Reports of the Academy of Sciences of the USSR

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964, Volume 157, No. 3

PHYSICAL CHEMISTRY

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PARAMAGNETIC RELAXATION IN SOLUTIONS OF GADOLINIUM NITRATE

(Presented by Academician B. A. Arbuzov, March 12, 1964)

Paramagnetic absorption in liquid solutions of gadolinium salts was first noted in (^{1}). For a long time, however, these solutions were not studied in detail by the EPR method because of the large line widths. Recently a paper was published (^{2}) in which the dependence of ΔH in liquid Gd^{3+} solutions on temperature, concentration, and viscosity was investigated. However, data on paramagnetic relaxation times in solutions were lacking, apart from indirect estimates of τ_s made on the basis of studies of proton relaxation (^{3}, ^{4}).

In the present work, by the Q-meter method (^{5}), measurements of paramagnetic absorption were carried out in parallel and perpendicular fields for aqueous solutions of gadolinium nitrate at concentrations from 0.5 to ~ 4 mol/l in the temperature range from 293 to 368°K. The frequencies used in the measurements were 12, 24, 34, and 44 MHz. Using the procedure described in (^{5}, ^{6}), the principal parameters of paramagnetic relaxation were determined: the spin-lattice relaxation time ρ_L, the spin-spin relaxation time ρ_s, and the constant b/c, which characterizes the internal field in the paramagnetic substance.

Table 1

$\rho_L \cdot 10^8$, sec.

C, mol/l	H, Oe	H, Oe	H, Oe	H, Oe	H, Oe	H, Oe
	0	2000	2800	3600	4400	5200
4	1.32	1.49	1.62	1.72	1.79	
3	1.32	1.46	1.62	1.72	1.77	1.83
2	1.35	1.6	1.67	1.75	1.83	1.89
1	1.36	1.64	1.87	2	2.18	2.29
0.5	1.44	1.69	2.06	2.3	2.46	2.55

It turned out that the spin-lattice relaxation time in aqueous gadolinium solutions is of the order of 10^{-8} sec. The absolute values of ρ_L and the dependence of the spin-lattice relaxation time on concentration and temperature for aqueous gadolinium solutions are very close to the corresponding values of ρ_L for manganese solutions (^{6}).

Table 1 gives data on spin-lattice relaxation times for $Gd(NO_3)_3$ solutions at room temperature and at various values of concentration and constant-field strength H_0.

The dependence of ρ_L on the constant-field strength is described by the Bloembergen–Van Vleck formula

$$\rho_L = \rho_0 \frac{b/c + H^2}{b/c + pH^2}. \tag{1}$$

Here ρ_0 is the spin-lattice relaxation time at $H = 0$, and p is a constant ($p < 1$).

From the data of Table 1 it is seen that ρ_L depends only very weakly on dilution; moreover, in the concentration range 2–4 mol/l the time values practically coincide, and only with a further decrease in concentration do the spin-lattice relaxation times become slightly longer. First of all it should be noted that such behavior of ρ_L cannot be explained by dipole-dipole interactions. Apparently, even for high concentrations the most probable mechanism responsible for relaxation will be a mechanism analogous to the MacConnell mechanism (^{7}) or to the Altshuler–Valiev mechanism (^{8}, ^{9}). (Exchange in gadolinium solutions is unlikely.)

The constancy of ρ_L at high concentrations (2-4 mole/liter) is apparently due to the existence in solution of aggregates of particles (so-called "crystallites"). Upon further dilution these groups begin to break down and ρ_L increases slightly. When such groups have completely disappeared, further dilution should no longer affect the spin-lattice relaxation time (this region has not yet been reached for Gd^{3+} solutions at a concentration of 0.5 mole/liter). A similar picture was observed in solutions of manganese nitrate$^{(6)}$.

The temperature dependence of the spin-lattice relaxation time at an ion concentration Gd^{3+} of 0.5 mole/liter is presented in Fig. 1. It turned out that ρ_L changes only slightly with temperature, but nevertheless a clear maximum appears on the $\rho_L(T^\circ)$ dependence curve at a temperature of $\sim 333^\circ$K. The same maximum is observed at a concentration of 1 mole/liter. With a further increase in concentration, the inflection on the $\rho_L(T^\circ)$ curve disappears. An analogous dependence of ρ_L on temperature is observed in equimolar solutions of Mn^{2+} $^{(10)}$.

(Figure: Figure 1)

Fig. 1. $Gd(NO_3)_3$, $C = 0.5$ mole/liter.
1 $-\rho_L$ at $H_0 = 2800$ oersted,
2 $-\rho_L$ at $H_0 = 3600$ oersted,
3 $-\rho_L$ at $H_0 = 4400$ oersted

Such a dependence of the spin-lattice relaxation time on temperature in solutions of ions in an S-state can be explained from the standpoint of the Al' tshuler-Valiev theory (8), the results of which were subsequently improved in works (9,11,12). In (11,12) it was suggested that better agreement with experiment can be achieved if the anharmonicity of internal vibrations and the phenomenon of complex dissociation are taken into account. The influence of the anharmonicity of internal vibrations of the complex on the temperature dependence of the spin-lattice relaxation rate was studied in detail in (12). Comparison of our experimental results with the theoretical curve for the relaxation rate, taking into account only anharmonicity, showed that in the temperature region up to $\sim$ 340°K the agreement is good. With a further increase in temperature, however, the experimental curve rises more steeply than the theoretical one. Apparently, it is also necessary to take into account the phenomenon of complex dissociation, as was done for the paramagnetic relaxation time of protons in (11).

Table 2

$\rho_s \cdot 10^9$, sec.

C, mole/liter	T, °K			
	293	318	343	368
4	0.67	0.9	1.1	1.32
3	1			
2	1.65			
1	2.48			
0.75	2.75	3.4	5.7	7.5
0.5	3.1	5.6	7	10

The spin-spin relaxation times ρ_s were also calculated from the experimental data. It turned out that the spin-spin relaxation time in aqueous Gd^{3+} solutions is approximately half as long as ρ_s in equimolar Mn^{2+} solutions. This is understandable, since for the Gd^{3+} ion $S = 7/2$, whereas for Mn^{2+}, $S = 5/2$. Table 2 gives the values of ρ_s for the investigated concentrations of aqueous $Gd(NO_3)_3$ solutions in the temperature range from 293 to 368°K. It turned out that the spin-spin relaxation time changes with temperature more strongly than the spin-lattice relaxation time and increases with increasing ρ_s according to a linear law, which agrees well with the results of work (13) for dipole-dipole interactions. From the data in Table 2 it is evident that the change of ρ_s with temperature for high concentrations is weaker than for low ones. At high concentrations, when the structure of the solution approaches the structure of a crystalline hydrate (14), an increase in temperature has a weaker effect on dipole-dipole interactions than in dilute solutions, where we are dealing with a "true liquid."

Using the values of the spin-spin and spin-lattice relaxation times that we obtained, we calculated the line width ΔH (denoting it ΔH_{relax}) and compared our data with the results of works (2) and (15), carried out by EPR methods. It turned out that the dependence of the line widths obtained by the two different methods on the concentration of Gd^{3+} ions in solution is completely identical. At the same time, however, the values of ΔH_{relax} are approximately a factor of two smaller than the ΔH values measured by the EPR method. Apparently, this difference is explained by the fact that ΔH (EPR) is not purely relaxation in character; it is broadened due to incompletely averaged fine structure, which is already clearly manifested in glycerol solutions (2). Indeed, the line shape for aqueous solutions, even at the lowest concentrations, turns out not to be Lorentzian but purely Gaussian (15) (ratio of moments = 1.31).

(Figure: Fig. 2. Dependence of b/c on the concentration of Gd^{3+} ions in water at room temperature)

Fig. 2. Dependence of b/c on the concentration of Gd^{3+} ions in water at room temperature

The study of the dependence of the internal-field constant b/c on concentration also indicates the presence, in the heat capacity, of a significant dilution-independent term associated with splittings in the local electric field (see Fig. 2). The study of the dependence $\Delta H_{\text{relax}}(T)$ made it possible, from the tangent of the slope angle of the straight line $\ln(\Delta H) = f\left(\frac{1}{T}\right)$, to determine the activation energy for the molecular motion of the hydrated ion. It was found to be 2.43 kcal/g-mole, which is in very good agreement with the data of works (2) and (16), carried out by EPR and NMR methods.

In conclusion the author expresses deep gratitude to B. M. Kozyrev for guidance and constant assistance in the work, and to M. M. Zaripov for participation in the discussion of the results.

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Received
7 III 1964

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