Studies of Polymers by Nuclear Magnetic Resonance at Magic Angle Rotation. II. Characterization of Ion-Exchange Resins by High Resolution Nuclear Magnetic Resonance

D. Doskočilová and B. Schneider*

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia. *Received August 25, 1971*

ABSTRACT: It is shown that the broadening of nmr lines caused by differences of magnetic susceptibility in liquids containing suspended solid particles may be eliminated by measurement with rotation about an axis inclined at the angle 54.7° with respect to the stationary magnetic field direction, at spinning speeds of a few hundred cycles per second; a high-resolution spectrum of the liquid phase can thus be obtained. The method is illustrated by the example of styrene–divinylbenzene cation exchangers in equilibrium with water and with methanol.

It is well known that nmr spectra of sulfonated styrene–divinylbenzene cation-exchange resins in the H$^+$ form [further, styrene–DVB resins (H$^+$)] in equilibrium with water exhibit separate signals of protons in water molecules outside and inside the resin particles.[1,2] The chemical shift between these two lines is a measure of the content of water in the resin phase and is currently used for resin characterization. A further parameter which might be of use for characterization of kinetic processes in ion exchangers, the width of the nmr bands,[3] cannot be quantitatively determined from these spectra because the width of the lines is modified by differences of magnetic susceptibility in the heterogeneous sample. In this paper, we wish to show that by magic angle rotation it is possible to eliminate the influence of the heterogeneity of the medium and to investigate the actual shape of the bands as determined by the dynamics of diffusion and chemical processes.

Relation between Magnetic Susceptibility and Nmr Spectra of Heterogeneous Systems

In measurements of high-resolution nmr spectra of liquids containing dispersed particles, nmr lines are broadened due to local perturbing magnetic fields which are generated by magnetic moments induced in the solid particles.

A macroscopic solid particle i of spherical shape (Figure 1) generates at the site of the liquid molecule j a perturbing magnetic field H_{ij}, of magnitude[4]

$$H_{ij} = (\mu_i/r_{ij}^3)(1 - 3\cos^2\vartheta_{ij})$$

where μ_i is the total magnetic moment of the solid sphere (supposed to be localized in its center), r_{ij} is the distance of the liquid molecule j from the center of the sphere i, and ϑ_{ij} is the angle between the vector $\mathbf{r}_{ij}$ and the static field direction $\mathbf{H}_0$. The magnetic moment μ_i of a solid sphere of magnetic susceptibility χ_v, immersed in a medium of susceptibility χ_{v0}, is given by the relation

$$\mu_i = (4/3)\pi R^3\Delta\chi H_0$$

where $\Delta\chi = \chi_v - \chi_{v0}$, R is the radius of the sphere, and H_0 is the static magnetic field.

If the solid sphere is of macroscopic dimensions, then the motion of a liquid molecule with respect to this sphere may be neglected. The interaction of the magnetic field of the solid sphere with the nuclear spin carried by the liquid molecule has in this case a form similar to the dipole–dipole interactions in solids. For a liquid molecule at a distance r_{ij} from the center of the solid sphere, the signal would be split into a doublet with a line spacing

$$\Delta\nu = (8/3)\pi(R^3/r_{ij}^3)\Delta\chi H_0(1 - 3\cos^2\vartheta_{ij})$$

By integration of the angular factor over all orientations ϑ_{ij}, we obtain a function analogous to the "powder function" of polycrystalline materials,[4] with maxima at ± 1. With increasing r_{ij}, the number of molecules in layer j increases in proportion to r_{ij}^2. The resulting width of the nmr signal of a liquid layer of thickness $(r_{j_{\max}} - R)$, surrounding a sphere of radius R, will approximately be given by the expression

$$2\Delta\nu_{1/2} = \frac{2\mu_i}{R^3}\sum\left(\frac{R}{r_{ij}}\right)^3 N_j$$

where N_j is the fraction of molecules in layer j. The expression $2\mu_i/R^3$ corresponds to the line width for the liquid layer directly on the surface of the solid sphere. This limiting (maximum) line width has at 60 Mcps the value $2\Delta\nu_{1/2\mathrm{lim}} = 500\Delta\chi \times 10^6$. At any larger content of the liquid phase, as well as at any other geometrical arrangement of the liquid and the solid spheres, the line width will be smaller than $2\Delta\nu_{1/2\mathrm{lim}}$.

As already stated, the interaction between the magnetized sphere and the surrounding liquid is characterized by similar relations, as the dipole–dipole interactions in solids, and for this reason it can be eliminated by rotation about an axis inclined by the magic angle (54.7°) with respect to H_0,[5,6] as long as the frequency of this rotation is comparable with or larger than the line width in the static spectrum. The value $2\Delta\nu_{1/2\mathrm{lim}}$ thus determines the minimum frequency sufficient for elimination of line broadening due to differences of magnetic susceptibility. For most substances of current interest, the values of $\Delta\chi \times 10^6$ are of the order of a unit or smaller, so that the necessary rotation frequencies are expected to be of the order of several hundred cycles per second.

---

(1) J. E. Gordon, *J. Phys. Chem.*, **66**, 1150 (1962).

(2) J. P. de Villiers and J. R. Parish, *J. Polym. Sci., Part A* **2**, 1331 (1964).

(3) A. Daříčková, D. Doskočilová, S. Ševčík, and J. Štamberg, *ibid., Part B*, **8**, 259 (1970).

(4) A. Lösche, "Kerninduktion," Deutscher Verlag der Wissenschaften, Berlin, 1957.

(5) E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature (London)*, **182**, 1659 (1958); **183**, 1802 (1959).

(6) I. J. Löwe, *Phys. Rev. Lett.*, **2**, 285 (1959).

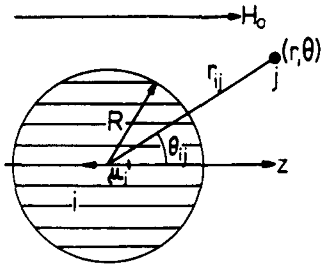

Figure 1.

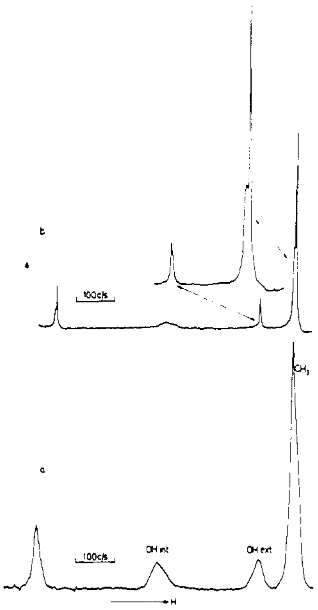

Figure 2. Nmr spectra of a styrene–DVB resin (H^+) in methanol: (a) sample rotated about axis perpendicular to H_0; (b) sample rotated about axis inclined at 54.7° with respect to H_0. (Band at lowest field is a modulation band used for calibration.)

Table I
Line Widths of Liquid Dispersed between Spheres of Cross-Linked Polystyrene[a]

		$\delta\nu$, cps			
		Perpendicular axis		Axis at magic angle	
Substance	$\Delta\chi \times 10^6$	Static	Rotated	Static	Rotated
Acetonitrile	0.210	130	67	120	4.1
Benzene	0.060			58	3.3

[a] 16% DVB, 160–100 mesh.

Experimental Section

All nmr spectra of the studied solid–liquid dispersions were measured on the JNM-3-60 (Jeolco) nmr spectrometer at 60 Mcps, with an apparatus described in previous papers of this series.[7–9] We used hollow Teflon turbines of 3-mm i.d. These could spin smoothly in the frequency range 30–3000 cps. Contrary to the magic angle rotation experiments with solids, described in the preceding paper,[9] mechanical properties of the turbines are not so critical in these experiments, because it is not necessary to work at extremely high spinning frequencies. However, in the construction of the apparatus great care had to be taken in order to preserve the maximum possible field homogeneity. Even so, resolution is always somewhat worse in magic angle rotation experiments, as compared to conventional measurements, because of the inclination of the measuring cell in the pole gap. With pure liquids (benzene, methanol, hexamethyldisiloxane), line widths of 1.5 cps were obtained in our Teflon cells (resolution in conventional measurement 0.6 cps).

The measured polystyrene spheres were cross-linked with 16% divinylbenzene and a fraction with sphere size 100–160 mesh was used. Sulfonated polystyrene resins were prepared by sulfonation of styrene–divinylbenzene copolymers of various degree of cross-linking, swollen in dichloroethane. Fractions with sphere size 250–500 mesh were measured. In the experiment with methanol, the commercial Zerolit 225 with nominal 8% divinylbenzene was used, with a sphere size 52–100 mesh.

Results and Discussion

In order to demonstrate that by magic angle rotation it is actually possible to eliminate the line broadening caused by differences of magnetic susceptibility in heterogeneous medium, we have measured the spectra of a system composed of spheres of cross-linked polystyrene immersed in acetonitrile ($\Delta\chi = 0.210 \times 10^{-6}$) and in benzene ($\Delta\chi = 0.060 \times 10^{-6}$). As seen from Table I, in both cases line width can be reduced to 3 cps by magic angle rotation, although in conventional measurement with rotation about a vertical axis the line widths are much larger and different in the two cases. It is remarkable that in this system, even after line-width reduction by magic angle rotation, benzene exhibits only a single peak, although the cross-linked polystyrene used evidently swells in benzene. From this it follows that the chemical shift of benzene inside and outside the spheres is less than 3 cps.

A second example is shown in Figure 2, exhibiting the spectrum of the system methanol–styrene–DVB resin (H^+). In conventional measurement, this system exhibits three bands in the nmr spectrum, corresponding to the CH_3 group and to OH groups of methanol inside and outside the spheres. All these lines are of comparable width. By magic angle rotation, the bands of the CH_3 groups and of the OH group in external methanol reduce again to *ca.* 3 cps, whereas the OH group band in internal methanol remains very broad. The CH_3 band is split into two components with a chemical shift difference of about 3 cps. From the band area ratio of internal and external OH, and from the ratio of the two components of the CH_3 band, it is evident that the line at higher field corresponds to CH_3 group in internal methanol and the band at lower field to external methanol. The fact that the CH_3 line is equally narrow both for molecules inside and outside the resin spheres indicates that the broadening of the OH band of internal methanol can only be caused by some kinetic process; in our case, this is evidently the exchange process $CH_3OH \longleftrightarrow CH_3OH_2^+$.

A typical spectrum of the system water–styrene–DVB resin (H^+) is shown in Figure 3. We see that similarly as with methanol, quite a narrow line (about 3 cps) of external water is obtained, whereas the line of internal water is somewhat wider. We measured a series of samples with a different degree of cross-linking, and from the results summarized in Figure 4 it is seen that with increasing degree of cross-linking the chemical shift between the lines of internal and external water increases, the width of the line of external water remains constant, and the width of the line of internal water increases very rapidly. This indicates that the degree of cross-linking affects not only the amount of water entering the resin, which deter-

---

(7) D. Doskočilová and B. Schneider, *Chem. Phys. Lett.*, **6**, 381 (1970).

(8) J. Babka, D. Doskočilová, H. Pivocová, Z. Růžička, and B. Schneider, "Magnetic Resonance and Related Phenomena," I. Ursu, Ed., Publishing House of the Academy, Bucharest, Romania, 1971, pp 785–788.

(9) B. Schneider, H. Pivcová, and D. Doskočilová, *Macromolecules*, **5**, 120 (1972).

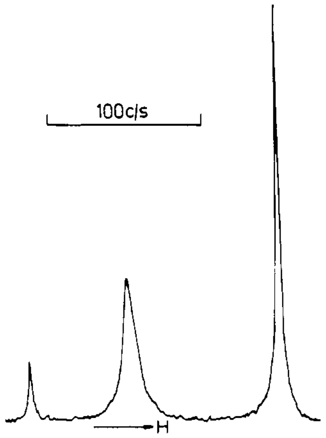

Figure 3. Nmr spectrum of a styrene–DVB resin (H^+) in water; sample rotated about an axis inclined at 54.7° with respect to H_0. (Band at lowest field is a modulation band used for calibration.)

mines the chemical shift between the two lines, but also the dynamics of the exchange reactions in the solid phase.

If we assume that the broadening of the internal water line is determined by the velocity of the exchange reaction $H_3O^+ + H_2O \longleftrightarrow H_2O + H_3O^+$, we can determine the mean lifetime of the molecules H_3O^+ and H_2O in the resin phase, $(\tau_{H_3O^+} + \tau_{H_2O})$, from the line width using the relation[10,11]

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{T_2''} = \frac{1}{T_2'} + p_{H_3O^+}{}^2 p_{H_2O}{}^2(\omega_{H_3O^+} - \omega_{H_2O})^2(\tau_{H_3O^+} + \tau_{H_2O})$$

where $1/T_2$ is the experimentally determined width of the line (assumed to be Lorentzian) at half maximum height in radians per second, $1/T_2''$ is the component of this line width corresponding to the exchange process, $1/T_2'$ is the component corresponding to all other relaxation mechanisms, including field inhomogeneity, $p_{H_3O^+}$ and p_{H_2O} are the mole fractions of the corresponding molecules in the water phase inside the resin, fulfilling the relation $p_{H_2O} + p_{H_3O^+} = 1$, and $(\omega_{H_3O^+} - \omega_{H_2O}) = 2\pi(\nu_{H_3O^+} - \nu_{H_2O})$ is the chemical shift between the signals of the pure hypothetical forms H_2O and H_3O^+ in radians per second.

It is well known that the measured chemical shift between the signals of internal and external water is a linear function of molality,[2] *i.e.*, of the concentration of H_3O^+ ions, similarly as in solutions of strong monobasic acids. From the values of molality, defined as the ratio of weight capacity and swelling ratio and given in milliequivalents per grams of H_2O in the resin phase, $p_{H_3O^+}$ can be calculated. By extrapolation of the chemical shift dependence on $p_{H_3O^+}$, the value of $\nu_{H_3O^+} - \nu_{H_2O} = 16.5$ ppm can be obtained. Using these values, we obtain for the series of measured resins (Figure 4) a mean lifetime $(\tau_{H_3O^+} + \tau_{H_2O})$ increasing with cross-linking from 0.95×10^{-4} sec (4.2% DVB) to 1.1×10^{-4} sec (10.3% DVB), *i.e.*, only very little. The broadening of the internal water line, rapidly increasing with cross-link density, is seen to be caused in this case primarily by the change of the populations $p_{H_3O^+} + p_{H_2O}$, in consequence of the lower content of water in the more strongly cross-linked resins.

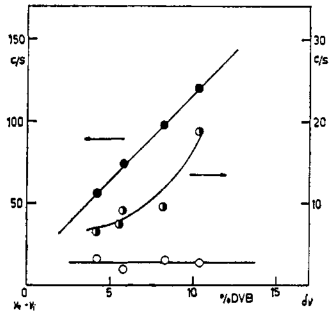

Figure 4. Nmr parameters of styrene–DVB resins (H^+) in water at different degrees of cross-linking; $\nu_e - \nu_1$ = the chemical shift between signals of water outside and inside resin sphere and $\delta\nu$ = the line width: (○) external water, (◑) internal water.

Conclusions

Previous studies of ion-exchange resins by high-resolution nmr spectroscopy were practically limited to styrene–DVB resins swollen with water, where, thanks to a fortuitous near equality of the magnetic susceptibilities of resin and of water, line widths are not intolerably broad even in conventional measurements. The method of magic angle rotation makes it possible to use nmr spectroscopy for the study of any heterogeneous system, disregarding the magnetic susceptibility of the components, as demonstrated on the system styrene–DVB resin–methanol. It makes it possible to utilize, in addition to chemical shift values, line width parameters for the characterization of the dynamics of processes proceeding in such heterogeneous systems.

---

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 222.

(11) S. Meiboom, Z. Luz, and D. Gill, *J. Chem. Phys.*, 27, 1411 (1957).