

A CIDEP study of photolyzed *p*-benzosemiquinone radical in homogeneous solvents and micellar solutions

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Abstract

A comparative study of CIDEP spectra was made, using a highly time-resolved ESR spectrometer, of photolyzed *p*-benzosemiquinone radicals in homogeneous solvents and TX-100 (Triton X-100) micellar solutions. The spectrum obtained from an EG (ethylene glycol)–H₂O homogeneous solution of *p*-benzoquinone (PBQ) contains six major peaks of PBQH· and three minor peaks of PBQ·⁻. In TX-100 EG–H₂O micellar solutions of PBQ, the intensities of PBQ·⁻ peaks increase and become stronger than those of PBQH·. In acid solution, more H₂SO₄ is added to the micellar system than to the homogeneous system to obtain a similar spectrum with an alternating linewidth caused by the proton exchange of PBQH·. Based on the mechanism that polarization of PBQ·⁻ is transferred from PBQH· through its dissociation reaction, special properties of the bound water in the polyethylene glycol shell of TX-100 micelles where photolyzed *p*-benzosemiquinone radicals are generated are discussed to explain these results. © 1997 Elsevier Science B.V.

Keywords: *p*-benzosemiquinone; CIDEP; Micelle; Radical; Triton X-100

1. Introduction

The phenomenon of transient populations of electron spin states differing from the Boltzmann distribution is known as chemically induced dynamic electron polarization CIDEP [1]. There have been studies on the CIDEP of the *p*-benzosemiquinone radical PBQH· in different solvents [2–6], with emphasis on the polarization mechanism of the radicals, but few investigations relate to the CIDEP of the other *p*-benzosemiquinone radicals with different configurations from PBQH·. Smith and Carrington [7] found three configurations of *p*-benzosemiquinone radicals (i.e.

the anion radical PBQ·⁻, single-protonated radical PBQH· and double-protonated cation radical PBQH₂⁺· when studying the dependence of their equilibrated ESR on pH. Pedersen [2] observed a TRESR spectrum from a solution of PBQ which showed peaks from both PBQH· and PBQ·⁻, using a square-wave xenon illuminator and an ESR spectrometer operated with the high-frequency field modulation technique. However, the intensity of the PBQ·⁻ peaks was much weaker than that of the PBQH· peaks, without a sufficient amount of PBQ·⁻ being obtained. In recent years, the behavior (such as CIDEP) of transient radicals in micellar systems has become both of experimental and of theoretical interest [8,9]. The unusual spectra of these radicals have shown some effects of micelles on the CIDEP mechanism, but few of

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them revealed other influences such as the effect on the proton exchange of radicals.

In this work, the CIDEP spectra of photolyzed *p*-benzosemiquinone radicals in Triton X-100 (TX-100) micellar solutions and solutions without added surfactant were studied with a highly time-resolved ESR spectrometer. The CIDEP signals of the three kinds of *p*-benzosemiquinone radicals ($\text{PBQH}\cdot$, $\text{PBQ}\cdot^-$ and $\text{PBQH}_2\cdot^+$) were obtained under different conditions. On the basis of the special properties of the microenvironment where the laser flash photolysis reaction of PBQ takes place, the effect of TX-100 micelles on the spin polarization of the different *p*-benzosemiquinone radicals and upon proton exchange are discussed.

2. Experimental

All spectra were recorded on a time-resolved ESR spectrometer, which has been illustrated in detail elsewhere [10,11]. The instrument mainly consists of a conventional X-band ESR spectrometer, an SRS 252 boxcar integrator, a PM 2556 digital oscilloscope and a broadband preamplifier with a response time of 50 ns. An excimer laser was used for photolysis of the samples. The laser, a Lambda Physik LPX 105 excimer laser (Xe-HCl gas mixture), operating at 308 nm with a pulse energy of 60 mJ/pulse, was fired at repetition rate of 20 Hz. The experiments were performed with a flowing system consisting of a flat (0.3 mm) cell. pH values were measured with a PHS-2 acidometer. All chemicals used were of a A.R. grade. Water was distilled and PBQ was purified by sublimation. Solutions were prepared with ethylene glycol (EG) or a mixture of EG and water (1:1 volume ratio) as solvents, with a 0.01 mol l^{-1} concentration of PBQ in all solutions. The concentration of TX-100 varied from 0.032 to 0.081 mol l^{-1} , all above the critical micelle concentration (cmc).

3. Results and discussion

3.1. Effect of TX-100 micelles on the generation of spin-polarized $\text{PBQ}\cdot^-$ radical

Before considering the results, it is necessary to recall the CIDEP mechanism of $\text{PBQH}\cdot$ radicals

photolyzed by laser flash [2]. The first three steps in the generally accepted reaction scheme for phototypically excited quinones may be applied to PBQ as follows:



The superscripts 1 and 3 indicate excited singlet and triplet states. RH is the hydrogen donor which, as in the experiments reported here, may be solvents (i.e. EG). The polarization of $\text{PBQH}\cdot$ due to the TM origin results in emissive peaks of all radicals in the CIDEP spectrum. Fig. 1(a) shows the TRESR spectrum obtained by direct detection of a laser flash photolyzed EG solution of PBQ (0.01 M). The spectrum represents the electron spin polarization at $1.2 \mu\text{s}$ after the excimer laser flash, averaged with the boxcar averager with a $0.3 \mu\text{s}$ gate aperture. The spectrum contains six major emissive peaks of $\text{PBQH}\cdot$ identical with those reported previously [5]. The coupling constants for $\text{PBQH}\cdot$ are 0.48 and 0.17 mT. Moreover, three minor peaks marked by arrows can be resolved among the major six peaks. With the mixture of EG and H_2O (1:1 volume ratio) as solvent, as observed in Fig. 1(b), six major peaks become wider than those in Fig. 1(a) were observed. However, the three minor peaks still exist.

Interestingly, the three minor peaks among the $\text{PBQH}\cdot$ major peaks increase in intensity with the addition of TX-100 to the solution in Fig. 1(b). The more TX-100 is added, the more the minor peaks' increase in intensity. Fig. 2 shows the TRESR spectra obtained from EG- H_2O solutions of TX-100 of different concentrations containing PBQ.

To confirm the assignment of the minor peaks, the time-resolved curves for all peaks in the above system (Fig. 2(b)) were recorded. It was found that the six major peaks of $\text{PBQH}\cdot$ have the same decay rate of the TRESR intensity ($1/T_1^{\text{eff}}$) and so do the three minor peaks. However, the decay rate of the minor peaks is different from that of the major peaks. Fig. 3 indicates the time-dependent

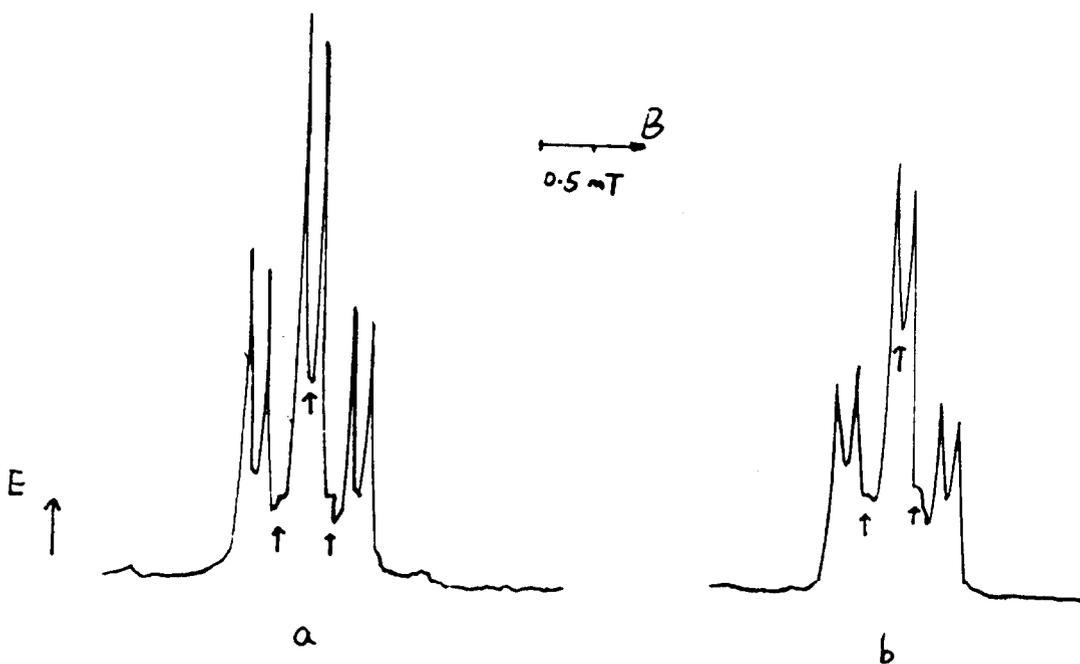


Fig. 1. TRESR spectra taken 1.2 μ s after excitation of PBQ in (a) EG and (b) EG-H₂O solution (0.01 M). In this and all subsequent figures, signals above the baseline are in emission and those below are in absorption.

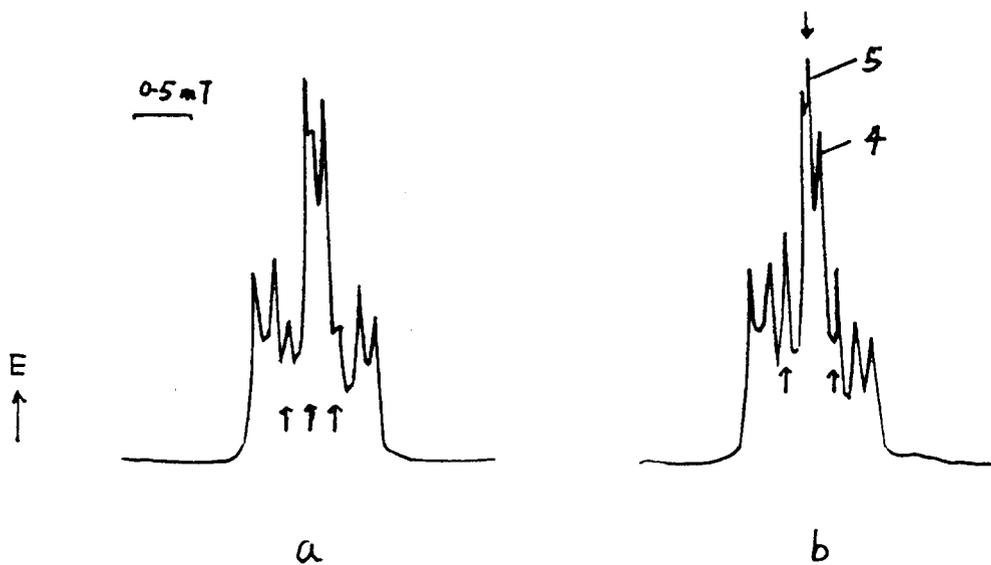


Fig. 2. TRESR spectra taken 0.8 μ s after excitation of PBQ in EG-H₂O solutions of TX-100 at concentrations of (a) 0.032 and (b) 0.081 M.

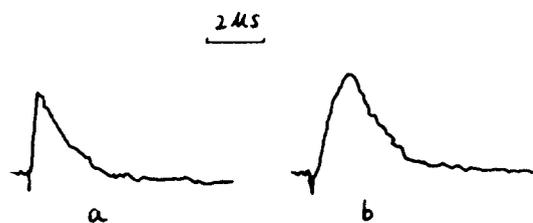
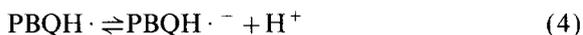


Fig. 3. Time-dependent intensity curves for (a) peak 4 and (b) peak 5 with 4 mW microwave power.

intensity curves for peak 5 (one of the minor peaks) and peak 4 (one of the major peaks).

It can be calculated that the relaxation time T_1 for peak 4 is 1.6 μs and that for peak 5 is 2.2 μs . It takes peak 4 0.3 μs to increase in intensity from zero to the maximum but peak 5 takes only 1.1 μs . The two different T_1 s and the two different times of the signal's increment indicate that the minor peaks can be assigned to a *p*-benzosemiquinone radical with another configuration (i.e. *p*-benzosemiquinone anion radical $\text{PBQ}\cdot^-$), according to Pedersen et al. [2]. Fig. 2 shows the overlap of peaks from both $\text{PBQH}\cdot$ and $\text{PBQ}\cdot^-$. There are five hyperfine lines for $\text{PBQ}\cdot^-$ with the coupling constant being 0.22 mT, in agreement with the literature [2]. However, the two sidelines in the low and high field, for $\text{PBQ}\cdot^-$ are too weak to be resolved, so only three peaks can be seen in Fig. 2. It was found that the intensity of the five $\text{PBQ}\cdot^-$ peaks increases when NaOH was added to the system in Fig. 2b and the $\text{PBQH}\cdot$ peaks decrease at the same time. As shown in Fig. 4, there are only five peaks of $\text{PBQ}\cdot^-$ remaining in the spectrum when the pH reaches 10.02. This phenomenon gives further good evidence of the minor peaks' assignment to $\text{PBQ}\cdot^-$, as the polarization of $\text{PBQ}\cdot^-$ is transferred from $\text{PBQH}\cdot$ in the forward reaction of the scheme [4]:



Hence both T_1 and the time for the intensity of the TRESR peaks to increase from zero to the maximum of $\text{PBQ}\cdot^-$ are longer those for $\text{PBQH}\cdot$, as for the results calculated from Fig. 3. If the dissociation rate of $\text{PBQH}\cdot$ is greater than the decay rate by relaxation, $\text{PBQH}\cdot$ will transfer its polarization energy effectively to $\text{PBQ}\cdot^-$. Since

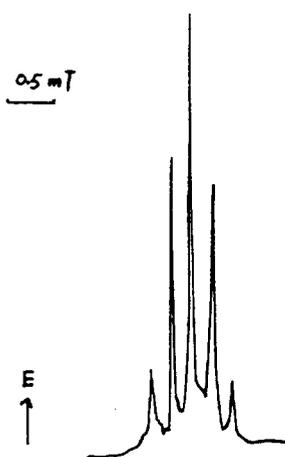


Fig. 4. TRESR spectrum taken 0.8 μs after excitation of PBQ in an EG-H₂O solution of TX-100 with [TX-100]=0.081 M and pH=10.02.

the spin angular momentum as well as the polarization phase remain constant in the course of transfer, $\text{PBQ}\cdot^-$ gives emissive peaks in the spectrum just as $\text{PBQH}\cdot$ does. By increasing the pH of the system, the dissociation of $\text{PBQH}\cdot$ will be facilitated and more $\text{PBQ}\cdot^-$ radicals will be produced. As shown in Fig. 4, the peaks from $\text{PBQ}\cdot^-$ become the major ones in the spectrum. In an EG solution of PBQ without TX-100, the CIDEP signal of $\text{PBQ}\cdot^-$ is much weaker than that of $\text{PBQH}\cdot$ since the dissociation of $\text{PBQH}\cdot$ is difficult because of the small dielectric constant of EG solvent. The same applies in a solution with EG-H₂O as solvent because of the slight acidity (pH=5.5) of the system, although the dielectric constant is higher than that of EG solution. As shown in Fig. 1, the spectra of both systems mainly contain emissive peaks from $\text{PBQH}\cdot$. The results from Fig. 2 showing that the peak intensities of $\text{PBQ}\cdot^-$ increase when TX-100 is added indicate that TX-100 plays almost the same role as NaOH. The micellar environment provided by TX-100 is the cause.

Some properties, such as the dielectric constant and microviscosity of the bound water in micelles or microemulsions, are different from those for the free water in the bulk solution. It has been found by Barbaric and Luisi [12] while preparing bulk and micellar solutions with the same apparent pH

value that the pH reflected by the bound water in the latter was higher than that by the free water in the former, and sometimes the pH difference reached as high as 4.5.

Being a small organic molecule with some polarity, PBQ is solubilized in micelles and the solubilization position can be assessed on the basis of some theoretical work [13]. For TX-100 micelles PBQ is solubilized in the polyethylene glycol shell where bound water (by hydrogen bonding between TX-100 and H₂O) gives a higher pH value than in bulk solution. Thus the photolyzed PBQH· radicals dissociate more easily. On the other hand, the hydrogen atom located in the OH group of PBQH· is slightly positively charged because of the attraction of π -bonding of the benzene ring to electrons of the OH group. This intensifies the hydrogen bonding attraction between the oxygen atom in the polyethylene glycol chain of TX-100 and the above-mentioned hydrogen atom of PBQH·, which helps the dissociation of PBQH·. Owing to the above two factors, more secondary PBQ radicals are produced and the CIDEP signals of PBQ·⁻ increase greatly in TX-100 micellar solution.

3.2. Effect of TX-100 micelles on the proton exchange of PBQH· radicals

Although the theory of electron exchange is well documented [14], and the behaviour of equilibrated radicals is well known [15], the case of proton exchange has not been considered previously with regard to spin polarized radicals. Here the situation which leads to alternating linewidths is considered. It will be seen that alternating linewidths also arise in spin polarized systems.

When H₂SO₄ is added to the above-mentioned systems, the spectra change markedly. We begin with the EG–H₂O homogeneous solution of PBQ without TX-100 (Fig. 1b system). The spectra are shown in Fig. 5. With increasing acidity the six high-emissive peaks (Fig. 5a) change into three wider peaks (Fig. 5b), then gradually evolve into five wide peaks (Fig. 5c) and finally into five sharp peaks (Fig. 5d). The pH values of the system to obtain three wide and five sharp peaks are 2.90 and 2.02, respectively. The five sharp peaks are

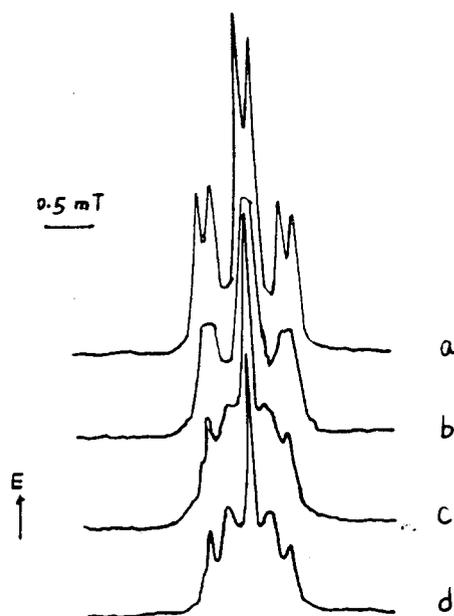
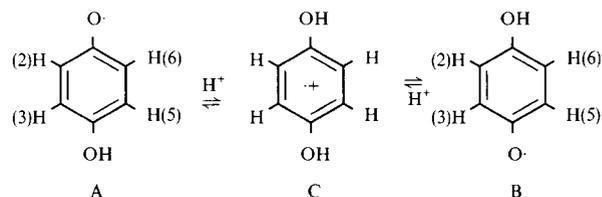


Fig. 5. TRESR spectra taken at 0.8 μ s after excitation of PBQ in EG–H₂O solution at pH (a) 5.5, (b) 2.90, (c) 2.65 and (d) 2.02.

assigned to the doubly protonated cation radical PBQH₂^{·+} with a hyperfine coupling constant of 0.22 mT.

The above changes are due to proton exchange of PBQH·. The exchange rate depends on the proton concentration in the solution. PBQH· has two configurations, A and B, which are thermodynamically equivalent to each other [7]:



The proton of OH transfers from A to B through medium C (i.e. PBQH₂^{·+} radical). Protons located at positions 2 and 6 are not completely equivalent to those in positions 3 and 5 both for configurations A and B. This leads to a series of changes in the TRESR spectra with the exchange rate increasing. In a system of pH 5.5 with weak acidity, protons exchange very slowly and the spectrum

gives six peaks which are characteristic of $\text{PBQH}\cdot$ (Fig. 5a). With increasing $[\text{H}^+]$ the proton exchange process speeds up and results in alternating linewidth in the TRESR spectra in Figs. 5b and c. At the maximum rate of exchange (Fig. 5d system) the spectrum shows five sharp peaks of $\text{PBQH}\cdot_2^+$ radical owing to the four equivalent protons of the benzene ring.

Once again, important new phenomena arise when the time dependence of the spectra is studied. The different hyperfine lines decay with time at different rates because the proton exchange process has different effects on different hyperfine lines. Fig. 6 shows the time dependence of five sharp peaks of $\text{PBQH}\cdot_2^+$ at pH 2.02. The outer lines of $M = \pm 2$ decay first, followed by the central lines of $M = 0$ and eventually the $M = \pm 1$ hyperfine lines decay. It can be concluded that the $M = \pm 1$ hyperfine lines are affected by the proton exchange most, then the $M = 0$ and the $M = \pm 2$ lines the least of all.

H_2SO_4 was then added to the EG– H_2O TX-100 micellar solution of PBQ with a 0.081 M concentration of TX-100. At first, the $\text{PBQ}\cdot^-$ peaks gradually decay with the addition of H_2SO_4 and only the six peaks of $\text{PBQH}\cdot$ remain in the

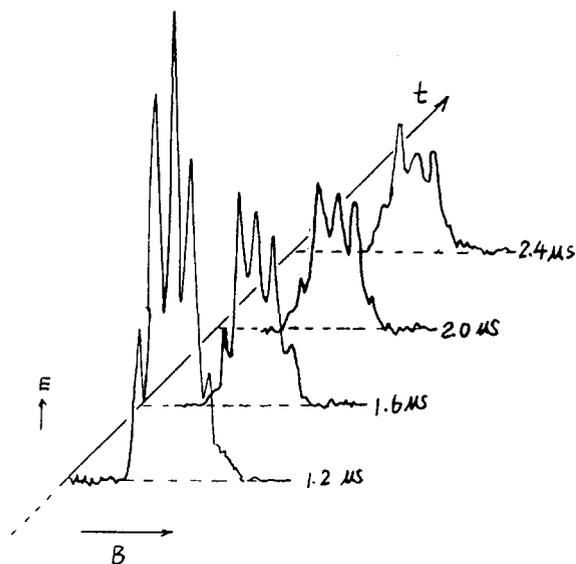


Fig. 6. Variation with time in the TRESR spectrum of the system of PBQH_2^+ radicals at pH 2.02.

spectrum at a definite pH value. When further H_2SO_4 is added, the evolution from six peaks to three wide peaks (pH 2.65) and eventually to five sharp peaks (pH 1.60) occurs again in the spectra as shown in Fig. 5. However, more H_2SO_4 is needed for the micellar solution to obtain a similar change in the spectra caused by proton exchange of $\text{PBQH}\cdot$. For example, the spectrum of the TX-100 micellar solution evolves from alternating linewidth to five sharp $\text{PBQH}\cdot_2^+$ peaks at a lower pH (1.60) than the homogeneous system (2.02). In other words, TX-100 micelles decrease the rate of proton exchange of $\text{PBQH}\cdot$ radicals. The concentration of TX-100 influences the pH for the five sharp peaks of $\text{PBQH}\cdot_2^+$, which is shown in Table 1. Also, $\Delta[\text{H}^+]$ (the H^+ deviation of TX-100 micellar solution to obtain $\text{PBQH}\cdot_2^+$ peaks from homogeneous solution) can be calculated from the data in Table 1. $\Delta[\text{H}^+]$ increases with increase in $[\text{TX-100}]$, as shown in Fig. 7. Hence at a higher TX-100 concentration, the proton exchange rate will be decreased to a greater degree.

TX-100 micelles show effects something like capturing the H^+ in the solution studied above. Therefore, the $\text{PBQH}\cdot$ proton is hindered from exchange through $\text{PBQH}\cdot_2^+$ medium. With PBQ solubilized in the polyethylene glycol shell of TX-100 micelles, a higher pH value in the local area is caused by the bound water and hydrogen bondings. This has been analyzed in the above discussion. It is just the decrease in $[\text{H}^+]$ compared with the bulk solution that hinders the proton exchange process from taking place in the microenvironment supplied by TX-100 micelles.

4. Conclusion

Through the CIDEP study of transient *p*-benzo-semiquinone radicals in homogeneous solution and micellar solution, we believe that some behaviors of transient radicals may be influenced by micelles. Concerning TX-100 micellar solutions because of the higher pH caused by the bound water in the TX-100 micelles polyethylene glycol shell, spin polarized $\text{PBQH}\cdot$ radicals are more easily dissociated into $\text{PBQ}\cdot^-$. More $\text{PBQ}\cdot^-$ radicals are produced, with polarization transferred from $\text{PBQH}\cdot$

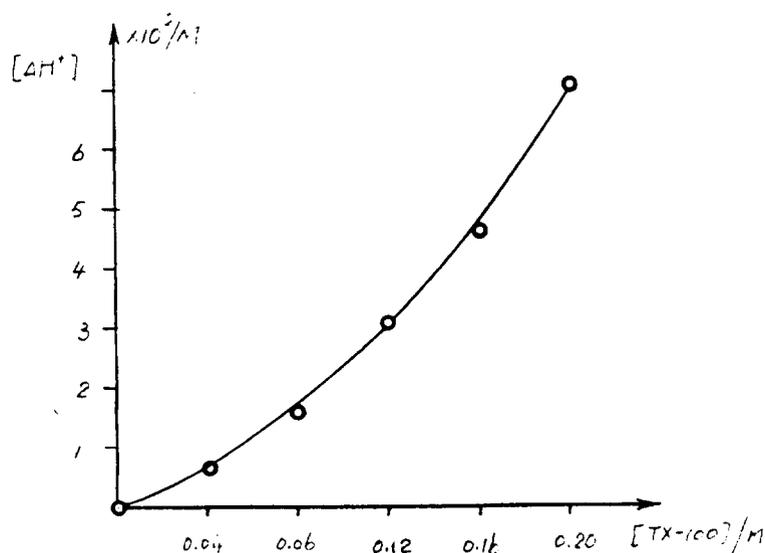
Fig. 7. Curves of $\Delta[\text{H}^+]$ vs. $[\text{TX-100}]$.

Table 1

pH values of systems with different TX-100 concentrations to obtain five sharp peaks of $\text{PBQH} \cdot ^{+2}$

TX-100 (M)	pH	TX-100 (M)	pH
0	2.02	0.12	1.40
0.04	1.80	0.16	1.26
0.08	1.60	1.10	1.10

radicals more effectively. Hence $\text{PBQ} \cdot ^-$ peaks in the spectra of TX-100 micellar solutions are more intense than $\text{PBQH} \cdot$ peaks. For the same reason proton exchange of $\text{PBQH} \cdot$ is hindered by TX-100 micelles under acidic conditions.

Acknowledgement

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