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NMR-RELAXATION STUDY OF DIAMAGNETIC ION SOLVATION IN METHANOL SOLUTIONS

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Selective measurements of the proton relaxation time T_1 of CH_3 and OH groups of methanol solutions of the diamagnetic salts: LiCl, LiBr, LiJ, $LiClO_4$, NaJ, $NaClO_4$, NaSCN, KJ, KSCN were performed. Positive as well as negative solvation effects of monovalent ions were determined. Performed analysis evidences that the correct interpretation of NMR relaxation data is possible only when the influence of internal rotation of the methyl group is taken into account. ^7Li spin-lattice relaxation time measurements suggest that ion-ion interactions play no role at low concentrations.

Introduction

Diamagnetic ions when in solutions undergo solvation. This process perturbs the structure of the solvent e. g. by the disruption of hydrogen bonds. Within the framework of the model of Gurney [1] and Samoylov [2], the solution of a diamagnetic electrolyte comprises three sub-liquids. The one, denoted by "0", represents the part of the solvent unaffected by the ions. The other two, denoted by "+" and "−" consists, of molecules belonging to the solvation spheres of cations and anions respectively. The mobility of the solvent molecules is different in each of the three sub-liquids. The solvation spheres of the ions consist of n_s^+ (cation) and n_s^- (anion) molecules of the solvent (solvation numbers). Some ions are enclosed in solvation spheres, the solvent molecules of which have a lower mobility than that of molecules in the pure solvent, whereas others are in spheres where the mobility of solvent molecules is higher than in the pure solvent. In the first case, the ions are said to possess positive solvation, to be of the structure forming type, in the second, we refer to them as ions with negative solvation, or ones of the structure breaking type. One of the methods providing information on the diffusional motion of molecules in solvation spheres of ions resides in the application of nuclear magnetic resonance (NMR). Aqueous solutions have been dealt with in numerous papers, the authors of which measured the spin-lattice relaxation time T_1 of the protons of water. The information on

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molecular dynamics provided by the measurements of spin-lattice relaxation times T_1 for all protons of the molecule can be inadequate in the case of nonaqueous solutions. This can be caused by the intramolecular motions leading to shortening of T_1 for some groups of protons. Thus it seemed interesting to carry out a study of diamagnetic ions solvation in non-aqueous solution by the method of selective T_1-measurement for chemically inequivalent proton groups [3–6]. The choice of methanol suggested itself since, for this solvent, studies of the average relaxation time T_1 [7–9] and of chemical shift [10–12] yielded contradictory results regarding the influence of ions on the structure of the solvent.

1. *Basic equations*

The proton spin-lattice relaxation rate T_1 is the sum of the intramolecular and intermolecular contributions [6]:

$$(1/T_1) = (1/T_1)_{\mathrm{intra}} + (1/T_1)_{\mathrm{inter}}. \tag{1}$$

In solutions of diamagnetic salts, both contributions undergo a change in value. According to the Hertz theory [13] the value of T_1^{-1} is, in a first approximation, modulated by the variations in diffusion coefficient D_I of the solvent molecules in a solution

$$(1/T_1)_{\mathrm{inter}} = \tfrac{17}{30} \frac{\pi \gamma_I c_I}{a D_I} \tag{2}$$

with a — the diameter of the solvent molecule, and c_I — the number of spins per 1 cm^3. The intramolecular part of T_1^{-1} is given by the well known BPP formula [14]

$$(1/T_1)_{\mathrm{intra}} = \tfrac{3}{2} \frac{\pi \gamma_I^4 \hbar^2}{r_{ij}} \tau_c \tag{3}$$

with r_{ij} — the interproton distance, and τ_0 — the correlation time of isotropic reorientation of the solvent molecules.

If ideal microdynamical conditions [15] are fulfilled in the diamagnetic salt solution, τ_c is the weighted average of contributions from molecules belonging to the sub-liquids (+), (−), (0) [15, 16]

$$\tau_c = x^+ \tau_c^+ + x^- \tau_c^- + (1 - x^+ - x^-) \tau_c^0, \tag{4}$$

where $x^\pm = \dfrac{N^\pm}{N^0}$ — concentration of molecules in the solvation spheres of cations and anions, $N^\pm$ — the number of solvent molecules in the solvation spheres of the positive or negative ions, N^0 — the number of all solvent molecules in the solution, and $\tau_c^{\pm,0}$ — the value of τ_c in each of the sub-liquids.

Hence we see that the value of $T_{1\,\mathrm{intra}}^{-1}$ in the solution has to be available in order to obtain information concerning the microdynamical parameters τ_c^+, τ_c^-, τ_c^0, characterizing the solvation spheres of the ions.

In order to make Eq. (4) applicable to our further analysis, it has to be brought to a form in which τ_c is no longer expressed as a function of the concentration of molecules in the solvation spheres but rather as a function of the salt concentration-c

$$\tau_c = \tau_c^0(1+B''c), \tag{5}$$

where

$$B'' = \frac{M_r}{1000d_r}\left[n_s^+ v^+ \left(\frac{\tau_c^+}{\tau^0} - 1\right) + n_s^- v^- \left(\frac{\tau_c^-}{\tau^0} - 1\right)\right] \tag{6}$$

(if c is expressed in moles of the salt per 1 l of the solvent), or

$$B'' = \frac{1}{55.5}\left[n_s^+ v^+ \left(\frac{\tau_c^+}{\tau_c^0} - 1\right) + n_s^- v^- \left(\frac{\tau_c^-}{\tau_c^0} - 1\right)\right] \tag{7}$$

(if c is in aquamolality scale i. e. in moles of the salt per 55.5 moles of the solvent), or

$$B'' = \frac{M_r}{1000}\left[n_s^+ v^+ \left(\frac{\tau_c^+}{\tau_c^0} - 1\right) + n_s^- v^- \left(\frac{\tau_c^-}{\tau_c^0} - 1\right)\right] \tag{8}$$

(if c is determined in units of mole of the salt per 1 kg of the solvent), with the notation: M_r — molecular mass of the solvent, d_r — density of the pure solvent, and $v^{\pm}$ — valency of the ions.

The correlation time of the isotropic reorientation of the solvent molecules is thus seen to depend linearly on the salt concentration. Eq. (5) is derived for rigid molecules of the solvent, since in this case τ_c depends on reorientation of the molecule as a whole only.

If the molecule is not rigid, the correlation time determined from NMR measurements depends also on internal reorientation [17]. This is the case for methanol, used here as a solvent. The methyl group, in addition to isotropic reorientation of the methanol molecule as a whole, is involved in internal rotational motion about its triad axis C_3 and about the OH bond (Fig. 1). O'Reilly and Peterson assumed [18], for the motion of the interproton vector of the methyl group about the C_3-axis a model of reorienta-

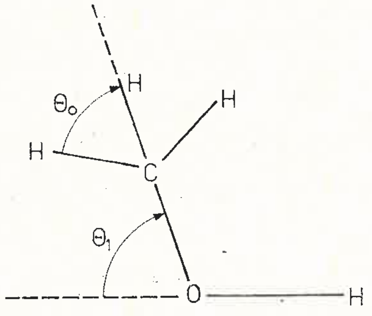

Fig. 1. The model of methanol molecule, $\theta_0 \theta_1$ – the angles characterizing the internal rotations of CH_3-group

tion by large 120° rotational jumps. Reorientation of the C_3-axis is anisotropic — it rotates about the axis of the OH-bond which, in turn, performs isotropic reorientation together with the molecule. O'Reilly and Peterson generalized the formula of Woessner [17] to describe the effective correlation time of the CH_3-group in the case when its rotation about the symmetry axis is much faster than the rotation about the OH-bond and isotropic reorientation of the molecule

$$\tau_c^{CH_3} = \tfrac{1}{4}(3\cos^2\theta_0-1)\{\tfrac{1}{4}(3\cos^2\theta_1-1)^2\tau_c+3\sin^2\theta_1\cos^2\theta_1\tau_{2t}^{(1)}+\tfrac{3}{4}\sin^4\theta_1\tau_{2t}^{(2)}\}$$
$$+(3\sin^2\theta_0\cos^2\theta_0+\tfrac{3}{4}\sin^4\theta_0)\frac{\tau_r\tau_c}{\tau_r+\tau_c}, \qquad (9)$$

where θ_0 is the angle of rotation between the interproton vector and the symmetry axis of the CH_3 — group; θ_1 — the angle between the C_3 — axis of the methyl-group and the direction of the OH-bond; τ_c — the correlation time of the isotropic reorientation of molecules of the solvent; τ_r — the correlation time of methyl group rotation about its C_3 axis;

$$\tau_{2t}^{(m)} = \left\{\frac{1-\langle\cos m\phi\rangle_{av}}{\tau_w}+\frac{1}{\tau_c}\right\}^{-1}, \qquad m = 1,2$$

τ_w is the correlation time for rotation about the OH-bond axis; $\langle\cos m\phi\rangle_{av}$ — the mean value of $\cos\phi(\tau)$; and $\phi(\tau)$ — the angle through which the orientation of the interproton vector varies during the time τ at rotation about the OH-axis.

Since the value of $\langle\cos m\phi\rangle_{av}$ is unknown, it is generally not easy to determine $\tau_{2t}^{(m)}$. O'Reilly and Peterson, nonetheless, determine $\tau_{2t}^{(m)}$ approximately assuming that rotation of the C_3-axis about the OH-bond represents a case of rotational diffusion by small angles. In this case,

$$\tau_{2t}^{(1)} = D_w+6D, \qquad (10)$$

$$\tau_{2t}^{(2)} = 4D_w+6D, \qquad (11)$$

where D is the diffusion coefficient for isotropic reorientation of the molecule $\left(\tau_c = \dfrac{1}{6D}\right)$, and D_w — that of internal rotation about the OH-bond.

2. *Experimental*

Measurements of the relaxation time T_1 of protons of the methyl and hydroxyl groups in methanol were performed with a Bruker SXP-4-100 pulse spectrometer operating at 90 MHz, by the method of $(180°-\tau-90°)$ pulses [19]. The frequency spectrum obtained by the Fourier transform of the free precession signal of the protons with a BNC-12 computer, exhibited good separation of the lines of the CH_3 and CH groups. T_1 was determined from the slope of $\ln(A_0-A(\tau)) = f(\tau)$, where A_0 is the FT FID amplitude after the 90° pulse and $A(\tau)$ that after a sequence of $(180°-\tau-90°)$ pulses for different values of τ. To obtain correct values of $A(\tau)$, each measurement was preceded by a period of rest of $5T_1$ sufficient for the system of spins to return to thermal equilibrium. The accuracy of measurement was 5%.

The viscosity of the solutions was measured with an Ubbelohde viscometer, thermostatized to ±1°. Density measurements were carried out by weighing. The samples were prepared by dilution of an initial solution, their concentrations being determined by the weight method. The samples for T_1 measurements were degassed to eliminate paramagnetic oxygen from the liquid by well known freeze-pump-thaw technique.

The anhydrous salts LiCl, LiBr, $LiClO_4$, NaJ, $NaClO_4$ and hydrated $LiJ{\cdot}2H_2O$ of "zur Analyse" grade, were obtained from E. Merck, Darmstadt. Anhydrous KJ, NaSCN and KSCN of "pro analysi" purity, as well as 99.9% methanol "pro analysi", were obtained from Polskie Odczynniki Chemiczne, Gliwice. All the salts, and methanol, were dried carefully. It proved impossible to dehydrate lithium iodide, supplied as the hydrate $LiJ \cdot 2H_2O$, in the usual way, so that hydrate crystals were dissolved in dried methanol and the solution was then dried with freshly calcinated (at 250°C) molecular sieves of the type 3A from Fluka AG Buchs SG. After drying, the solution was filtrated through a hard paper filter in a dark dry-box, carefully dried with phosphor pentoxide. The efficacy of drying was checked with Karl Fischer reagent [20]. Sodium and potassium rhodanides were additionally purified, previous to drying, the former by crystallisation from methanol and the latter by fractionated precipitation with ethyl ether from methanol.

3. *Results*

Our results obtained when measuring the relaxation times T_1 versus the salt concentration at 20°C are plotted in the relaxation rate curves $T_1^{-1} = f(c)$ of Figs 2—4, where c is the salt concentration in moles per 1 l of the solvent. The small difference in T_1 between CH_3 and OH in pure methanol increases considerably in the salt solutions depending on the type of salt. The variations in T_1 observed for lithium salts in methanol are much larger than those observed vs. concentration in aqueous solution. The least changes in T_1 as a function of concentration were found by us for potassium rhodanide. For all the salts in methanol solution studied, we observed a shortening of T_1. Regrettably, the low solubility of some salts in methanol prevented us from pursuing our study on ones with large monovalent ions, like CsJ and RbJ.

The relaxation times T_1 of CH_3 and OH groups of pure methanol measured by us amounted to $T_1^{CH_3} = 7.5(s)$ and $T_1^{OH} = 7.2(s)$ in good agreement with previously published results [3]. In our study, it was essential to know the exact value of the intramolecular part of T_1. To obtain this value, we had to calculate the intermolecular contribution $T_{1\,\mathrm{inter}}$. The spin-lattice relaxation rates of the two chemically inequivalent groups of methanol fulfil the following equations [6]

$$(1/T_1)^{CH_3} = (1/T_1)_{\mathrm{intra}}^{CH_3} + (1/T_1)_{\mathrm{inter}}, \tag{12}$$

$$(1/T_1)^{OH} = (1/T_1)_{\mathrm{intra}}^{OH} + (1/T_1)_{\mathrm{inter}}, \tag{13}$$

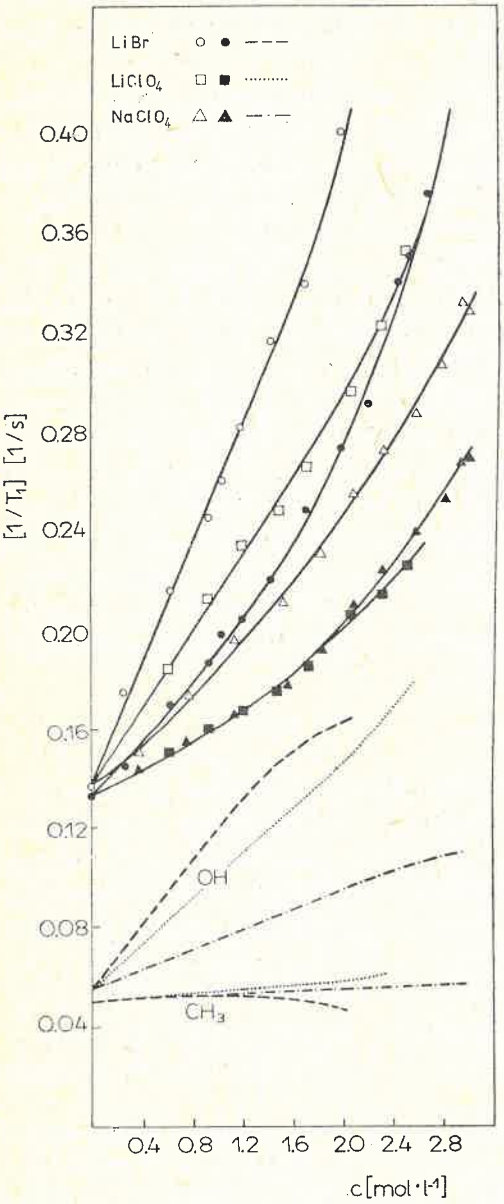

Fig. 2

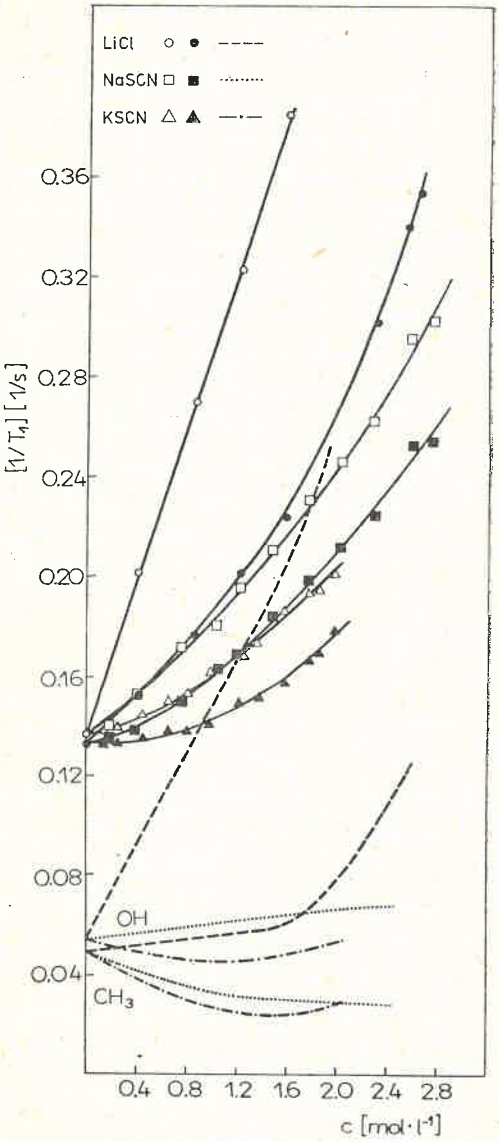

Fig. 3

Fig. 2. Proton spin-lattice relaxation rates for methanol solutions of LiBr, $LiClO_4$, $NaClO_4$. Open points – OH group, black points – CH_3 group, dashed, dotted, and dotted-dashed lines – intramolecular contributions

Fig. 3. Proton spin-lattice relaxation rates for methanol solutions of LiCl, NaSCN, KSCN. Open points – OH group, black points – CH_3 group, dashed, dotted-dashed, and dotted lines – intramolecular contributions

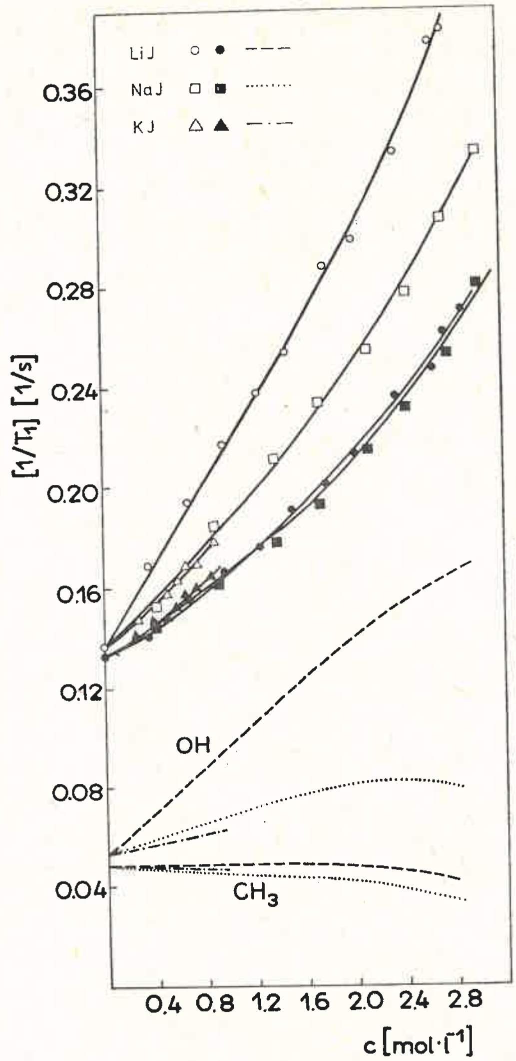

Fig. 4. Proton spin-lattice relaxation rates for methanol solutions of LiJ, NaJ, KJ. Open points – OH group, black points – CH_3 group, dashed, dotted, and dotted-dashed lines – intramolecular contributions

where

$$(1/T_1)^{CH_3}_{intra} = \tfrac{3}{2}\,\gamma_I^4 \hbar^4 \Big(\sum_{j=1}^{4} r_{ij}^{-6}\Big)^{CH_3} \tau_c^{CH_3}, \tag{14}$$

$$(1/T_1)^{OH}_{intra} = \tfrac{3}{2}\,\gamma_I^4 \hbar^4 \Big(\sum_{j=1}^{4} r_{ij}^{-6}\Big)^{OH} \tau_c^{OH}. \tag{15}$$

The values of $\sum r_{ij}^{-6}$ calculated by us for CH_3 and OH in methanol amount to $(\sum r_{ij}^{-6})^{OH} = 0.016\times 10^{48}$ cm^{-1} and $(\sum r_{ij}^{-6})^{CH_3} = 0.066\times 10^{48}$ cm^{-1}. The values of $(T_1)_{inter}$ were calculated by Eq. (2) [21] for the pure liquids as well as for the solutions. In determining the diffusion coefficients D_i we had recourse to the simple Stokes–Einstein relation

$$D_i = 6\pi\eta_i r, \qquad (16)$$

where r is the radius of the methanol molecule, η_i the viscosity of the solutions. Thus, we determined $(T_1)_{\text{inter}}$ from the measurement of viscosity of methanol or its solutions. (The viscosities of studied solutions are plotted in Fig. 5). Applying Eqs (12)—(15) we then determined τ_c for the methyl and hydroxyl group of pure methanol as $\tau_c^{CH_3} = 0.88$ (ps) and $\tau_c^{OH} = 4.5$ (ps). Since the values of correlation times depend on the model applied for calculating of $T_{1\,\text{inter}}$, we thought it essentially important to compare the determined values of τ_c with the values accessible to direct determination from measurements of T_1 for deuterium in d-methanol. O'Reilly and Peterson [18] obtained the reorientation correlation times $\tau_c^{OD} = 5.4$ (ps) for the OD the group in CH_3OD and $\tau_c^{CD_3} = 0.96$ (ps) for the CD_3 group in CD_3OH. They consider τ_c^{OD} to be the correlation time characterizing the reorientational motion of entire methanol molecules. The time $\tau_c^{CD_3}$ is less than one quarter of τ_c^{OD}. Now, by Woessner's formula [16] the ratio should be one to four for the methyl group. Their unexpected results led O'Reilly and Peterson to assume complex rotational motion for the methyl group [17]. The values $\tau_c^{CH_3}$ and τ_c^{OH} calculated by us are in excellent agreement with the values reported by O'Reilly and Peterson from their experiments.

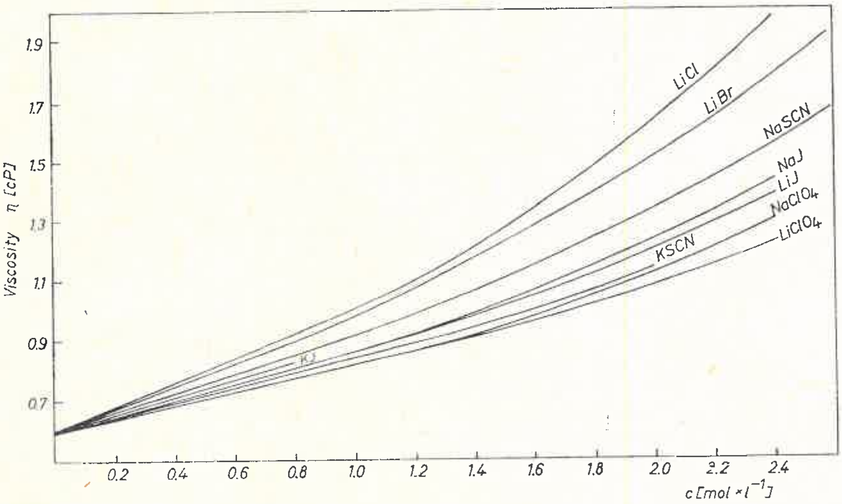

Fig. 5. Viscosities of LiCl, LiJ, $LiClO_4$, LiBr, NaJ, NaSCN, $NaClO_4$, KJ and KSCN methanol solutions

4. Effects of positive and negative solvation of the ions

At first sight, the shortening of T_1 as observed by us in solutions of diamagnetic salts in methanol might suggest that, in all cases, solvation of the ions was positive. Solutions of ions with negative solvation should exhibit an increase in T_1, as in fact is the case for solutions in water, and in glycol. The situation, however, has to be evaluated with more circumspection. Chemical shift studies on solutions of diamagnetic salts in methanol show, for salt like KJ, NaSCN, LiJ and KSCN, a shift in OH-signal towards higher fields. This can be explained as being due to the presence of a structure breaking effect in the solutions [10–12]. On the other hand, the analysis of total relaxation time T_1 in methanol solutions of diamagnetic salts shows no evidence of a structure breaking effect [7]. However, neither the lack of T_1-lengthening or the last-cited analysis appears to be a proof for an absence of negative solvation in methanolic solutions. A shortening of T_1 is also observed in aqueous solutions of e.g. lithium iodide in spite of the fact that iodine is an ion with negative solvation.

The use of Eq. (4) for the analysis of results bearing on the mean relaxation time T_1 of the protons of methanol is incorrect. The methanol molecule is by no means rigid. Hence the mean time T_1 depends, in addition to reorientation of the entire molecule, on its inner reorientation as well.

In this work, we shall restrict the use of Eq. (4) to the analysis of T_1-measurements for the OH-group only. In fact, according to O'Reilly and Peterson, only the rotational correlation time of this group can be interpreted as the correlation time of isotropic reorientation of the whole molecule, i.e. $\tau_c^{OH} = \tau_c$. The presence of the ions modifies the reorientation of the methanol molecule but does not affect its internal rotation. Hence their presence should affect strongly the τ_c-value of the OH-group not necessarily modifying the reorientation correlation time of the CH_3-group, since $\tau_c^{CH_3}$ depends mainly on the internal rotations of this group.

In order to obtain the values of the intramolecular contributions $T_{1\,\mathrm{intra}}$ for CH_3 and OH groups, we had recourse to Eqs (12), (13) and (2) as well as to the simple Stokes–Einstein relation. The obtained values of $(T_1^{-1})_{\mathrm{intra}}^{OH}$ and $(T_1^{-1})_{\mathrm{intra}}^{CH_3}$ vs. the salt concentration are plotted in Figs 2—4, showing that the changes in intramolecular OH-contribution depended on the type of salt in solution; the intramolecular CH_3-contribution remained almost unaffected (except for the CH_3 rhodanide solutions). This unexpected behaviour of $T_{1\,\mathrm{intra}}^{OH}$ and $T_{1\,\mathrm{intra}}^{CH_3}$ was already reported by us [22]. The independence of $T_{1\,\mathrm{intra}}$ on the salt concentration found in our experiments was subsequently confirmed by Hertz's et al. [23] measurements of the deuterium relaxation time of the CD_3 in methanol versus the salt concentration for NaJ, KJ and $NaClO_4$. The changes in $(T_1^{-1})^{CD_3}$ were but quite insignificant in those solutions. The agreement of our results with those obtained by Hertz as well as the above mentioned agreement for pure methanol with O'Reilly and Peterson's data proves the correctness of applying the Stokes–Einstein model for calculating the intermolecular contribution to T_1 for diamagnetic salt solutions in methanol. For diamagnetic salt solution in ammonia this model was also successfully applied for calculating diffusion coefficients [24]. The linear dependence of $(T_1^{-1})_{\mathrm{intra}}^{OH}$ on concentration enables one to calculate the coefficients B'' from Eqs (5) and (15). Table I gives the values of B'' for the studied solutions (to facilitate comparison: when defining the concentration in mole salt per litre methanol (column 1), in mole salt per kg methanol (column 3) and aquamolality units (column 2).

All obtained coefficients B'' are positive except for the solutions of potassium rhodan-

TABLE I

Values of the coefficients $B'' = \frac{(1/T_1)_{\text{intra}} - (1/T_1)^{c\to 0}_{\text{intra}}}{c(1/T_1)^{c\to 0}_{\text{intra}}}$

Salt	B''		
	c mole/l	c aquamole	c mole/kg
LiCl	1.57	0.78	1.24
LiBr	1.16	0.58	0.92
$LiClO_4$	0.82	0.41	0.65
LiJ	0.82	0.41	0.65
$NaClO_4$	0.34	0.17	0.27
NaJ	0.34	0.17*	0.27
KJ	0.17	0.08	0.13
NaSCN	0.13	0.06	0.10
KSCN	−0.12	−0.06	−0.09

* The same value was obtained by Hertz from deuterium relaxation in CH_3OD solution [23].

ide. On the basis of evaluated values of B'', we can now proceed to calculate the microdynamical parameters $\tau_c^{\mp}/\tau_c^0$. First, however, we have to check the additivity conditions for the ionic contributions

$$B'' = B''^{+} + B''^{-}, \tag{17}$$

where

$$B''^{\pm} = \frac{M_r}{1000\, d_r}\, n_s^{\pm} \nu^{\pm} \left(\frac{\tau_c^{\pm}}{\tau_c^0} - 1\right). \tag{18}$$

As reported in our earlier paper [22], this condition was very well fulfilled for all the salts except rhodanides.

The absolute values of B''^{+}, B''^{-} are calculated on the assumption of identical changes in mobility of the solvent molecules in solvation spheres of the ions Cl^- and K^+, i.e. $B''^{+}(K) = B''^{-}(Cl)$. For solutions of salts in methanol, the assumption is justified with regard to the equal transfer numbers of chlorine and potassium ions in methanol [7]. Since KCl is practically insoluble in methanol we had recourse to three other salts in order to calculate the ionic contribution $B''^{-}(Cl)$ for the chlorine ion

$$B''^{-}(Cl) = 1/2[B''(LiCl) + B''(KJ) - B(LiJ)].$$

For the other ions, we calculated $B''^{\pm}$ from Eq. (17) and the data of Table I (for concentrations in mole per litre only). Table II gives the coefficients $B''^{\pm}$, and the ratios $\tau_c^{\pm}/\tau_c^0$ calculated from Eq. (18), for the selected solvation numbers $n_s = 4, 6, 8, 10, 12, 14, 16, 18, 20$. Obviously, the values of $\tau_c^{\pm}/\tau_c^0$ are independent of the concentration units applied when calculating B''.

In Table II, the coefficients $B''^{\pm}$ and ratios $\tau_c^{\pm}/\tau_c^0$ are seen to be negative for J^-, ClO_4^- and SCN^-. For the other ions, $\tau_c^{\pm}/\tau_c^0$ decreases as follows: $Li^+ > Na^+ > K^+ = Cl^- > Br^-$.

TABLE II

Values of the coefficient $B''^{\pm}$ and ratios $\tau_c^{\pm}/\tau_c^0$, calculated for selected solvation numbers of the various ions in solution in methanol. Column 2 gives the crystallographical radii of the ions

Ion	R [Å]	$B''^{\pm}$	$\tau_c^{\pm}/\tau_c^0$								
			$n_s = 4$	$n_s = 6$	$n_s = 8$	$n_s = 10$	$n_s = 12$	$n_s = 14$	$n_s = 16$	$n_s = 18$	$n_s = 20$
Li^+	0.78	1.11	7.9	5.6	4.4	3.7	3.3	2.9	2.7	2.5	2.4
Na^+	0.98	0.63	4.9	3.6	2.9	2.6	2.3	2.1	2.0	1.9	1.8
K^+	1.33	0.46	3.8	2.6	2.4	2.1	1.9	1.8	1.7	1.63	1.57
Cl^-	1.81	0.46	3.8	2.6	2.4	2.1	1.9	1.8	1.7	1.63	1.57
Br^-	1.95	0.05	1.31	1.20	1.15	1.12	1.10	1.09	1.08	1.07	1.06
J^-	2.20	−0.29	—	—	0.10	0.28	0.40	0.49	0.56	0.60	0.64
ClO_4^-	2.84	−0.29	—	—	0.10	0.28	0.40	0.49	0.56	0.60	0.64
SCN^-	2.34	−0.50*	—	—	—	—	—	0.12	0.22	0.31	0.38
		−0.58*	—	—	—	—	—	—	0.10	0.20	0.28

* Two contributions $B''^{\pm}$ for the rhodanide ion result from calculation for KSCN and NaSCN.

Thus, the rotational correlation time τ_c of methanol molecules in the solvation spheres of the ions J^-, ClO_4^-, SCN^- is less than τ_c^0 — the rotational correlation time of methanol molecules in the pure liquid. Hence, in methanol solutions there appears an *effect of negative solvation* (structure breaking) for the ions J^-, ClO_4^-, SCN^-. The ions Li^+, Na^+, K^+. Cl^-, Br^- exhibit positive solvation (structure forming). The most strong structure forming effect is observed for the lithium ion. The bromine ion has almost no effect altogether on the structure of methanol.

TABLE III

Some examples of $B''^{\pm}$ values (for c in mole per litre) for ions in methanol as derived from the data of Table I, on the assumption of $B''^{-}(Cl) < B''^{+}(Li)$. The last column corresponds to the situation when chlorine and potassium ions have equal coefficients $B''^{\pm}$ (the $B''^{\pm}$ values of this column served for working out the values of the ratios $\tau_c^{\pm}/\tau_c^0$ given in Table II)

Ion	$B''^{\pm}$					
Li^+	0.82	0.84	0.86	0.90	1.00	1.11
Cl^-	0.75	0.73	0.71	0.67	0.57	0.46
Br^-	0.34	0.32	0.30	0.26	0.16	0.05
ClO_4^-	0.00	−0.02	−0.04	−0.08	−0.18	−0.29
J^-	0.00	−0.02	−0.04	−0.08	−0.18	−0.29
Na^+	0.34	0.36	0.38	0.42	0.52	0.63
K^+	0.17	0.19	0.21	0.25	0.35	0.46
SCN^-	−0.21	−0.23	−0.25	−0.29	−0.39	−0.50
	−0.29	−0.31	−0.33	−0.37	−0.47	−0.58

It should be stressed that the assumption of $B''^{+}(K) = B''^{-}(Cl)$ is by no means decisive for the qualitative establishment of negative solvation in methanol solutions. The value of the ionic contribution can be assumed for one of the ions, for the others it can be calculated from Eq. (17). It is obvious that Li^+ polarizes the structure strongly. Certainly, the cation contribution $B''^{+}(\mathrm{Li})$ to the coefficient e.g. $B''(\mathrm{LiCl})$ is larger than the anion contribution $B''^{-}(\mathrm{Cl})$. Thus, taking into consideration the assumption $B''^{-}(\mathrm{Cl}) < B''^{+}(\mathrm{Li})$, selecting values of $B''^{-}(\mathrm{Cl})$, and then carrying out exact calculations of B''^{+} for the other ions with Eq. (17), one always arrives at negative values for the ionic contributions B''^{-} of ClO_4^-, J^-, SCN^-. Examples of the values of $B''^{\pm}$ are given in Table III. The fact that $B''^{-} < 0$ for ClO_4^-, J^- and SCN^- is sufficient proof of the presence of negative solvation of these ions in methanol. The correlation time ratios τ_c^+/τ_c^0 for Li^+ and Na^+ determined in Table II are larger than in aqueous solution, for the same solvation numbers. This points to a strongly polarizing influence of the ions Li^+ and Na^+ on the molecules of methanol.

5. *Intramolecular motions of the* CH_3*-group of methanol*

As stated in Section 4 $(T_1^{-1})_{\mathrm{intra}}^{CH_3}$ is insensitive to the presence of ions in the solution. In the case of lithium chloride, iodide, bromide and perchlorate as well as sodium iodide and perchlorate, $(T_1^{-1})_{\mathrm{intra}}^{CH_3}$ varies insignificantly up to concentrations of 1.8 mole/l and, for weakly soluble potassium iodide, up to 0.9 mole/l. Exceptionally, for sodium and potassium rhodanide, $T_{1\,\mathrm{intra}}^{-1}$ for the CH_3-group of methanol decreases with growing concentration.

From the calculations to follow, the independence of $(T_1^{-1})_{\mathrm{intra}}^{CH_3}$ on salt concentration can be explained only on the basis of O'Reilly and Peterson's model of complex reorientation of the CH_3-group in methanol. Since the presence of ions can reasonably be thought to affect reorientation of the solvent molecules leaving unaffected the internal reorientations of the CH_3-group, only τ_c can be variable in O'Reilly and Peterson's formula for the effective rotational time of the CH_3-group, the other quantities remaining constant: $\tau_r = 0.78$ ps, $D_{\parallel} = 13 \times 10^{10}\ s^{-1}$, $\theta_0 = 90°$, $\theta_1 = 71°$ [17]. In Table IV, we give the numerical values of $\tau_{\mathrm{eff}}^{CH_3}$ as functions of τ_c determined from Eq. (9) and taking into account Eqs (10), (11). Since, after O'Reilly and Peterson, one can assume that $\tau_c^{OH} = \tau_c$, the variable parameter in the first row of Table IV, represents the changes in rotational correlation time of the OH-group. The second row gives the effective correlation time of the CH_3-group shortened in comparison with τ_c as a result of complex reorientation rotation of the CH_3-group, in accordance with Eq. (9).

TABLE IV

$\tau_c^{CH_3}$ as a function of τ_c from Eq. (9)

τ_c [ps]	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8	9	10	11	12	13
$\tau_c^{CH_3}$ [ps]	0.53	0.69	0.79	0.86	0.91	0.95	0.98	1.03	1.05	1.06	1.08	1.10	1.11

Table IV shows that although τ_c varies very considerably e.g. from 4.0 to 13 ps, $\tau_c^{CH_3}$ changes insignificantly from 0.86 to 1.11 ps.

Fig. 6 represents the dependence of the intramolecular part $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ on $(T_1^{-1})_{\text{intra}}^{\text{OH}}$ determined from Eqs (14), (15) and Table IV. The values corresponding to pure methanol are denoted by arrow. It is seen that $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ varies but little even if $(T_1^{-1})_{\text{intra}}^{\text{OH}}$ varies strongly. This, in fact, is the situation observed in solutions of the salts under investigation. For instance, in Fig. 2 for $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ and $(T_1^{-1})_{\text{intra}}^{\text{OH}}$ vs. the LiBr concentration, $(T_1^{-1})_{\text{intra}}^{\text{OH}}$ changes from about 0.056 s^{-1} to 0.16 s^{-1} whereas $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ changes from about 0.049 to 0.053. Hence on the basis of O'Reilly and Peterson's model, the change in the motion of the whole methanol molecules (observed as a function of the concentration of certain diamagnetic salts) bears but insignificantly on the intramolecular contribution to the spin-lattice relaxation rate of the CH_3-group. $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ is dependent mainly on the complex rotational motion of the methyl group which is much more rapid than the isotropic reorientation of the molecule as a whole.

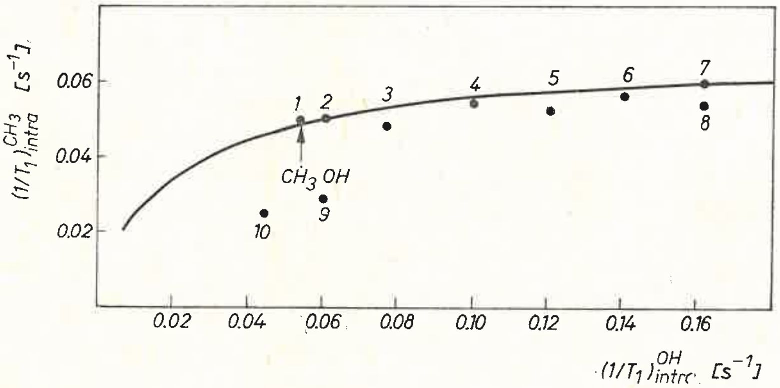

Fig. 6. Theoretical values of $(1/T_1)_{\text{intra}}^{\text{CH}_3}$ as function of $(1/T_1)_{\text{intra}}^{\text{OH}}$ (from Eq. (9), $\tau_c = \tau_c^{\text{HO}}$ is the independent variable). Experimental points are for: pure methanol – *1* and methanol solutions of KJ ($c = 0.8$ mol × l^{-1}) – *2*, NaJ ($c = 1.6$ mol × l^{-1}) – *3*, $NaClO_4$ ($c = 2.3$ mol × l^{-1}) – *4*, LiJ ($c = 1.6$ mol × l^{-1}) – *5*, $LiClO_4$ ($c = 1.9$ mol × l^{-1}) – *6*, LiCl ($c = 1.1$ mol × l^{-1}) – *7*, LiBr ($c = 1.6$ mol × l^{-1}) – *8*, NaSCN ($c = 1.5$ mol × l^{-1}) – *9*, KSCN ($c = 1.6$ mol × l^{-1}) – *10*

The O'Reilly–Peterson model accounts well for the concentrational dependence of $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ in solutions of the diamagnetic salts LiCl, LiJ, LiBr, $LiClO_4$, NaJ, KJ in methanol, but not for the case of KSCN and NaSCN. In solutions of NaSCN, $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ decreases, with increasing concentration of the salt whereas $(T_1^{-1})_{\text{intra}}^{\text{OH}}$ increases. In solutions of KSCN, $(T_1^{-1})_{\text{intra}}^{\text{CH}_3}$ decreases more strongly compared with the decrease in $(T_1^{-1})_{\text{intra}}^{\text{OH}}$ vs concentration than one would expect from the model (see Fig. 6).

Thus, this detailed analysis shows clearly that, in the case of solvent molecules with complex internal motions, the equations resulting from the theory of Hertz [15] and Beckert and Pfeifer [16] are applicable only if the influence of internal rotation is taken into account. Otherwise, analyses based on those equations can lead to erroneous conclusions. The preceding statement can be also extended to the equations of Zimmerman and Brittin [25] widely applied in studies on nuclear magnetic relaxation in multi-phase systems.

6. *Ion association in solutions of lithium chloride in methanol*

At higher concentrations, association can take place between the ions of diamagnetic salts in solutions. According to Bjerrum [26], the critical concentration above which ions can form pairs amounts, in methanol, to 1.3 mole/l for monovalent ions. Solutions of LiCl in methanol belong to those systems for which the formation of ionic contact pairs has been suggested [27]. Since we are applying Hertz's theory, which is based on the assumption that no ionic interactions are present in the solution, the problem requires some discussion. The linear dependence of $(T_1^{-1})^{\mathrm{OH}}_{\mathrm{intra}}$ vs the LiCl concentration shows that at least up to 1.8 mole/l ideal microdynamical conditions exist within the solution.

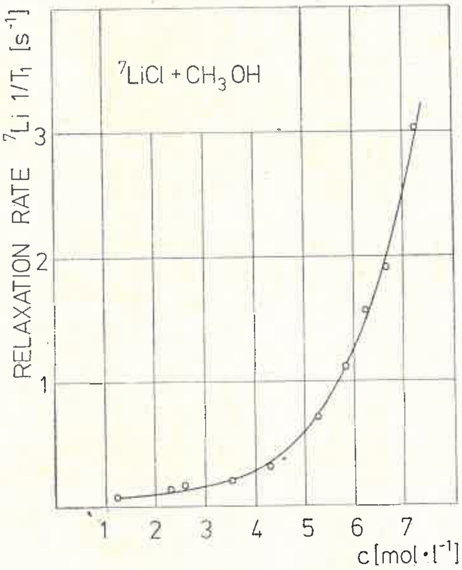

Fig. 7. Spin-lattice relaxation rates for ^{7}Li nuclei for LiCl methanol solutions

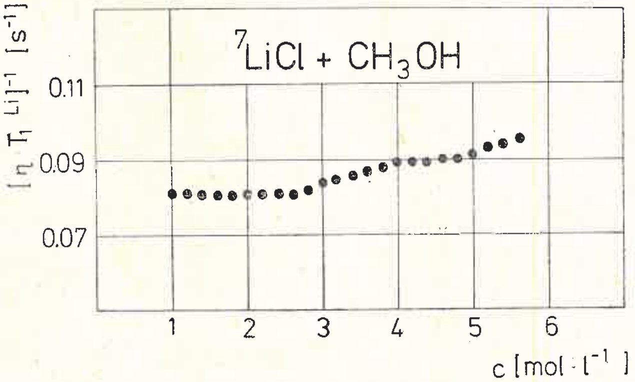

Fig. 8. $1/\eta T_1^{7\mathrm{Li}}$ as a function of LiCl concentration in methanol solution

The problem of the presence, or absence, of ionic associates can be dealt with from the viewpoint of spin-lattice relaxation time measurements for nuclei of ions in solutions of diamagnetic salts [28–30]. If the relaxation rate T_1^{-1} of the nuclei depends mainly on ion-solvent interaction, the dependence of T_1^{-1} on η/T has to be linear (η — viscosity of the solution, T_1 — relaxation time of the ion, T — temperature) [28–30]. Any deviation from linearity can point to association. In this work we performed measurements of the relaxation time T_1 of ^{7}Li nuclei (by the $180°-\tau-90°$ method) with an SXP4-100 Bruker spectrometer in methanol solutions of LiCl (Fig. 7). Fig. 8 shows $1/\eta T_1$ as a function of the salt concentration. The independence of this value on concentration up to about 2 mole/l evidences that ion-ion interactions play no role in investigated solutions of LiCl in methanol.

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