On the Viscosity Correction of Line Width in ^{35}Cl NMR

Tadashi Sugawara, Masako Yudasaka,† Katsuo Takahashi,†† Reita Tamamushi,††
Hiizu Iwamura,* and Tsunetake Fujiyama**
Institute for Molecular Science, Myodaiji, Okazaki 444
†*Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240*
††*The Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama 351*

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From the view point of the effect of viscosity, the ^{35}Cl NMR line widths and the electrical conductivities were compared for the aqueous solutions of sodium chloride in the presence of polyethylene glycol. A criterion was proposed on the validity of the viscosity correction treatment for the NMR line width.

The line width of ^{35}Cl NMR, $\Delta\nu_{1/2}$, is governed by quadrupolar relaxation, and it is proportional to the product of the square of the quadrupolar coupling constant, e^2Qq, and the correlation time, τ_C, for molecular reorientation,

$$\Delta\nu_{1/2} \propto (e^2Qq)^2\tau_c. \tag{1}$$

In order to obtain information about the change in the field gradient, q, around a ^{35}Cl nucleus and to utilize the line width as a probe for investigating the condition of the nearest neighbours around a ^{35}Cl ion, the effect of τ_C on the line width has been eliminated effectively by dividing the line width by the macroscopic viscosity using the Einstein-Stokes relation, $\tau_c = 4\pi a^3\eta/3kT$, where a is an ion radius, η is viscosity, and $3kT$ is thermal energy.[1,2] The validity and limitation of this viscosity correction treatment, however, have to be examined carefully, because the viscosity η should be microscopic in nature instead of macroscopic. Here we wish to present an example to discuss this problem and show a criterion on the validity of this viscosity correction treatment for the line width.

As a measure for the microscopic viscosity, we focus our attention on the electrical conductivity, κ, because it is well known that this relationship holds between the electrical conductivity and viscosity.

$$\kappa\eta = \text{constant}, \tag{2}$$

so far as Stokes' law is satisfied for a slowly moving sphere in a liquid. It is also known that this simple relation is valid only when we use the microscopic viscosity for η.[3,4]

Aqueous solutions of sodium chloride (0.1 mol kg^{-1}) in the presence of polyethylene glycol (PEG) with various molecular weights were studied, since the electrical conductivity of aqueous sodium chloride was determined in these solutions, the macroscopic viscosities of which range from 0.9 to 138 cP (1 cP$=10^{-3}$ Pa s).[5] The composition of the solution, macroscopic viscosity, electrical conductivity, Walden product, and ^{35}Cl line width are summarized in Table 1. The results were quite straightforward. It is noticeable that both $\Delta\nu_{1/2}$ and κ^{-1} do not correlate with the macroscopic viscosity, which is illustrated in Fig. 1. These results arise from the fact that Eqs. 1 and 2 can be satisfied only for microscopic viscosity. A reasonably good linear correlation was found, on the other hand, in the $\Delta\nu_{1/2}$ against κ^{-1} plot of Fig. 2. This result indicates that $\Delta\nu_{1/2}$ and κ^{-1} are governed by the same physical quantity, namely, microscopic viscosity, although they correspond to different dynamical motions, namely, rotational and translational ones, respectively. It is also noticeable in Fig. 1 that a linear correlation could be recognized between $\Delta\nu_{1/2}$ and κ, or between κ^{-1} and η, for the entries 1, 2, and 6. The Walden products of these three are close to 1.0.

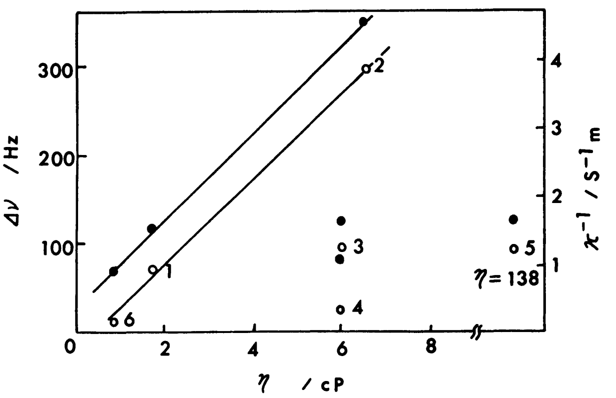

Fig. 1. Plots of the ^{35}Cl line width (○), and the inverse of electrical conductivity (●), *vs.* macroscopic viscosity η.

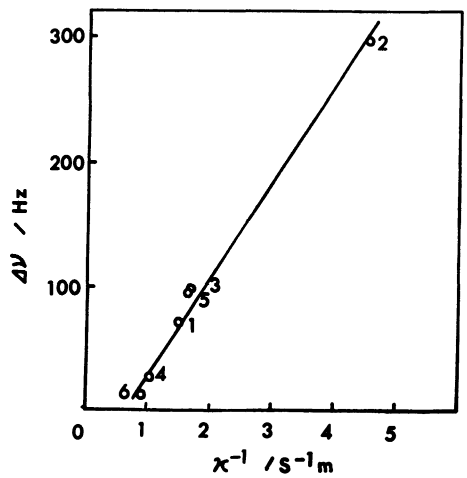

Fig. 2. The correlation between ^{35}Cl line width $\Delta\nu_{1/2}$ and the inverse of electrical conductivity κ^{-1}.

Based upon the above results, we propose a criterion to judge whether macroscopic viscosity can be used for the correction of line width in place of the microscopic one. The Walden product for a certain concentration of aqueous sodium chloride is to be determined

** Deceased November 18, 1981.

Table 1. The viscosity, electrical conductivity, reciprocal conductivity, and ^{35}Cl line width of sodium chloride in aqueous polyethylene glycol

Entry	Polymers	Concn of PEG/wt%	η/cP	κ/S m^{-1}	κ^{-1}/S^{-1} m	$\Delta\nu$/Hz	$\eta\kappa$
1	PEG 200	20	1.786	0.647	1.546	71	1.15
2	PEG 200	50	6.577	0.220	4.545	298	1.45
3	PEG 4000	20	6.058	0.608	1.645	96	3.68
4	PEG 20000	5	5.98	0.932	1.073	25	5.57
5	PEG 20000	20	138	0.605	1.653	95	83.5
6	none	0	0.890	1.066	0.938	12	0.949

a) Concentration of sodium chloride was 0.1 mol kg^{-1} at 25 °C.

from conductivity and viscosity measurements in the absence of additives. If the Walden product of aqueous sodium chloride in the presence of additives (PEG in the present case) is close to the former value, microscopic viscosity can be replaced with macroscopic one in this solution. The idea obtained here would be quite useful for analyzing NMR line width on ionic species of quadrupolar nuclei.

Experimental

Polyethylene glycol (PEG 200, 4000, 20000) were supplied by Wako Pure Chemical Industries Ltd.[3] Sodium chloride was purchased as a special grade and used without further purification.

^{35}Cl FT-NMR was recorded on Varian's FT 80A in the same condition as described elsewhere.[2] The temperature of the probe was kept at 25±0.5 °C by the temperature variation accessary.

References

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