. From the slope of the line, the activation energy (E_η) for the viscosity of 3-propyl-4-ethylsydnone is found to be 29.7 kJ mol^{-1}. The value is very large compared with those of many organic solvents and close to that of 3-butylsydnone (29.3 kJ mol^{-1}).[8] According to the high viscosity and dielectric constant, in spite of a small molecular weight, it seems reasonable to assume that an associated compound (aggregate) is formed in 3-propyl-4-ethylsydnone like other 3-alkylsydnones. The formation of the associated compounds in 3-propyl-4-ethyl-
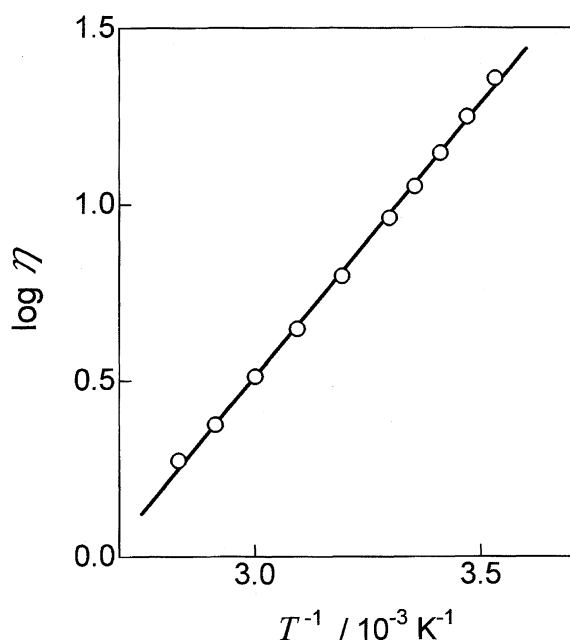

Fig. 8. Plot of the logarithm of viscosity vs. $1/T$ for 3-propyl-4-ethylsydnone.

sydnone should be further investigated. When 3-propyl-4-ethylsydnone is applied to the electrolytes, the problem of low conductivity owing to its high viscosity will be solved by addition of a low viscosity solvent. In Table 1, the physical properties of 3-propyl-4-methylsydnone in a bulk at 25, 40, and 60 °C are summarized to compare them with those of 3-alkylsydnones.

From the point of view of the microscopic properties, the donor number (DN) and acceptor number (AN) were estimated by NMR spectroscopic measurements. Donor numbers of sydnone compounds are obtained indirectly by ^{29}Si NMR spectroscopic methods by way of the literature.[12,15] This method gives fairly good calibration curves that are very convenient in many empirical methods.[25—28] The solvent effect is attributed to hydrogen bonding between the hydroxyl proton of the silanol and an electron pair of the solvent. In Table 2, the observed ^{29}Si NMR chemical shifts of triphenylsilanol in various solvents are shown. The solvent basicity varies from benzene to hexamethylphosphoric triamide. Some solvents that have high viscosity, high dielectric constant, and association are included for using with sydnone compounds. In this study, all of the chemical shifts are strongly dependent on solvent basicity (ranges > 5 ppm) and have upfield shifts of the ^{29}Si resonance with increasing solvent basicity. The chemical shifts of many solvents give an excellent linear correlation with Gutmann's donor number, as shown in Fig. 9. The coefficient of correlation (r) value is 0.99. It is possible to estimate the donor numbers of sydnone compounds from linear correlation in Fig. 9. The ^{29}Si NMR spectra in 3-propyl-4-ethylsydnone, 3-propylsydnone, and 3-butylsydnone give sharp peaks as well as other solvents above. The donor number of 3-propyl-4-ethylsydnone $(\delta\ ^{29}$Si/ppm $= -17.20)$ is estimated to be about $25._3$. Those of 3-propylsydnone (-16.57) and 3-butylsydnone (-16.67) are about $21._2$ and $21._8$, respectively. The donor number of 3-propyl-4-ethyl-

Table 1. Physycal Properties of Sydnone Compounds

		3-Propylsydnone[a]	3-Butylsydnone[a]	3-Propyl-4-ethylsydnone
ε (1 MHz)	25 °C	93.0	77.9	64.6
	40 °C	87.1	71.6	60.7
	60 °C	79.2	64.5	55.9
n_D	25 °C	1.499_8	1.493_8	1.472_0
	40 °C	1.493_8	1.487_8	1.466_0
	60 °C	1.484_8	1.479_8	1.457_6
$\rho/10^3$ kg m^{-3}	25 °C	1.161_6	1.115_2	1.068_4
	40 °C	1.148_9	1.103_4	1.054_3
	60 °C	1.132_3	1.088_3	1.035_3
η/cP	25 °C	10.3	11.3	11.2
	40 °C	6.2	6.3	6.3
	60 °C	3.5	3.3	3.2
E_η/kJ mol^{-1}		26.2	29.3	29.7

a) Ref. 9.

M. Handa et al.

Bull. Chem. Soc. Jpn., 70, No. 2 (1997)   319

Table 2. ^{29}Si NMR Chemical Shifts of Trimethylsilanol in Various Donor Solvents

No.	Solvent	DN[a]	$\Delta\ \delta$[b]
1	Benzene	0.1	−13.52
2	Acetic anhydride	10.5	−14.91
3	Dioxane	14.8	−15.81
4	Propylene carbonate	15.1	−15.67
5	Diethyl carbonate	16.0	−15.46
6	Acetone	17.0	−15.69
7	Ethyl acetate	17.1	−15.55
8	Methanol	(19)	−15.97
9	Diethyl ether	19.2	−16.20
10	Ethanol	(20)	−16.26
11	Acetic acid	(20)	−16.53
12	Tetrahydrofuran	20.0	−16.69
13	N,N-Dimethylformamide	26.6	−17.24
14	N-Methylpyrrolidinone	27.2	−17.52
15	N,N-Dimethylacetamide	32.1	−17.84
16	1-Buthanol	(29)	−17.39
17	Pyridine	33.1	−18.51
18	Hexamethylphosphoric triamide	38.8	−19.47

a) Ref. 15, values in parentheses have been obtained indirectly.
b) ^{29}Si NMR chemical shifts in ppm from external TMS.
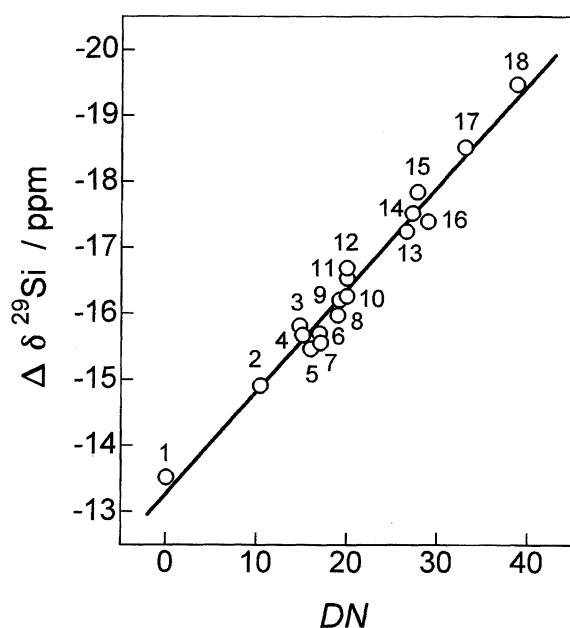
Fig. 9.   Plot of ^{29}Si NMR chemical shifts vs. donor number of the solvents. For explanation of 1—18 see Table 2.

sydnone is larger than those of 3-propylsydnone, 3-butyl-sydnone, and propylene carbonate. The large donor number allows it to increase in the solvation toward cations, which influences the solubility of the electrolytes.

Acceptor numbers of sydnone compounds are also obtained indirectly by ^{13}C NMR spectroscopic methods by way of the literature.[13—15] The general trend is a shift of the ^{13}C=O resonance signals to a lower field with increasing acceptor number, indicating an increasing polarization of the C=O double bond. The ^{13}C=O NMR chemical shifts of acetone in solvents with various acidities from hexane to methyl acetate

are shown in Table 3. Figure 10 shows a relationship between acceptor numbers and ^{13}C=O chemical shifts of acetone obtained in this study, which is a good correlation ($r = 0.94$) and enough to approximate acceptor numbers. The small irregularities of the relationship are presumably due to the fact that the sp^2 hybridized carbon atom is less shielded towards contact interaction with the solvents.[14] The ^{13}C chemical shifts of 3-propylsydnone, 3-butylsydnone, and 3-propyl-4-ethylsydnone are 1.04, 0.64, and −0.15 ppm, respectively. The line provides acceptor numbers of 3-propylsydnone, 3-butylsydnone, and 3-propyl-4-ethylsydnone, which decrease in that order, in the range 23—18. According to the value of the acceptor number, sydnone compounds should solvate toward anions as well as propylene carbonate.

Donor and acceptor numbers of 3-propylsydnone, 3-butylsydnone, and 3-propyl-4-ethylsydnone were reported as mentioned above. It was shown that both donor and acceptor numbers of sydnone compounds depend on the alkyl groups in the 3-, 4-positions of the sydnone ring. The donor

Table 3. ^{13}C=O NMR Chemical Shifts of Acetone in Various Acceptor Solvents

No.	Solvent	AN[a]	$\Delta\ \delta$[b]
1	Hexane	0.0	−4.46
2	Diethyl ether	3.9	−2.98
3	Tetrahydrofuran	8.0	−2.03
4	Benzene	8.2	−2.20
5	Hexamethylphosphoric triamide	10.6	−0.87
6	Dioxane	10.8	−0.91
7	Acetone	12.5	0.0
8	N,N-Dimethylacetamide	13.6	0.03
9	N,N-Dimethylformamide	16.0	0.49
10	Propylene carbonate	18.3	0.35
11	Acetonitrile	19.3	1.32
12	Dimethylsulfoxide	19.3	1.48
13	Chloroform	23.1	1.02
14	Ethanol	37.1	1.92
15	Methanol	41.3	3.35
16	Acetic acid	52.9	5.25
17	Water	54.8	9.47

a) Ref. 15. b) ^{13}C NMR chemical shifts in ppm referred to solvent acetone.
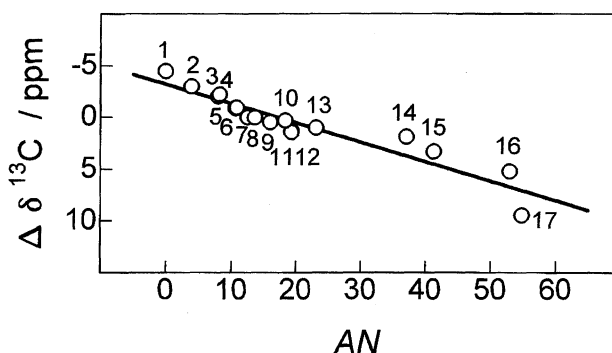
Fig. 10.   Plot of ^{13}C=O NMR chemical shifts vs. acceptor number of the solvents. For explanation of 1—17 see Table 3.

numbers lead to the sequence of the basicities of sydnone compounds, 3-propylsydnone < 3-butylsydnone < 3-propyl-4-ethylsydnone. Inversely, acceptor numbers lead to the sequence of the acidities of sydnone compounds, 3-propylsydnone > 3-butylsydnone > 3-propyl-4-ethylsydnone. The donor number tends to increase with lengthening of the chain of the alkyl substituents. It is suggested that the electron-donating alkyl group affects the sydnone ring system. The longer alkyl substituents would result in higher electron density of the sydnone ring. The positive charge of a sydnone ring system may be weakened by the electron-donor effect of alkyl groups. Thus the basicity of the electron-donor atom, which may be an oxygen atom, seems to be strengthened by the electron-donor effect of alkyl groups through the sydnone ring. On the contrary, the acceptor number tends to decrease with lengthening of the chain of the alkyl substituents. The acidities of the sydnone compounds are affected by the alkyl groups. This result seems reasonable upon considering the acceptor numbers of compounds that have an alkyl group, typically such as a series of alcohols[15] like methanol (AN=41.3), ethanol (AN=37.1), and isopropyl alcohol (AN = 33.5), etc.

In conclusion, the bulk physical properties of 3-propyl-4-ethylsydnone are elucidated at various temperatures. 3-Propyl-4-ethylsydnone will be expected to be a good solvent for the electrolytes as an alternative to propylene carbonate because of the high dielectric constant and very large dipole moment. The donor and acceptor numbers of 3-propylsydnone, 3-butylsydnone, and 3-propyl-4-ethylsydnone are estimated. The higher donor and acceptor numbers of 3-propyl-4-ethylsydnone indicate increasing in solvation toward both cations and anions more than those of many organic polar solvents. 3-Propyl-4-ethylsydnone must be superior in solvating toward cations to other 3-alkylsydnones and propylene carbonate. In addition, it is clear that both bulk physical properties and microscopic donor–acceptor properties of the sydnone compounds are definitely changed by the influence of alkyl substituent groups in the 3-, 4-positions of the sydnone ring. The substitution will make it possible to control the properties of sydnone compounds.

References

1) W. Baker and W. D. Ollis, *Q. Rev., Chem. Soc.*, **11**, 15 (1957).

2) F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964).

3) M. Ohta and H. Kato, "Non-benzenoid Aromatics," Academic Press, New York (1969), Vol. 1, Chap. 4, p. 117.

4) G. H. Schmid, *J. Mol. Struct.*, **5**, 236 (1970).

5) R. J. Lemire and P. G. Sears, *J. Chem. Eng. Data*, **22**, 376 (1977).

6) R. J. Lemire and P. G. Sears, *J. Solution Chem.*, **9**, 553 (1980).

7) Y. Sasaki and Y. Ishibashi, *Bull. Chem. Soc. Jpn.*, **63**, 1422 (1990).

8) Y. Sasaki, T. Koshiba, H. Taniguchi, and Y. Takeya, *Nippon Kagaku Kaishi*, **1992**, 140.

9) Y. Sasaki, I. Komiya, and M. Handa, *Bull. Chem. Soc. Jpn.*, **67**, 2571 (1994).

10) Y. Sasaki, K. Miyagawa, N. Wataru, and H. Kaido, *Bull. Chem. Soc. Jpn.*, **66**, 1608 (1993).

11) Y. Sasaki, H. Ohashi, S. Okahata, H. Kaido, K. Mori, and M. Handa, *Nippon Kagaku Kaishi*, **1993**, 1217.

12) E. A. Williams, J. D. Cargioli, and R. W. Larochelle, *J. Organomet. Chem.*, **108**, 153 (1976).

13) G. E. Maciel and G. C. Ruben, *J. Am. Chem. Soc.*, **85**, 3903 (1963).

14) U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).

15) V. Gutmann, *Electrochim. Acta*, **21**, 661 (1976).

16) L. B. Kier and D. Dhawan, *J. Pharm. Sci.*, **51**, 1058 (1962).

17) D. Dhawan and L. B. Kier, *J. Pharm. Sci.*, **53**, 83 (1964).

18) J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Organic Solvents," 4th ed, John Wiley and Sons, Inc., New York (1986).

19) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

20) R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 385 (1941).

21) E. G. Runwald and K.-C. Pan, *J. Phys. Chem.*, **80**, 2929 (1976).

22) J. O'M. Bockris and A. K. Reddy, "Modern Electrochemistry," Prenum Press, New York (1970), Vol. 1, p. 152.

23) E. Grundwald, *J. Am. Chem. Soc.*, **108**, 5719 (1986).

24) S. Glasstone and D. Lewis, "Elements of physical Chemistry," D. Van Nostrand Co. Inc., Maruzen Co., Ltd., Tokyo (1960), p. 149.

25) P. Spaziante and V. Gutmann, *Inorg. Chim. Acta*, **5**, 273 (1971).

26) R. H. Erlich, R. Roach, and A. I. Popov, *J. Am. Chem. Soc.*, **92**, 4989 (1970).

27) R. H. Erlich and A. I. Popov, *J. Am. Chem. Soc.*, **93**, 5620 (1971).

28) V. Gutmann and R. Schmid, *Monatsh. Chem.*, **100**, 2113 (1969).