BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1022—1027 (1970)

Solvent Effects on the *g* Factors of Semiquinones

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(Received October 17, 1969)

The dependence of the *g* factors of *p*-benzosemiquinone and its tetrahalogenated derivatives on the solvent composition has been studied in the dimethyl sulfoxide-water system. When the water content of the solvent increases, the *g* factor of *p*-benzosemiquinone decreases, that of tetrachloro-*p*-benzosemiquinone scarcely changes, and the *g* factors of tetrabromo- and tetraiodo-*p*-benzosemiquinones increase. These phenomena are interpreted qualitatively by assuming that the water molecule solvates to the carbonyl oxygen atom of semiquinones and by using Stone's equation for the *g* factor of the polyatomic radical. The dependence of the *g* factor of *p*-benzosemiquinone on the solvent composition is quantitatively studied by means of the theory of solvent effects proposed by Gendell, Freed and Fraenkel and by using the 2-site model of Stone and Maki and also the 4-site model. The former model assumes that one carbonyl oxygen atom has one site occupied by a solvent molecule, thus resulting in a dominant *g* shift. In the later model, two solvent molecules interact with one carbonyl oxygen atom. Both models predict the same relation between the *g* shift and the solvent composition; this experiment cannot confirm which model is more adequate, although the deduced values of the equilibrium constants indicate that the 4-site model is preferable.

In two previous papers[1,2] we have studied the effects of solvents on the *g* factors of diphenyl nitric oxide and di-*t*-butyl nitric oxide; these investigations gave useful information about solvent-solute interactions, especially regarding the hydrogen-bond.

Although the solvent effects on the hyperfine coupling constants of the proton, carbon-13, and oxygen-17 of semiquinones have been extensively investigated,[3-7] the solvent effects on their *g* factors have attracted little attention[8]; therefore, a further extensive investigation of the solvent

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[1] T. Kawamura, S. Matsunami, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1935 (1965).

[2] T. Kawamura, S. Matsunami and T. Yonezawa, *ibid.*, **40**, 1111 (1967).

[3] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

[4] J. Gendell, J. H. Freed and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).

[5] E. W. Stone and A. H. Maki, *J. Amer. Chem. Soc.*, **87**, 454 (1965).

[6] M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

[7] W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 4119 (1966).

[8] R. J. Zandstra, *J. Chem. Phys.*, **41**, 3655 (1966).

effect on the *g* factors of semiquinones seems to be required.

p-Benzosemiquinone and its tetrahalogenated derivatives are generated electrochemically in the mixed solvent system of water and dimethyl sulfoxide (DMSO). The *g* factors of these radicals are measured in solvents of various compositions. These data are quantitatively explained in terms of the Gendell, Freed, and Fraenkel (GFF) theory;[4] this procedure accounts for these solvent effects on the assumption that the solvent forms localized complexes with oxygen atoms in carbonyl groups. Moreover, the shifts in the *g* factors of these semiquinones can be quantitatively explained by means of Stone's theory[9] regarding *g* factor of the polyatomic radical.

Experimental

p-Benzoquinone and chloranil were obtained commercially and were purified by recrystallization. The bromanil and iodanil were synthesized by the method of Torrey and Hunter[10] and were subsequently purified by recrystallization.

Semiquinones were generated by diffusion-controlled electroreduction within the microwave cavity of a 10^{-3} mol/*l* solution of quinone in DMSO, water, and various mixtures of both solvents under a vacuum. The reduction potential was controlled as the yellow color of the semiquinone arose near the mercury cathode. The supporting electrolyte was 0.05M tetraethylammonium perchlorate or sodium perchlorate in solutions with mole fractions of water less than or greater than 0.5 respectively.[5]

The water content of the mixed solvent was determined by means of the Karl-Fisher method.[11]

The electron spin resonance (ESR) spectra were observed by means of a JEOL JES-3BSX instrument with a 100 kHz field modulation and operating at a nominal frequency of 9.4 GHz.

For the measurement of the *g* factor, a glass capillary was attached to the sample tube. The capillary was filled with a reference compound, an alkaline aqueous solution of the potassium peroxylamine disulfonate or the tetracene cation radical in concentrated sulfuric acid, the *g* factors of which were assumed to be 2.005590 or 2.002604[12] respectively.

Results and Discussion

Table 1 lists the experimental values of the *g* factor of *p*-benzosemiquinone (I) for various mole fractions of water, designated by N_W, in mixture with DMSO. The values of the *g* factors decrease

TABLE 1. *g* FACTOR OF *p*-BENZOSEMIQUINONE IN MIXTURES OF WATER AND DIMETHYL SULFOXIDE

N_w[a]	g[b]
0.000	2.005182±0.000003
0.014	2.005169±0.000003
0.043	2.005147±0.000002
0.083	2.005125±0.000004
0.196	2.005065±0.000002
0.268	2.005030±0.000004
0.489	2.004928±0.000007
0.650	2.004845±0.000003
0.777	2.004778±0.000004
0.892	2.004722±0.000004
0.950	2.004693±0.000006
0.980	2.004670±0.000002
1.000	2.004659±0.000003

a) Mole fraction of water.
d) Determined by using an alkaline aqueous solution of potassium peroxylamine disulfonate as a reference, *g* factor of which is assumed to be 2.005590.

TABLE 2. *g* FACTOR OF TETRACHLORO-*p*-BENZOSEMIQUINONE IN MIXTURES OF WATER AND DIMETHYL SULFOXIDE

N_w[a]	g[b]
0.00	2.005859±0.000005
0.10	2.005852±0.000007
0.20	2.005847±0.000005
0.40	2.005868±0.000008
0.60	2.005875±0.000008

a) Mole fraction of water.
Maximum error: ±0.02.
d) Determined by using tetracene cation radical in conc. sulfuric acid as a reference, *g* factor of which is assumed to be 2.002604.

TABLE 3. *g* FACTOR OF TETRABROMO-*p*-BENZOSEMIQUINONE IN MIXTURES OF WATER AND DIMEHYL SULFOXIDE

N_w[a]	g[b]
0.00	2.008433±0.000016
0.10	2.008482±0.000007
0.20	2.008486±0.000016
0.40	2.008596±0.000007
0.60	2.008700±0.000007

a) Mole fraction of water.
Maximum error: ±0.02.
d) Determined by using an alkaline aqueous solution of potassium peroxylamine disulfonate as a reference, *g* factor of which is assumed to be 2.005590.

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[9] A. J. Stone, *Proc. Roy. Soc. Ser. A* **271**, 424 (1963); *Mol. Phys.*, **6**, 509 (1963).

[10] H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).

[11] C. D. McKinney, Jr., and R. T. Hall, *Ind. Eng. Chem.*, **15**, 460 (1943).

[12] B. G. Segal, M. Kaplan and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

TABLE 4. *g* FACTOR OF TETRAIODO-*p*-BENZOSEMIQUINONE IN MIXTURES OF WATER AND DIMETHYL SUIFOXIDE

N_w[a)]	g[b)]
0.000	2.011399±0.000003
0.049	2.011439±0.000003
0.090	2.011469±0.000003
0.211	2.011559±0.000010
0.282	2.011631±0.000007
0.394	2.011791±0.000010
0.503	2.011971±0.000003

a) Mole fraction of water.
b) Determined by using an alkaline aqueous solution of potassium peroxylamine disulfonate as a reference, *g* factor of which is assumed to be 2.005590.

with the increase in N_W.

The experimental values of the *g* factors of tetrachloro-*p*-benzosemiquinone (II), tetrabromo-*p*-benzosemiquinone (III), and tetraiodo-*p*-benzosemiquinone (IV) are summarized in Tables 2, 3, and 4 respectively. Since tetrahalogenated derivatives of *p*-benzoquinone do not dissolve in water, the *g* factors of semiquinones derived from these quinones can not be obtained for high values of N_W.

Shifts of the *g* Factors of *p*-Benzosemiquinone and Its Tetrahalogenated Derivatives. Figure 1 shows plots of the *g* factors of *p*-benzosemiquinone and its tetrahalogenated derivatives against N_W. As N_W increases, the *g* factor of I decreases, and that of II scarcely changes, while that of III increases and the *g* factor of IV increases even more steeply than that of III.

According to Stone's equation for the *g* factor of a polyatomic radical,[9)] the *g* factors of these semiquinones can be approximately given as:[13)]

$$g \simeq 2.00232 + 2\Delta g_O + 4\Delta g_X \qquad (1)^{14)}$$

$$\Delta g_O = \frac{a\zeta_O C_O^2 \ \rho_O{}^\pi}{\Delta E_O} \qquad (2)$$

$$\Delta g_X = \frac{b\zeta_X C_{X\sigma}^2 \rho_X{}^\pi}{\Delta E_X} \qquad (3)$$

where *a* and *b* are positive constants; ζ_O and ζ_X are the L–S coupling constants about oxygen and halogen nuclei; $C_{O\sigma}{}^2$ or $C_{X\sigma}{}^2$ implies the square of the coefficient of the p_σ atomic orbitals of oxygen or halogen in lone-pair orbitals on it, and $\rho_O{}^\pi$ and $\rho_X{}^\pi$ denote the odd-electron density on the oxygen and on the halogen atoms respectively. ΔE_O or ΔE_X is the energy for a transition of a lone pair electron localized on oxygen or halogen atoms to the odd electron π orbital, respectively.

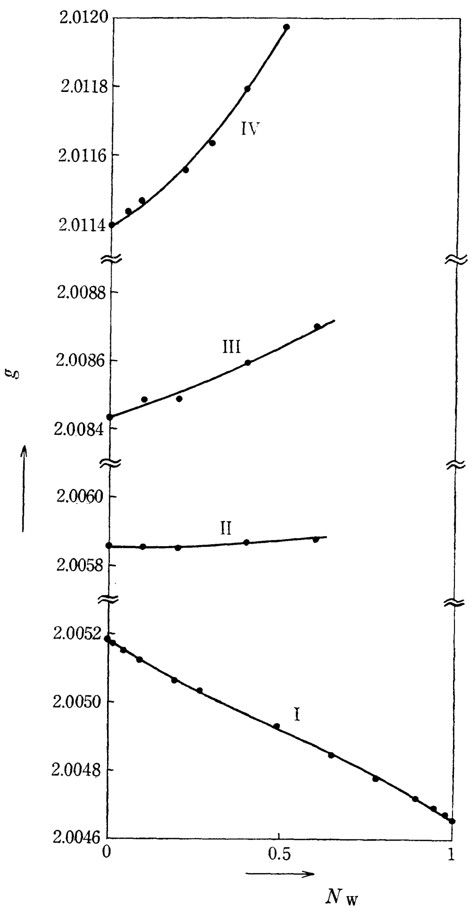


Fig. 1. Observed *g* factors of *p*-benzosemiquinone (I), tetrachloro-*p*-benzosemiquinone (II), tetrabromo-*p*-benzosemiquinone (III), and tetraiodo-*p*-benzosemiquinone (IV) *vs.* mole fraction of water in solution of DMSO-water.
The curve for I expresses calculated behavior (See text).

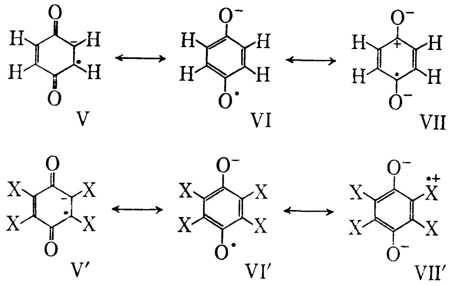
Δg_X and Δg_O then, indicate the contributions of lone parirs on oxygen and halogen respectively to the *g* factor. The L–S coupling constants of oxygen and halogen are greater than that of carbon (ζ_C=28 cm^{-1}, ζ_O=152 cm^{-1} ζ_{Cl}=587 cm^{-1}, ζ_{Br}=2460 cm^{-1}, ζ_I=5060 cm^{-1}),[15)] and the σ–π^* and π–σ^* transition energies are greater than ΔE_O and ΔE_X; hence, the other terms contribute only a little to the *g* factors of semiquinones and are neglected in this discussion. Changes in the electronic structure and a resulting shift in the *g* factor, accompanied by a change in the solvent from DMSO to water, are denoted by δ. For example, when *g* is the *g* factor in DMSO, $g+\delta g$ is that in water.

[13)] See also H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

[14)] In the case of *p*-benzosemiquinone, the last term in Eq. (1) should be ignored.

[15)] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

We assume that semiquinones in water form a hydrogen bond between their lone pairs on the oxygen atom and the solvent molecule, but not between their halogen atoms and the water molecule. Hydrogen-bond formation to the oxygen atom in a carbonyl group affects the odd-electron distribution through increasing the effective electronegativity of oxygen, while it decreases the odd-electron density on oxygen and increases that on halogen.



(4)

(X: halogen)

When the effective electronegativity of oxygen increases, the weight of the structure VII or VII′ can be expected to increase in resonance (4). Therefore, as to the changes in ρ_O^π and ρ_X^π,

$$\delta\rho_O^\pi < 0 \tag{5}$$

$$\delta\rho_X^\pi > 0 \tag{6}$$

are expected. Broze, Luz, and Silver[16] have reported that the absolute values of the oxygen-17 hyperfine coupling constants of *p*-benzosemiquinone and tetrachloro-*p*-benzosemiquinone in aprotic solvents are larger than those in protic solvents. These results also confirm the inequality (5).

A hydrogen-bond formation changes ΔE_O and $\Delta C_{O\sigma}{}^2$ thus:

$$\delta\Delta E_O > 0 \tag{7}$$

$$\delta C_{O\sigma}^2 < 0, \tag{8}$$

these phenomena are known as the blue-shift of the *n*–π^* transition and the delocalization of lone-pair electrons onto hydrogen respectively.[17] By comparing Eqs. (2) and (3) and the inequalities, (5)—(8), we obtain:

$$\delta\Delta g_O < 0 \tag{9}$$

$$\delta\Delta g_X > 0. \tag{10}$$

Since the L–S coupling constants of halogens decrease in the following order:

$$\zeta_{Cl} < \zeta_{Br} < \zeta_I, \tag{11}$$

we may expect:

$$0 < \delta\Delta g_{Cl} < \delta\Delta g_{Br} < \delta\Delta g_I.$$

The discussion above can explain the interesting feature shown in Fig. 1, since:

$$\delta g_{I} = 2\delta g_O < 0$$

$$\delta g_{II} = 2\delta g_O + 4\delta\Delta g_{Cl} \simeq 0$$

$$\delta g_{III} = 2\delta\Delta g_O + 4\delta\Delta g_{Br} > 0$$

$$\delta g_{IV} = 2\delta\Delta g_O + 4\delta\Delta g_I > \delta g_{III}.$$

Analysis of the Dependence of the *g* Factor of *p*-Benzosemiquinone on *N*w. Gendell, Freed, and Fraenkel[4] assume that the electronic structure of a radical is affected by radical-solvent complexing, and that each type of complex is characterize by a unique value of the coupling constant, *a*. The formation and decomposition of complexes is so rapid in our case, however, that only a single averaged coupling constant, $\bar{a}$, is observed, *i. e.*:

$$\bar{a} = \sum_i p_i a_i \quad (\text{with} \sum_i p_i = 1) \tag{12}$$

where a_i is the coupling constant characteristic of the *i*th solvent-radical complex, with represents a fraction, p_i, of the total concentration of the radical. The p_i can be evaluated in terms of a series of solvent-radical association equilibria. Although the GFF theory has been proposed in accounting for solvent effects on the coupling constant, this theory is also applicable at discussion of solvent effects on the *g* factor, for

$$\bar{g} = \sum_i g_i p_i, \tag{13}$$

where $\bar{g}$ is an observed *g* factor, g_i denotes the *g* factor of the *i*th complex, and p_i has the same meaning as in Eq. (12).

Stone and Maki[5] studied the ^{13}C coupling constant of *p*-benzosemiquinone-1-^{13}C in a DMSO-water mixed solvent and explained their data quantitatively by assuming three types of solvated species, DRD, WRD, and WRW, where R is the radical anion, D is a DMSO molecule, and W is a water molecule. Their model for solvated complexes assumes that two solvent molecules solvate to one semiquinone molecule; it is referred to as the 2-site model in this work. We used this model in discussing solvent effects on the *g* factor of *p*-benzosemiquinone. We also analyzed the present data with the 4-site model. This model assumes that 4 solvent molecules solvate to one semiquinone molecule.

2-Sitie Model. The equilibria proposed by Stone and Maki[5] are:

$$\text{DRD} + \text{W} \overset{K_1}{\rightleftarrows} \text{DRW (and WRD)} + \text{D}$$

$$\text{DRW} \overset{K_s}{\rightleftarrows} \text{WRD}$$

$$\text{W} + \text{DRW (and WRD)} \overset{K_2}{\rightleftarrows} \text{WRW} + \text{D}. \tag{14}$$

They assumed, in the complex formation, that one carbonyl group of the radical has one site occupied by a solvent molecule and that the electronic state of the radical is perturbed. In Eq. (14), DRW

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16) M. Broze, Z. Luz and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967).

17) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman Co., San Francisco (1960).

or WRD refers to a complex in which the water molecule is complexed with one carbonyl or with the other carbonyl respectively, and it is assumed that $K_3=1$. When the equilibria in (14) are assumed to explain the solvent effects on the g factor of p-benzosemiquinone, the g factor is given by:

$$\bar{g}=\frac{g_1+K_1g_2S+K_1K_2g_3S^2}{1+K_1S+K_1K_2S^2} \qquad (15)$$

where $S=[\mathrm{W}]/[\mathrm{D}]$ is the ratio of the mole fraction of water and DMSO. The notations, g_1, g_2, and g_3, are the g factors of DRD, of the average of DRW and WRD, and of WRW respectively.

If these radical-solvent complexes are assumed, g_2 becomes

$$g_2=(g_1+g_3)/2$$

and Eq. (15) simplifies to:

$$\bar{g}=\frac{g_1(2+K_1S)+g_3(K_1S+2K_1K_2S^2)}{2(1+K_1S+K_1K_2S)} \qquad (16)$$

Since we have taken three types of equilibria (14) into consideration, g_1 and g_3 may be interpreted as the experimental g factors in nonaqueous DMSO and in pure water respectively.

According to Stone and Maki's treatment, an equation equivalent to Eq. (16) is given with the $Q\equiv S^{-1}$ parameter as the variable:

$$\bar{g}=\frac{g_3(2+K_2^{-1}Q)+g_1[2(K_1K_2)^{-1}Q^2+K_2^{-1}Q]}{2[1+K_2^{-1}Q+(K_1K_2)^{-1}Q^2]} \qquad (17)$$

Taking the experimental values of 2.005182 and 2.004659 for g_1 and g_3 respectively, we obtain $K_1=2.6$ from the initial slope of Eq. (16):

$$\left(\frac{d\bar{g}}{ds}\right)_{S=0}=K_1(g_3-g_1)/2$$

and $K_2=0.41$ from the initial slope of Eq. (17):

$$\left(\frac{d\bar{g}}{dQ}\right)_{Q=0}=K_2^{-1}(g_1-g_3)/2.$$

By adopting the equilibrium constants thus obtained, we have plotted the g factors calculated by means of Eqs. (16) and (17) in Fig. 1, with N_W as the abscissa. The experimental plots agree with Eqs. (16) and (17) over the entire range of solvent composition.

The obtained values of the equlibrium constants of $K_1=2.6>1$ and $K_2=0.41<1$ show that the first solvation of the water molecule to one carbonyl group of the semiquinone tends to occur and that the second solvation of the water molecule to the other carbonyl group of the radical is, rather, prevented. The distance between the two carbonyl oxygen atoms is 5.4 Å.[18] The interaction of the hydrogen bond is a rather localized one. Therefore, the results of $K_1>1$ and $K_2<1$ obtained with Stone and Maki's 2-site model of solvent-radical complexing seems somewhat unreasonable.

4-Site Model. Senti and Harker[19] and Pasternak[20] showed that, in a crystal of acetoamide or succinamide, two N–H hydrogen atoms interact with one carbonyl oxygen atom to form a planar hydrogen-bond structure. On the basis of the infrared spectroscopic study of a hydrogen-bond formation between p-benzoquinone and phenol in a carbon tetrachloride solution, Fritzsche[21] reported that each carbonyl group of p-benzoquinone has two sites occupied by a phenol molecule forming a hydrogen-bond between its OH hydrogen and the lone-pair electrons of the quinone.

On the basis of these experimental observations, we attempted to analyze solvent effects on the g factor of p-benzosemiquinone with a model (4-site model) in which each carbonyl group has two sites which the solvent molecule occupies, thus shifting the g factor of the radical dominantly. The postulated equilibria are:

$$\mathrm{DDRDD}+\mathrm{W}\xrightleftharpoons{K_1'}$$
$$\mathrm{WDRDD\ (DWRDD,\ DDRWD,\ and\ DDRDW)}+\mathrm{D}$$

$$\mathrm{DWRDD\ (WDRDD,\ DDRWD,\ and\ DDRDW)}+\mathrm{W}$$
$$\xrightleftharpoons{K_2'}\mathrm{WWRDD\ (and\ DDRWW)}+\mathrm{D}$$

$$\mathrm{DWRDD\ (WDRDD,\ DDRWD,\ and\ DDRDW)}+\mathrm{W}$$
$$\xrightleftharpoons{K_1'}\mathrm{DWRDW\ (DWRWD,\ WDRDW,\ and\ WDRWD)}+\mathrm{D}$$

$$\mathrm{WWRDD\ (and\ DDRWW)}+\mathrm{W}\xrightleftharpoons{K_1'}$$
$$\mathrm{WWRWD\ (WWRDW,\ DWRWW,\ and\ WDRWW)}+\mathrm{D}$$

$$\mathrm{DWRDW\ (WDRDW,\ DWRWD,\ and\ WDRWD)}+\mathrm{W}$$
$$\xrightleftharpoons{K_2'}\mathrm{WWRDW\ (WWRWD,\ DWRWW,\ and\ WDRWW)}+\mathrm{D}$$

$$\mathrm{WWRWD\ (WWRDW,\ DWRWW,\ and\ WDRWW)}$$
$$+\mathrm{W}\xrightleftharpoons{K_2'}\mathrm{WWRWW}+\mathrm{D}, \qquad (17)$$

where WWRWD refers to the complex in which two water molecules solvate to one carbonyl group and in which the other carbonyl group interacts with one water molecule and one DMSO molecule. It is assumed that solvent molecules complexed with one carbonyl group do not affect the equilibrium constants concerned in the solvation of the other carbonyl, and that the number of solvated water molecules determines the g factor of the com-

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[18] S. M. Swingle, *J. Amer. Chem. Soc.*, **76**, 1409 (1954).

[19] F. Senti and D. Harker, *ibid.*, **62**, 2008 (1940).

[20] R. A. Pasternak, *Acta Cryst.*, **6**, 808 (1953).

[21] H. Fritzsche, *Z. Phys. Chem. Neue Folge*, **43**, 154 (1964).

plex and is proportional to the shift of the g factor; for example,

$$g_{\text{WWRDD}} = g_{\text{WDRWD}} = g_{\text{DDRDD}} + \frac{1}{2}(g_{\text{WWRWW}} - g_{\text{DDRDD}}).$$

g_{WWRWW} and g_{DDRDD} may be interpreted as the experimental g factors in pure water, g_{W}, and in nonaqueous DMSO, g_{D}, respectively.

On the assumptions stated above, the (17) equilibria and Eq. (13) give, as the g factor in the mixed solvent:

$$\bar{g} = g_{\text{D}} + \frac{K_1'K_2'S^2 + K_1'S}{K_1'K_2'S^2 + 2K_1'S + 1}(g_{\text{W}} - g_{\text{D}}). \qquad (18)$$

Eq. (18) coincides with the equation of the 2-site model, Eq. (15), when $K_1' = K_1/2$ and $K_2' = 2K_2$; that is, $K_1' = 1.3$ and $K_2' = 0.82$.

In the 4-site model, the obtained values of K_1' and K_2' are reasonable. $K_2' < 1$ shows that the second solvation of the water molecule, forming a hydrogen bond between an oxygen atom of a carbonyl group and a hydrogen atom of water, is hindered by the water molecule which has solvated to the same oxygen atom.

Stone and Maki's[5)] data on the solvent effects on ^{13}C coupling constants can be interpreted by means of the 4-site model as well as by means of their 2-site model. They reported that the solvation to the nonlabeled carbonyl group scarcely changes the odd-electron distribution near the labeled carbonyl of *p*-benzosemiquinone-1-^{13}C (see Eq. (5) of Ref. 5). Therefore, their a_1 value, the ^{13}C coupling constant in DMSO, may be regarded as the constants of the DDRSS complexes; their a_3 value, the ^{13}C coupling constant in water, as those of the WWRSS complexes, and their a_2 value, as those of the DWRSS and WDRSS complexes, where S denote D or W. In the complex representation above, the two prefixed letters refer to the solvent molecules solvated to the labeled carbonyl. With the approximations above, the equation derived from the 4-site model coincides with the 2-site model equation of solvent effects on the ^{13}C coupling constant.

Both Stone and Maki's 2-site model and the present 4-site model can interpret solvent effects on the g factor as well as on the ^{13}C coupling constant of *p*-benzosemiquinone. Although the 4-site model may be preferred on the basis of the physical meaning of the obtained values of K_2 and K_2', which are smaller than 1, neither the present experimental data on solvent effects on the g factor nor Stone and Maki's study of the ^{13}C coupling constant can experimentally confirm which model is more adequate.

The further study of such things as solvent effects on the ESR parameters of 2,6-di-*t*-butyl-*p*-benzosemiquinone and 2,5-di-*t*-butyl-*p*-benzosemiquinone seems to be desirable in order to ascertain how many water molecules, one or two, can solvate to one carbonyl oxygen atom forming hydrogen-bond in solution.