

NMR STUDY OF INDUCED DIELECTRIC ALIGNMENT IN PURE AND BINARY LIQUIDS

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ABSTRACT

The nmr spectra of polar liquids may be affected by application of a strong external electric field. Dipolar molecules are slightly aligned by this field and the nuclear quadrupole couplings and the direct spin-spin dipolar interactions may no longer be averaged to zero. The proton spectrum of *p*-nitrotoluene, modified by dipolar induced couplings, is given as an example. Quadrupolar electric field effects have been measured in the ^{14}N spectra of a series of pure nitriles and nitrocompounds. From these spectra the molecular alignment, induced by the electric field, has been obtained.

Alignments of both polar and nonpolar molecules have been detected in the nmr spectra of nitrobenzene-deuterobenzene mixtures. If the polar molecules are aligned by the electric field, the orientation is transferred to the nonpolar particles.

Theoretical expressions for the alignments in pure and binary liquids are discussed. Short range interactions between the molecules, giving rise to angular correlations, turn out to be important. This is particularly apparent in the case of the alignment of nonpolar molecules in mixtures.

INTRODUCTION

When an external electric field is applied to a polar liquid the molecular dipoles will tend to align themselves along this field. In competition with this effect the thermal motion disturbs the ordering but on the average the molecules will preserve a preferential orientation. As a result the nmr spectrum of the liquid may be modified because molecular tensor properties, which have no influence on the spectrum of an isotropic liquid, become manifest. Well known examples are the direct dipole-dipole interactions between nuclear spins and the quadrupole interaction between a nucleus and the inhomogeneous electric field originating from the surrounding electrons and nuclei.

The possibility of observing the effect of molecular alignment, induced by an electric field, in nuclear magnetic resonance phenomena was mentioned as early as 1954 by Hahn¹. Since then several attempts²⁻⁴ have been made to detect dipolar-induced electric field effects in nmr spectra. Most

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of these experiments suffered from an insufficient control of the electric currents through the sample. By the application of a special kind of electrodes, electro dialysis membranes, these difficulties could be overcome and recently quadrupolar and dipolar electric field effects have been detected^{5,6}.

From the nmr spectra the molecular alignment, induced by the applied electric field, can be calculated. Theoretical analysis of this quantity shows that the average orientation of the molecules does not only depend on the molecular dipole moment and the molecular polarizability but also on the angular correlations between the molecules in the liquid⁷⁻⁹.

In 1963 it was discovered by Saupe and Englert¹⁰, that nematic liquid crystals can provide an homogeneous anisotropic environment for solute molecules to be studied by nmr. This technique has been widely applied in subsequent years. The method is based on the fact, that in nematic solvents, the intermolecular forces are strongly anisotropic, imposing a preferential orientation on the solute molecules. One may wonder if, in an analogous way, the anisotropic character of the intermolecular forces in a normal liquid can become manifest. Therefore we have investigated the possibility of detecting the molecular alignment, induced by an electric field, of nonpolar molecules dissolved in a polar solvent. Transfer of the alignment from the polar to the nonpolar component would provide a direct experimental method to probe the angular correlations between the two different molecular species. Before discussing the experimental details and results we shall, for convenience sake, first summarize the basic equations needed for the interpretation of the spectra.

Let us assume the applied electric field E to be parallel to the static magnetic field H_0 . For a molecule in which the z -axis has been chosen along the molecular electric dipole moment, the induced dipolar splitting in hertz is given by

$$D_{ij}^{dd} = -\gamma_i \gamma_j (\hbar/2\pi) \langle 3 \cos^2 \theta - 1 \rangle_E [(\Delta z_{ij}^2 - \frac{1}{2} \Delta x_{ij}^2 - \frac{1}{2} \Delta y_{ij}^2) r_{ij}^{-5}] \quad (1)$$

Here $\Delta z_{ij} = z_i - z_j$, etc.; x_i , y_i and z_i are the coordinates of the i th nucleus in the molecular frame; θ is the angle between the magnetic field and the molecular electric dipole moment. The brackets $\langle \dots \rangle_E$ indicate an ensemble average over all molecular orientations and positions in the sample in the presence of an electric field.

The quadrupolar line splitting for a nucleus with $I = 1$ can be shown to be

$$D^Q = \frac{3}{4} \frac{e^2 q Q}{h} \langle 3 \cos^2 \theta - 1 \rangle_E \quad (2)$$

Again θ is the angle between the magnetic field and the molecular dipole moment. eq is the field gradient at the site of the nucleus in the direction of the molecular z -axis, i.e. the direction of the electric dipole moment.

In this paper we shall give examples of quadrupolar line splittings induced by an external electric field, obtained for some organic nitrocompounds and aliphatic nitriles. The experimental results are compared with predictions from the local field models of Lorentz, Onsager and Scholte. The influence of nonaveraged dipolar couplings in the proton spectrum of *p*-nitrotoluene will also be demonstrated. Furthermore it is shown that in a solution of

benzene in nitrobenzene the alignment is transferred from the polar to the nonpolar molecules. A brief discussion of the interpretation of the alignment, in terms of a statistical mechanical theory, will be given.

EXPERIMENTAL RESULTS

A representative example of the quadrupolar line splitting induced by an external electric field is reproduced in *Figure 1*. In the upper part the ^{14}N resonance of nitromethane is given. When an electric field is applied this line splits into a doublet (*Figure 1b*). The line splitting amounts to 117 Hz at 39kV cm^{-1} ($\text{E}\parallel\text{H}$). The central peak in *Figure 1c* appears when the r.f. field is increased. It is attributed to a double quantum transition. Under these conditions the neighbouring lines are partly saturated.

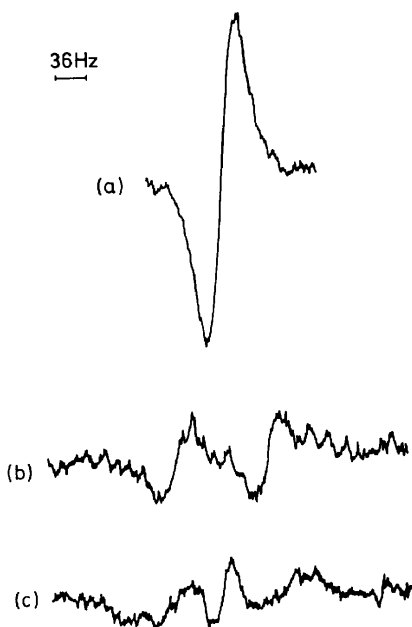


Figure 1. ^{14}N nmr spectrum of nitromethane, without (a) and with (b) an applied electric field. The central peak in (c) is attributed to a double quantum transition

The influence of an electric field on the proton spectrum of *p*-nitrotoluene dissolved in nitrobenzene is demonstrated in *Figure 2*. Again the upper part displays the spectrum, when no electric field is present. The peaks in the low field multiplet, caused by the ring protons, tend to shift towards each other under the influence of the electric field (compare *Figures 2a* and *b*). The absorption at high field, originating from the *p*-methyl group, splits into a triplet. In the presence of an electric field the high field part of the low field multiplet is somewhat broadened. This is due to the direct dipole-dipole

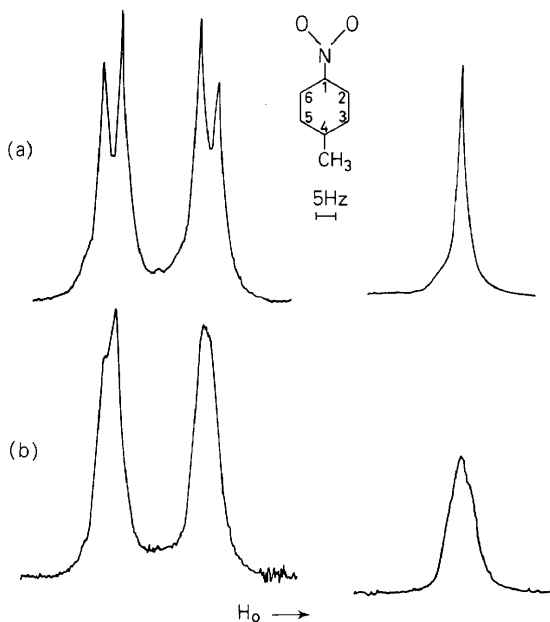


Figure 2. Proton spectrum of *p*-nitrotoluene, dissolved in deuterionitrobenzene, without (a) and with (b) an applied electric field (56.4 kV cm^{-1}). The high and the low field of the spectra have been recorded with different output levels

interactions between the methyl group and the ring protons 3 and 5 as has been demonstrated by a decoupling experiment. If the 3- and 5- ring protons are decoupled the triplet character of the methyl resonance is more pronounced (see Figure 3).

We have also detected the transfer of alignment from the polar to the nonpolar component in a mixture. When a mixture of 79.5 mole per cent nitrobenzene and 20.5 mole per cent perdeuterobenzene is exposed to an electric field of 55.3 kV cm^{-1} the deuterium absorption of the benzene splits into a doublet as is demonstrated in Figure 4. The experiments have been performed under the same conditions as the dipolar induced electric field experiments, i.e. the same precautions to obtain a sufficiently homogeneous electric and magnetic field have been taken. It should be noted that these

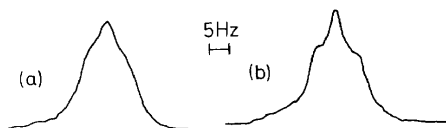


Figure 3. The methyl group resonance of *p*-nitrotoluene in the presence of an electric field, without (a) and with (b) ring protons 3 and 5 decoupled

splittings can easily be masked by the occurrence of double quantum transitions if the intensity of the r.f. field is too high.

When the quadrupole coupling constants are known the alignment $\langle 3 \cos^2 \theta - 1 \rangle_E$ can be determined from the induced quadrupolar line splittings. The alignments of a series of compounds are summarized in Table I.

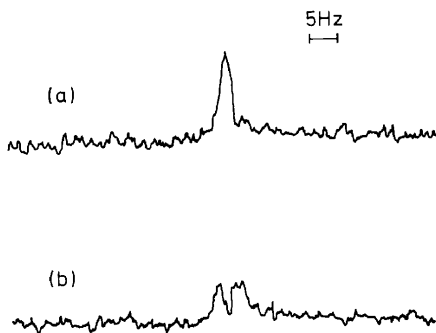


Figure 4. ^2D nmr spectrum of deuterobenzene, dissolved in nitrobenzene, (a) without, (b) with an applied electric field (55.3 kV cm^{-1} , $T = 25^\circ\text{C}$)

The quadrupolar line splitting of the ^2D nmr signal of the deuterobenzene is given by

$$D^Q = \frac{3}{4} \frac{e^2 q Q}{h} \langle 3 \cos^2 \theta' - 1 \rangle_E \frac{1}{2} (3 \cos^2 \gamma - 1) \quad (3)$$

θ' is the angle between the axis perpendicular to the molecular plane and the static magnetic field; γ is the angle between this axis and the principal axis of the electric field gradient at the ^2D nucleus. Assuming that this axis lies along the C—D bond, we have $\gamma = 90^\circ$. Substituting $(e^2 q Q/h) ^2\text{D} = 193 \text{ kHz}$ (from solid state¹¹) into equation 3 we obtain for the alignment of the nonpolar component at 25°C and 55.3 kV cm^{-1}

$$\langle 3 \cos^2 \theta' - 1 \rangle_E = \pm 5 \times 10^{-5}.$$

In addition, the alignment of the polar component, nitrobenzene, has been measured from the line splitting of its ^{14}N nmr signal. With $(e^2 q Q/h) ^{14}\text{N} = 0.95 \text{ MHz}^3$ we obtain at the same field strength and temperature

$$\langle 3 \cos^2 \theta - 1 \rangle_E = 5.7 \times 10^{-4}$$

It is noticed that the alignments $\langle 3 \cos^2 \theta - 1 \rangle_E$ of the polar component and $\langle 3 \cos^2 \theta' - 1 \rangle_E$ of the nonpolar component represent ensemble averages of the liquid mixture instead of those of the pure liquid.

Table 1. Comparison of experimental and theoretical alignments, calculated in terms of local field models

Substance	Formula	m	ϵ	n	$\langle 3 \cos^2 \theta - 1 \rangle_E / (E^M)^2 \times 10^8$ (e.s.u.)				
					Experimental	Lorentz	Onsager	Scholte	
Nitrobenzene	$C_6H_5NO_2$	4.1 ^a	34.8 ^f	1.55 ^f	1.94	19.7	0.59	0.35	
Nitromethane	CH_3NO_2	3.5 ^a	35.3 ^b	1.38 ^b	0.72	14.8	0.33	0.30	
Nitroethane	$C_2H_5NO_2$	3.7 ^a	27.7 ^b	1.39 ^b	0.60	10.4	0.39	—	
1-nitropropane	$C_3H_7NO_2$	3.72 ^a	23.1 ^b	1.40 ^b	0.51	7.6	0.39	—	
2-nitropropane	$(CH_3)_2CHNO_2$	3.73 ^a	25.1 ^b	1.40 ^b	0.64	8.7	0.39	—	
1-nitrobutane	$C_4H_9NO_2$	3.58 ^c	—	1.41 ^f	0.57	—	0.34	—	
1-nitropentane	$C_5H_{11}NO_2$	3.52 ^c	—	1.40	0.51	—	0.33	—	
Acetonitrile	CH_3CN	3.94 ^a	36.2 ^e	1.35 ^e	0.46	19.6	0.42	0.30	
Propionitrile	C_2H_5CN	4.00 ^a	28.6 ^e	1.37 ^e	0.43	12.9	0.43	—	
Isobutyronitrile	$(CH_3)_2CHCN$	4.0 ^a	20.4 ^d	1.37 ^d	0.47	5.1	0.42	—	
Chloroacetonitrile	$ClCH_2CN$	3.0 ^a	—	1.42 ^d	0.31	—	—	—	
Chloroacrin	Cl_3CNO_2	1.88 ^a	7.1 ^d	1.46 ^d	0.09	0.24	0.09	0.09	

^a Smyth, C. F., *Dielectric Behavior and Structure*, McGraw Hill, New York (1955).

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^d Mansingh, K. and Mansingh, A., *J. Chem. Phys.*, **42**, 2503 (1965).

^e *Ibidem*, **41**, 827 (1964).

^f *Handbook of Physics and Chemistry*, The Chemical Rubber Co., 48th edition (1967-1968).

INTERPRETATION OF THE RESULTS

(a) Pure liquids

We will now try to interpret the experimental values of the dielectric alignment for pure polar liquids in terms of molecular properties. Using Boltzmann statistics one can show that

$$\langle 3 \cos^2 \theta - 1 \rangle_E = \frac{2}{15} (pE_{\text{loc}}/kT)^2 \quad (4)$$

p is the effective molecular dipole moment in the liquid and E_{loc} is the local electric field in the liquid acting on a molecule. It is well known, that E_{loc} may differ considerably from the applied electric field. Several local field models have been developed to account for the dielectric properties of liquids, i.e. of Lorentz¹², Onsager¹³ and Scholte¹⁴.

Comparison with the experimental results in *Table 1* shows, that in the Lorentz model the alignments are predicted too high by about one order of magnitude. This inadequacy of the Lorentz model is in line with other experimental results. For instance dipole moments, calculated from measurements of the dielectric constant on the basis of this model are known to be erroneous.

The local field model of Onsager¹³ yields better agreement between theory and experiment (see *Table 1*), although the predicted values for nitrocompounds are too low. The failure of Onsager's model may in several instances be ascribed to the entire neglect of short-range interactions between the molecules.

Onsager's theory in its original form applies only to spherical dipoles. Extension to nonspherical molecules was proposed by Scholte¹⁴. For some liquids of *Table 1* the alignments according to the Scholte model¹⁵ have been calculated. The correspondence with experiment is disappointing.

In the following paragraphs the results of a statistical mechanical theory of the alignment are discussed. As expected, angular correlations between the molecules influence the experimental data. Let us consider a system consisting of nonpolarizable dipolar molecules. Taking the ensemble average of such a system we obtain for the alignment⁷⁻⁹

$$\begin{aligned} \langle 3 \cos^2 \theta_k - 1 \rangle_E = & \frac{2}{15} \left(\frac{mE^e}{kT} \right)^2 \left\{ 1 + \frac{1}{2}(N-1) \langle 3 \cos^2 \theta_{ki} - 1 \rangle_0 \right. \\ & + \frac{3}{2}(N-1)(N-2) \langle \cos \theta_{ki} \cos \theta_{kj} \rangle_0 \\ & \left. - \frac{1}{2}(N-1)(N-6) \langle \cos \theta_{ij} \rangle_0 \right\}. \end{aligned} \quad (5)$$

m is the permanent dipole moment, E^e the externally applied field; θ_{ki} is the angle between the electric dipole moments of molecules k and i . The brackets $\langle \dots \rangle_0$ represent an average over all molecular positions and orientations in the liquid in absence of an applied electric field. This formula demonstrates that the alignment is not only determined by the molecular dipole moment and by the externally applied electric field but also by two and three particle correlations between the molecules, which exist in the unperturbed liquid.

Numerical evaluation of the right hand side of equation 5 is not possible, however, because the two and three particle correlation functions are unknown for liquids. Moreover, in the present case the interpretation of the

averages is complicated by correlations between particles which are at macroscopic distances, due to the long range dipole-dipole interactions.

In order to simplify the interpretation of the averages one usually tries to separate these long range contributions. The remaining integrals, only depending on short range interactions, are a measure of the local order in the liquid. In a first approximation the separation is usually accomplished using electrostatic arguments^{7, 8}. In doing so one obtains for the alignment

$$\langle 3 \cos^2 \theta_k - 1 \rangle_E = \frac{2}{15} \left(\frac{mE^M}{kT} \right)^2 \left(\frac{3\epsilon}{2\epsilon + 1} \right)^2 \left\{ 1 + \frac{1}{2}(Z - 1) \langle 3 \cos^2 \theta_{ki} - 1 \rangle \right. \\ \left. + \frac{3}{2}(Z - 1)(Z - 2) \langle \cos \theta_{ki} \cos \theta_{kj} \rangle - \frac{1}{2}(Z - 1)(Z - 6) \langle \cos \theta_{ij} \rangle \right\}. \quad (6)$$

E^M is the Maxwell field; the brackets $\langle \dots \rangle$ indicate an integration, which is now performed over the positions and orientations of a molecule and its $(Z - 1)$ nearest neighbours. In absence of short range interactions we obtain an expression for the alignment, which is the same as that obtained from Onsager's theory for nonpolarizable molecules.

For an assembly of polarizable dipolar molecules an expression analogous to equation 3 can be derived, provided certain correlations existing in the liquid are neglected⁹.

(b) Mixtures

For pure liquids an impression about the role of short range interactions can be obtained by comparing the experimentally obtained alignment with the value predicted by Onsager's model. For mixtures, the existence of angular correlations between the molecules in the liquid is directly demonstrated by measuring the alignment of the nonpolar component, as has been performed in the mixture benzene-nitrobenzene. In a first approximation the nonpolar benzene molecules are not oriented by the applied electric field. If these molecules possess on the average a preferential orientation with respect to the nitrobenzene molecules the dielectric alignment may be transferred. These arguments can be made more quantitative by extension of the statistical mechanical theory of the preceding section to mixtures. For this purpose a system consisting of N_1 polar and N_2 nonpolar molecules is considered and again it is assumed that the particles are not polarizable. Using a distribution function, appropriate to the liquid mixture, the alignment for the nonpolar component is computed to be

$$\langle 3 \cos \theta_{k'} - 1 \rangle_E = \frac{2}{15} \left(\frac{mE^e}{kT} \right)^2 \left\{ \frac{1}{2} N_1 \langle 3 \cos^2 \theta_{k'i} - 1 \rangle_0 \right. \\ \left. + \frac{1}{2} N_1 (N_1 - 1) \langle 3 \cos \theta_{k'i} \cos \theta_{k'j} - \cos \theta_{ij} \rangle_0 \right\} \quad (7)$$

Here m is the electric dipole moment of the polar component; E^e is the externally applied electric field; $\theta_{k'i}$ is the angle between the z -axis of the nonpolar molecule k' and the direction of the dipole moment of the polar molecule i , and θ_{ij} is the angle between dipoles i and j . The brackets $\langle \dots \rangle_0$ again denote averages over the positions and orientations of the molecules in the absence of an electric field for the mixture.

The alignment of the polar component in the mixture can be shown to be

$$\begin{aligned} \langle 3 \cos^2 \theta_k - 1 \rangle_E = & \frac{2}{15} \left(\frac{mE^e}{kT} \right)^2 \left\{ 1 + \frac{1}{2}(N_1 - 1) \langle 3 \cos^2 \theta_{ki} - 1 \rangle_0 \right. \\ & \left. + \frac{3}{2}(N_1 - 1)(N_1 - 2) \langle \cos \theta_{ki} \cos \theta_{kj} \rangle_0 - \frac{1}{2}(N_1 - 1)(N_1 - 6) \langle \cos \theta_{ij} \rangle_0 \right\} \end{aligned} \quad (8)$$

θ_{ki} etc. is the angle between dipoles k and i . Evaluation of the averages $\langle \dots \rangle_0$ in equations 7 and 8 is even more difficult than the solution of the integrals of equation 5, representative of the pure liquid. Again they contain long range contributions, due to shape-dependent boundary effects. Separation of these contributions is necessary to obtain information about the short range interactions between a molecule, polar or nonpolar, and its nearest neighbours.

Although equations 7 and 8 give results for a system which is not physically realistic, the main features determining the alignment of the polar and nonpolar components are demonstrated by these formulae. The way in which they depend on the applied electric field and the dipole moment of the polar component is made explicit, as is the dependence on angular correlations between the polar molecules and between the polar and the nonpolar molecules in the mixture.

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