

## **Charge Effect on Relative Distance Distribution of Fremy's Radical Ions in Frozen Glassy Solution Studied by PELDOR**

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Received November 1, 1999

**Abstract.** The method of pulsed electron double resonance (PELDOR) was used to study the kinetics of phase relaxation due to dipole-dipole spin coupling of Fremy's radical ions and neutral nitroxyl radicals TEMPON in glassy solutions frozen to 77 K. It is shown that as compared with neutral radicals, in the case of Fremy's radical ions, the phase relaxation kinetics deviates from the exponential one. The observed low relaxation rate of Fremy's radical ions corresponds to electrostatic repulsion for the charged radical ions. It is shown that the relative space distribution of radical ions on the basis of the Debye-Hückel theory gives a satisfactory description of the dipole-dipole spin phase relaxation for charged radicals.

### **1 Introduction**

Pulse methods of electron spin resonance (ESR) spectroscopy have been successfully applied for studying the peculiarities of relative spatial arrangement of paramagnetic centers in the solid by analyzing phase relaxation of spins due to their dipole-dipole coupling [1–4]. The methods of electron spin echo (ESE) and pulsed electron double resonance (PELDOR) make it possible to study the weak dipole-dipole couplings of paramagnetic centers in solids hidden by strong inhomogeneous broadening of ESR spectra [5]. Theoretical analysis and experimental investigations by means of these methods show that for a random distribution of paramagnetic centers in solids, the kinetics of spin phase relaxation due to their dipole-dipole coupling, for example in the case of two-pulse ESE, is described by a conventional exponential law [1]

$$V(\tau) \propto \exp(-2b\tau), \quad (1)$$

where  $\tau$  is time interval between microwave (mw) pulses;  $b = 1/T_f$  is the relaxation rate,  $T_f$  is the phase relaxation time. The relaxation rate depends on the average concentration of spins in the sample.

Deviations from the random distribution of spins are manifested in the change of the kinetics law of phase relaxation process. For example, when the local concentration of spins exceeds the mean one (spin pairs, groups or clusters, radical tracks, etc.), then at short times  $\tau$ , there is fast relaxation due to the strong dipole-dipole coupling of the closely spaced spins. These deviations from the usual exponential dependence Eq. (1) have been frequently observed in phase relaxation processes in systems with a high local concentration of spins in solids [1, 3, 5].

Actually, the opposite case is possible where the relative approach of spins is, for some reasons, limited by rather large distances. Thus, in this case a fraction of the closely spaced spins, bonded by the strong dipole-dipole coupling, will be small. As a result, the relaxation rate at short times will be smaller than that estimated for random spin space distribution. This has been observed in [6] by means of PELDOR for the study of the phase relaxation of spin labels in the frozen solutions of the spin-labeled polyvinylpyridine polymer. It was shown [6] that the phase relaxation rate due to the intermolecular interaction of spin labels is small at short times and increases with time. This indicates the difficulties in the approach of spin labels belonging to different macromolecules. When comparing phase relaxation due to intramolecular and intermolecular dipole-dipole couplings of spin labels, it was assumed [6] that the main reason of the limitation of the mutual approach of spins is the electrostatic repulsion of charged polymeric molecules. At present, however, little is known about the feasible influence of electrostatic repulsion of charged radicals on both their relative distribution fixed in frozen solutions and its manifestation in phase relaxation. Therefore, it was necessary to study experimentally the influence of the Coulomb repulsion of radicals on the phase relaxation.

In this paper we studied the dipole-dipole spin relaxation for the frozen glassy solutions of radical ions in order to reveal a possible effect of electrostatic interaction on phase relaxation decay. We have studied the frozen solutions of Fremy's salt (potassium nitrosodisulfonate),  $(\text{KSO}_3)_2\text{NO}$ , because in liquid solutions it dissociates to form a double-charged nitroxyl anion radical (Fremy's radical) and two counterions of potassium [7]. The study of spin exchange in the Fremy's radical liquid solutions shows that a charge substantially hampers the relative approach of radicals [8-10]. This makes Fremy's radical promising for studying the effects of a charge on the spatial distribution of radicals in the solid phase assuming that upon freezing of solution the main pattern of radical ion spatial distribution will be preserved. As a solvent, we used a water-glycerin mixture frozen as a transparent glass. For comparison, under the same conditions, we have studied the phase relaxation of the uncharged stable nitroxyl radical TEMPON  $(\text{OC}_5\text{H}_2(\text{CH}_3)_4\text{NO})$  and Fremy's radical solutions with the addition of  $\text{K}_2\text{CO}_3$  increasing the ionic strength of solution.

In this paper, the phase relaxation decay has been studied by means of PELDOR. It allows us to distinguish phase relaxation due to the dipole-dipole coupling of spins and the inhomogeneous broadening of ESR spectra, and other

possible mechanisms of magnetic relaxation having no relation to the dipole-dipole coupling of spins [5].

## 2 PELDOR Principles

The PELDOR method is a modification of the ESE method. The PELDOR signal  $V(T)$  in Fig. 1) is the usual ESE signal measured in the presence of an additional pumping pulse which changes the dipole-dipole coupling of spins and thus the ESE decay. The PELDOR method has been described in detail in [5, 11]. Figure 1 shows a sequence of pulses in PELDOR (Fig. 1a) and the continuous-wave (cw) ESR spectrum of nitroxyl in solid in a frequency domain (Fig. 1b). Two microwave pulses 1 and 2 induce the ESE signal 3 at frequency  $\omega_A$  in a spin system. The spin echo signal arises at time  $2\tau$  after the first pulse. Between pulses 1 and 2 a pumping pulse 4 is applied at frequency  $\omega_B$  at time  $T$  after the first pulse. The spins are labeled as A spins (at  $\omega_A$ ) and B spins excited by the pumping pulse at  $\omega_B$ . The pumping pulse induces transitions between the Zeeman levels of B spins and thus changes local magnetic fields for A spins. This results in additional dephasing of A spins and hence in a decrease in the PELDOR signal. This decrease depends on the value of dipole-dipole spin coupling, time position and intensity of pumping pulse. The main decay of the PELDOR signal occurs within the time  $T \sim T_f$ , where  $T_f$  is the phase relaxation time. It depends on the value of dipole-dipole spin coupling between A and B spins. Usually in experiments, time  $\tau$  between pulses 1 and 2 is fixed and the PELDOR signal decay on time  $T$  is studied.

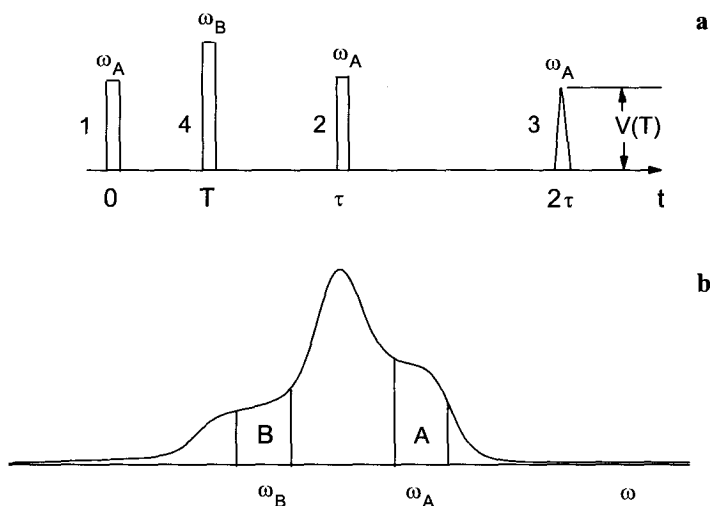


Fig. 1. Sequence of pulses in time (a) and their position in the frequency domain ESR spectrum (b); 1 and 2 are ESE-forming pulses; 3 is the spin echo signal; 4 is the pumping pulse.

### 3 Experimental

The cw ESR spectra of radicals under study were recorded on an ESP-380 Bruker spectrometer (X-band) at a modulation frequency of 100 kHz and modulation amplitude of 1 G in the absence of spectrum saturation. Experiments on PELDOR were performed using an X-band ESE spectrometer supplied with a bimodal resonator and an additional mw source for generating the pumping pulses [11]. The difference in the operating ( $\omega_A$ ) and pumping ( $\omega_B$ ) frequencies was about 100 MHz. The duration of pulses 1 and 2 was 40 and 70 ns, respectively. The pumping pulse duration was about 40 ns. To obtain the ESR spectra and PELDOR decay kinetics, the samples under study were placed in the Dewar flask filled with liquid nitrogen and located in the spectrometer resonator.

The samples were put into glass ampoules 0.5 cm in diameter containing from 50 to 100 ml of the solution under study. As a solvent, we used the water-glycerin mixture containing 30 mol% of water. Solutions were prepared by dissolving the corresponding weighed portions of Fremy's salt or TEMPON in water with subsequent addition of the required amount of glycerin. The samples were frozen by immersing the ampoules into liquid nitrogen. The water-glycerin mixture was frozen to form a transparent glass. We used "pure" glycerin with a density of 1.26 g/cm<sup>3</sup> without repurification. Fremy's salt was synthesized and purified as described in [7]. TEMPON was purified by recrystallization from hexane. The solution ionic strength was changed by adding the necessary amount of K<sub>2</sub>CO<sub>3</sub>. The number of radicals was determined by both the weighed portion and comparing the double integrals of the ESR spectra of the samples under study with the similar values for the CuCl<sub>2</sub>·2H<sub>2</sub>O crystals containing the known number of paramagnetic centers.

### 4 Experimental Results

The cw ESR spectra of TEMPON and Fremy's radical in frozen solutions are shown in Fig. 2. The spectrum shapes are independent of the concentration over the range studied. As follows from Fig. 2, the ESR spectrum shape of Fremy's radical differs from that of TEMPON. These differences are caused by the difference in the chemical structure of the radicals under study and therefore the different  $g$  and  $A$  tensor elements.

The time decay of the PELDOR signal amplitude  $V(T)$  has been obtained for a series of concentrations of TEMPON and Fremy's radical. These data are convenient to be analyzed and represented in coordinates  $\ln(V)/C$  vs.  $T$  where  $C$  is the radical concentration and  $V$  is the PELDOR signal amplitude normalized to 1 at  $T = 0$ . This is due to the fact that for the random distribution of radicals, the time and concentration dependence of  $V$  is exponential [5, 11] and has the form

$$V = \exp(-\alpha pCT) , \quad (2)$$

$$\alpha = \frac{8\pi^2}{9\sqrt{3}} \gamma^2 \hbar \approx 1.65 \cdot 10^{-12} \text{ cm}^3/\text{s} , \quad (3)$$

$$p = \int \frac{\gamma^2 H_1^2}{\gamma^2 H_1^2 + (\omega - \omega_B)^2} \sin^2 \left( \frac{t_p}{2} \sqrt{\gamma^2 H_1^2 + (\omega - \omega_B)^2} \right) g(\omega) d\omega, \quad (4)$$

where  $T$  is the time position of the pumping pulse at  $\omega_B$  after the first pulse at  $\omega_A$ ;  $p$  is the probability that the  $z$ -projection of the B spins changes under the pumping pulse;  $g$  is the gyromagnetic ratio for an electron;  $\hbar$  is a Planck constant;  $H_1$ ,  $t_p$ , and  $\omega_B$  are the amplitude, duration, and frequency of the pumping pulse, respectively;  $\omega$  is the spin frequency in the ESR spectrum in the frequency domain,  $g(\omega)$  is the ESR absorption line normalized to area in the frequency domain. Integration with respect to  $\omega$  is performed in Eq. (4) over the entire ESR spectrum  $g(\omega)$ , and  $p$  values are different for Fremy's and TEMPON radicals due to their different lineshapes.

If Eq. (2) holds, the experimental data should fit the general linear dependence  $\ln(V)/C = \alpha p T$ , where the values  $\alpha$  and  $p$  are set by Eqs. (3) and (4).

Figure 3 shows the experimental dependences of the PELDOR signal amplitude in the given coordinates for TEMPON at different radical concentrations. As follows from Fig. 3, within the error of determination of concentrations and spread in the  $p$  value for different samples, the experimental data for TEMPON fit the general linear dependence.

Figure 4 presents, in the same coordinates, the experimental and calculated dependences for the Fremy's radical solutions. The scattered points in Fig. 4 (dependences I, II, III and IV) show the experimental data obtained under the same conditions as for TEMPON but with another  $p$  value because of the difference in their ESR spectra (Fig. 2). Note that the experimental dependences II and IV were obtained at the same concentration of radical ions in solution, but depen-

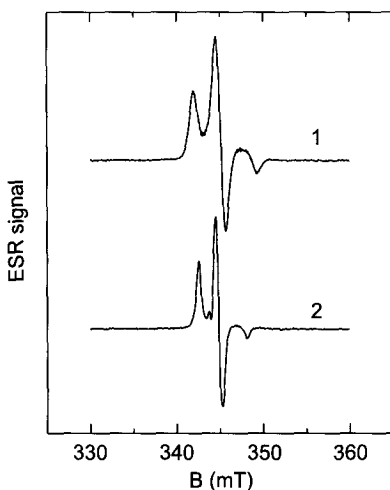


Fig. 2. ESR spectra of TEMPON (1) and Fremy's radical (2) in frozen water-glycerin solutions at 77 K.

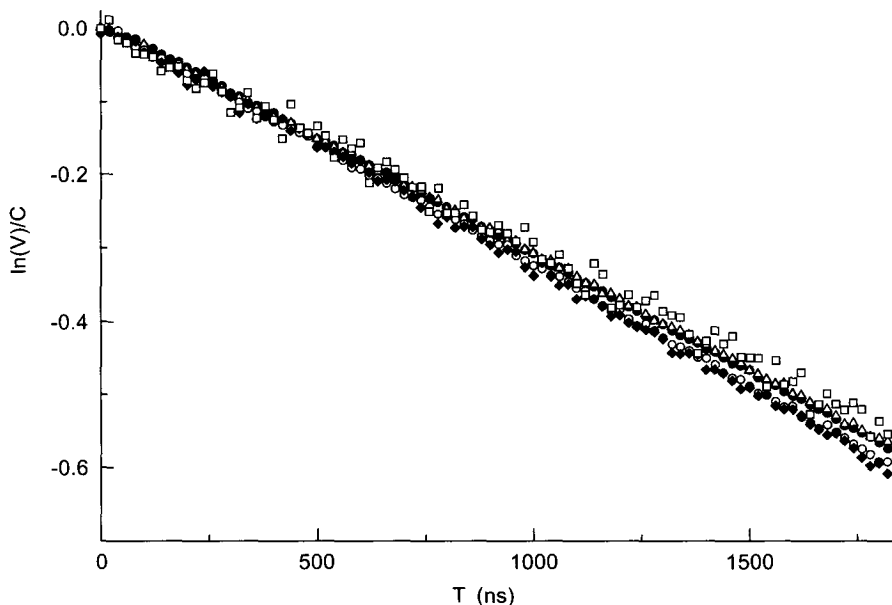
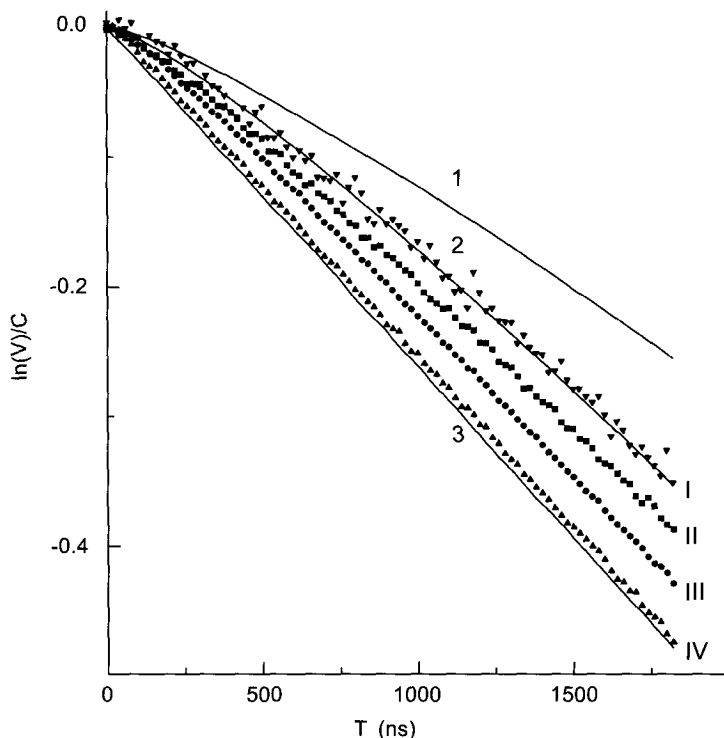


Fig. 3. Experimental dependences of  $\ln(V)/C$  on  $T$  for TEMPN in a frozen water-glycerin mixture at 77 K. Concentrations:  $\square$   $1.7 \cdot 10^{17} \text{ cm}^{-3}$ ;  $\blacklozenge$   $4 \cdot 10^{17} \text{ cm}^{-3}$ ;  $\circ$   $6 \cdot 10^{17} \text{ cm}^{-3}$ ;  $\triangle$   $9 \cdot 10^{17} \text{ cm}^{-3}$ ;  $\bullet$   $1.4 \cdot 10^{18} \text{ cm}^{-3}$ .

dence IV was obtained for the solution with  $\text{K}_2\text{CO}_3$  increasing the ionic strength. The ionic strength value, in this case, was 1 mol/l. The solid lines 1, 2 and 3 in Fig. 4 show the calculated dependences for the Fremy's radical solutions at different values of the ionic strength.

## 5 Discussion

The experimental data shown in Fig. 3 for TEMPN indicate that Eq. (2) is fulfilled and there is a random distribution of TEMPN radicals in a given system. The random distribution of TEMPN radicals in the frozen water-glycerin solution is, probably, due to the absence of specific interactions between these radicals, which can affect their relative arrangement at distances substantially exceeding the radical size. Limitations on the mutual approach of spins determined by the finite radical size can be manifested only at times  $T \approx d^3/\gamma^2\hbar$  where  $d$  is the radical size. For the typical radical size of several ångström, these times amount to tens of nanoseconds and can be compared with pulse durations which makes this type of analysis by PELDOR impossible at this time. Besides, a fraction of spins situated at a distance of nearest contact is small with respect to other spins. Therefore, limitations on nearest spin approach owing to the finite radical size should not cause distortions of exponential dependences in the basic time interval (50–1800 ns).



**Fig. 4.** Experimental and calculated dependences of  $\ln(V)/C$  on  $T$  for Fremy's radical in a frozen water-glycerin mixture at 77 K. Scattered points show the experimental data for the following concentrations: I  $2.6 \cdot 10^{17} \text{ cm}^{-3}$ ; II  $8 \cdot 10^{17} \text{ cm}^{-3}$ ; III  $2.2 \cdot 10^{18} \text{ cm}^{-3}$ ; IV  $8 \cdot 10^{17} \text{ cm}^{-3} + 0.3 \text{ mol/l K}_2\text{CO}_3$ . Solid lines 1, 2 and 3 are calculated for the Fremy's radical concentrations of  $2.6 \cdot 10^{17} \text{ cm}^{-3}$  and the following values of the ionic strength: 1  $I = 0$ ; 2  $I = 1.3 \cdot 10^{-3} \text{ mol/l}$ ; 3  $I = 1.0 \text{ mol/l}$ .

As compared with TEMPON, the data given in Fig. 4 for Fremy's radical do not fit the general dependence for the random radical distribution Eq. (2). Of interest is the nonlinear dependence  $\ln(V)/C$  on  $T$  which is most pronounced at low concentrations of Fremy's salt (Fig. 4). The peculiarity of deviations from linearity is that the relaxation rate at short  $T$  times ( $T \approx 100 \text{ ns}$ ) is considerably lower than that for uniformly distributed radicals and increases with time  $T$ . As the concentration of Fremy's radicals increases, the mean relaxation rate also increases and the  $\ln(V)/C$  function tends to be linear. After addition of  $\text{K}_2\text{CO}_3$ , the relaxation rate increases and  $\ln(V)/C$  becomes linear the same as for TEMPON. The difference in the slopes of curves for TEMPON and Fremy's radical with  $\text{K}_2\text{CO}_3$  addition is due to the difference in the  $p$  values. The  $p$  value was estimated from the slopes of curves for TEMPON and curve 3 in Fig. 4 for Fremy's radical to be 0.19 and 0.16, respectively, with an error of about 5%.

The low phase relaxation rate at short  $T$  times for Fremy's radical indicates that a fraction of the closely spaced spins with the fairly strong dipole-dipole coupling is small. Unlike TEMPON, Fremy's salt is observed in solutions in the

form of ions. Therefore, it is possible to assume that the relative repulsion of negatively charged Fremy's radical ions restricts the probability of the nearest approach in solution. Upon freezing, the peculiarities of the space arrangement of radicals are probably preserved which causes the observed deviations from exponential law Eq. (2) in phase relaxation.

Addition of  $K_2CO_3$  increases the ionic strength and screens the electrostatic interaction of radical ions. As a result, the relative arrangement of radical ions tends to the random distribution. A similar effect is likely to occur with increasing concentration of Fremy's salt in the solution in the absence of  $K_2CO_3$ . In this case, the ionic strength depends on the Fremy's salt concentration.

The influence of mutual repulsion of radical ions on the phase relaxation can be quantitatively described by the classical Debye-Hückel theory for the diluted ion solutions [12]. According to this theory, the concentration of radical ions with charge  $Z$  at a distance  $r$  from the isolated radical ion is given by the equation

$$C(r) = C \exp((-Q/r) \exp(-\chi r)) , \quad (5)$$

$$Q = \frac{Z^2 \varepsilon^2}{DkT} , \quad (6)$$

$$\chi^2 = \frac{8\pi \varepsilon^2}{DkT} I , \quad (7)$$

$$I = \frac{1}{2} \sum_i C_i Z_i^2 , \quad (8)$$

where  $C(r)$  is the concentration of radical ions at a distance  $r$  from a given ion;  $C$  is the mean concentration of radical ions;  $Z$  is the charge of the radical ion given in proton charge units,  $\varepsilon$  is the proton charge,  $D$  is the dielectric constant;  $k$  is the Boltzmann constant,  $T$  is the temperature in kelvin,  $\chi$  is the Debye-Hückel constant,  $I$  is the ionic strength of a solution,  $Z_i$  and  $C_i$  are the charge and concentration of  $i$ -th ions in solution, respectively.

Equation (5) can be used to describe the distance distribution of B spins with respect to A spins for Fremy's radical. This makes it possible to calculate the relaxation decay of PELDOR signal upon time  $T$  and spin concentration  $C$  with the general expression for the relaxation decay of ESE signal [1, 13] in the case of the time-dependent frequency of A spins.

$$V = \left\langle \exp \left( -i \int_0^{2\tau} s(t) \omega_A(t) dt \right) \right\rangle_{av} , \quad (9)$$

$$\omega_A(t) = \omega_A + \sum_B \omega_{AB}(t) , \quad (10)$$

$$\omega_{AB} = \frac{\gamma^2 \hbar (1 - 3 \cos^2(\theta_{AB}))}{r_{AB}^3} S_{BZ}(t) , \quad (11)$$



where  $t$  is the time counted from the first pulse;  $s(t) = 1$  at  $0 < t < \tau$ ,  $s(t) = -1$  at  $\tau < t < 2\tau$ ;  $\omega_A(t)$  is the dependence of the resonance frequency of A spins on time  $t$ ;  $\omega_{AB}(t)$  is the shift in the resonance frequency of A spin owing to the dipole-dipole coupling of A spin with B spin,  $r_{AB}$  is the distance between A and B spins,  $\theta_{AB}$  is the angle between vector  $r_{AB}$  and the direction of external magnetic field,  $S_{BZ}$  is the projection of B spin onto the external magnetic field;  $\langle \rangle_{av}$  is the averaging over all realizations of  $\omega_A(t)$  depending on  $r_{AB}$ ,  $\theta_{AB}$ ,  $p$  and  $t$ . In Eq. (10), summation is performed over all B spins.

The averaging in Eq. (9) was made over  $r_{AB}$ ,  $\theta_{AB}$  and all realizations of time dependence of  $\omega_A(t)$  by the Monte-Carlo technique. In the case of PELDOR, the  $\omega_{AB}(t)$  value, depending on  $r_{AB}$  and  $\theta_{AB}$ , changes its sign with probability  $p$  at  $t = T$  with a change in the  $z$ -projection of B spin under the pumping pulse at  $\omega_B$ . This type of the  $\omega_{AB}(t)$  time dependence makes the calculation of phase relaxation in a given system much easier. With Eq. (5) as the  $r_{AB}$  distribution function and setting  $\theta_{AB}$  random, we have calculated the PELDOR signal decay kinetics for Fremy's radical solutions using the real experimental values for radical concentrations and  $p$  parameters. We assumed that in the absence of  $K_2CO_3$ , the ionic strength of the solution is produced only by dissociation of Fremy's salt.

Results of calculation are given in Fig. 4 by the solid lines. It is seen that the experimental data are described by calculated dependences. Curve 1 is derived at zero ionic strength. It indicates the feasible maximum influence of the charge on the phase relaxation kinetics in a given system.

The choice of the temperature at which the radical distribution and the value of dielectric constant  $D$  in solution upon freezing are fixed, introduces some uncertainty in calculations. However, it has been established that in the studied concentration range, the results are almost independent of the  $DT$  value at a given ionic strength. This is due to the fact that the  $DT$  value is included in both  $Q$  and  $\chi$  of Eq. (5) which smoothes the influence of the  $DT$  value on the final result. Besides, the  $DT$  value does not practically change with temperature, because  $D$  varies close to  $1/T$  law. Taking this into consideration, the  $DT$  value was assumed constant and equal to  $1.64 \cdot 10^4$  at 253.6 K [14].

The  $Q$  and  $\chi$  values provide the scale of distances over which the approach of radical ions at a given ionic strength is rather difficult. Taking the distance  $r_0$  as a characteristic of the radical ion approach, at which concentration  $C(r_0) = 0.5C$ , we get  $r_0 \approx 30$  Å for the lowest concentration ( $2.6 \cdot 10^{17}$  cm<sup>-3</sup>) of Fremy's salt in experiment. This distance is substantially greater than the geometric radius of Fremy's radical amounting to several ångström and is manifested in the phase relaxation kinetics  $V(T)$  at times  $T \approx r_0^3/\gamma^2\hbar$  lying in the microsecond domain.

## 6 Conclusions

It was shown that the magnetic phase relaxation due to the dipole-dipole coupling of spins in the frozen glassy solutions of double-charged radical ions is sensitive to the radical ion distance distribution determined by the electrostatic repulsion of radical ions.

The influence of electrostatic interaction of the Fremy's radical ions on their relative spatial distribution in frozen glassy water-glycerin solutions has been established experimentally. It is shown that an increase in the ionic strength eliminates the effect of electrostatic interaction on the spatial distribution of radical ions. From the experimental data obtained it follows that the freezing of water-glycerin solutions down to 77 K in the form of a transparent glass preserves as in liquids the relative spatial distribution of the Fremy's radical ions. It was shown that at the lowest Fremy's salt concentration in solutions under study the characteristic distance of the Fremy's radical approach is about 30 Å. This value is substantially greater than the geometric radius of Fremy's radical.

The Debye-Hückel theory provides satisfactory description of the spatial distribution of radical dianions in frozen glassy solutions and can serve as a basis for a quantitative description of the processes of magnetic phase relaxation in such systems.

### Acknowledgements

The authors are grateful to I. E. Sokolov for the synthesis and purification of Fremy's salt and to A. G. Maryasov and J. Raap for fruitful discussions and help.

This work was performed at the Center of Chemical Radiospectroscopy of Reactive Intermediates (Novosibirsk) and was supported by Russian Basic Science Foundation (Grant no. 99-03-33149) and partly by Netherlands Organisation for Scientific Research (NWO) (Grant 047-006-009).

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