Electrochemical behavior of polymers in aprotic media. 1. Polyvinylnaphthalene and polyvinylanthracene

Tetsuo Saji, Nicholas F. Pasch, S. E. Webber, and Allen J. Bard

More About This Article

The permalink http://dx.doi.org/10.1021/j100499a002 provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

we suggest that this would be a more satisfactory state of affairs than dependence on an assumed chemical equilibrium model.

Conclusion

In this work we have applied familiar techniques to a familiar type of problem and in a sense there is nothing new here. However, the work does illustrate to some extent the physicochemical breadth of studies of radical ions.

References and Notes

(1) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

(2) See, e.g., L. Kevan and L. D. Kispert, "Electron Spin Double Resonance Spectroscopy", Wiley-Interscience, New York, N.Y., 1976, and references therein.

(3) A. P. Terent'ev, A. N. Grinev, and A. B. Terent'ev, *Zhr. Obshch. Khim.*, **24**, 1433 (1954).

(4) N. M. Atherton and P. A. Henshaw, *J. Chem. Soc., Perkin Trans.* 2, 258 (1975).

(5) J. H. Freed, *J. Chem. Phys.*, **43**, 2312 (1965).

(6) J. H. Freed, D. S. Leniart, and J. S. Hyde, *J. Chem. Phys.*, **47**, 2762 (1967).

(7) K. P. Dinse, K. Mobius, and R. Biehl, *Z. Naturforsch. A*, **28**, 1069 (1973).

(8) K. P. Dinse, R. Biehl, K. Möbius, and M. Plato, *J. Magn. Reson.*, **6**, 444 (1972).

(9) F. Gerson, J. Jachimowicz, K. Möbius, R. Biehl, J. S. Hyde, and D. S. Leniart, *J. Magn. Reson.*, **18**, 471 (1975).

(10) P. A. Kennedy, Ph.D. Thesis, University of Sheffield, 1976.

(11) See, e.g., N. M. Atherton, "Electron Spin Resonance", Ellis Horwood, Chichester, 1973, and references therein.

(12) A. D. Covington and A. K. Covington, *J. Chem. Soc., Faraday Trans.* 1, **71**, 831 (1975), and references therein.

(13) The analysis enables one to assign a particular coupling to the 5 position, possible because the principal axes of the coupling to the proton there are not parallel to those of the protons at the 3 and 6 positions. We are grateful to Mr. A. Smith for a preliminary analysis of the line widths and their interpretation in this way.

Electrochemical Behavior of Polymers in Aprotic Media.
1. Polyvinylnaphthalene and Polyvinylanthracene

Tetsuo Saji, Nicholas F. Pasch, S. E. Webber, and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 75712 (Received August 31, 1977)

The electrochemical behavior of poly-2-vinylnaphthalene (PVN) and poly-9-vinylanthracene (PVA) has been investigated in tetrahydrofuran and N,N-dimethylformamide (DMF) solutions by cyclic voltammetry and coulometry at a platinum electrode and by polarography. The results are consistent with reversible reduction of the polymer in an n_p electron reaction, where n_p is near or equal to the number of substituent electroactive naphthalene or anthracene groups per molecule. The shape of the voltammetric response suggests no interaction between these electroactive centers. Electrogenerated chemiluminescence (ecl) of PVA alone and in the presence of tri-p-tolylamine (TPTA), and of PVN–TPTA mixtures in DMF solutions was also observed.

Although there have been numerous studies of the electrochemical initiation of polymerization,[1,2] there has been very little work reported on the electrochemical behavior of the polymers themselves. There have been a number of studies of the electroreduction of biological macromolecules, such as proteins which usually involve molecules adsorbed on an electrode in aqueous media, but, aside from a recent paper on the oxidation of poly(vinylferrocene) at a platinum rotating disk electrode,[3] we have found no reports on the electrochemistry of vinyl polymers. The low solubility of the polymers in many of the solvents used in electrochemical studies certainly presents a major problem. However extensive electrochemical studies have been carried out in recent years in suitable, but highly resistive, solvents [e.g., tetrahydrofuran (THF) containing tetra-n-butylammonium perchlorate (TBAP) as supporting electrolyte] with accurate measurements made possible by using positive feedback to compensate for solution resistance effects. Moreover, the wide limits of potential that are available in these media before reduction or oxidation of the solvent or supporting electrolyte occurs should allow investigation of a number of substituent electroactive groups on the polymers.

Electrochemical studies of polymers are of interest for several reasons. They can provide a new means of analysis and characterization. Moreover, the location, size, and shape of the voltammetric waves depends upon the extent of interaction of the substituent groups on the polymer and the rate of electron transfer between these groups. Thus information about electron transfer between centers and along polymer chains and about the conformation of the polymer (paralleling studies of excitation transfer in polymers[4-6] or electron spin resonance studies of intramolecular electron transfer[7-9]) may be obtainable. Finally electroactive polymeric materials may find application in electrochemical devices (e.g., batteries, displays, electrosynthesis cells).

We report here electrochemical studies of the reduction of poly-2-vinylnaphthalene (PVN) and poly-9-vinyl-

I   II   III

PVN   PVA
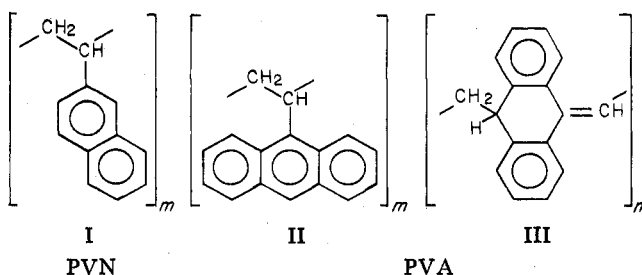
anthracene (PVA) by polarographic, cyclic voltammetric, and controlled potential coulometric techniques in $N,$-

TABLE I: Half-Wave Potentials and Number of Electrons (n_p) Involved in the Reduction of Vinyl Polymers

Species	Mol wt[a]	$E_{1/2}$[b]	$D_0(\times 10^7)$[c]	n_p[e]	DP[f]	Slope,[g] mV
PVN	2.0×10^4	−2.77	1.9	130	130	60
PVN	1.0×10^5	−2.77	0.78	430	670	57
PVN	3.0×10^5	−2.77	0.44	1200	1900	63
Naphthalene	128	−2.75	44[d]	1	(1)	
PVA	3.1×10^3	−1.79	5.5	17	15	57
Anthracene	178	−1.89	26[d]	1	(1)	

[a] Based on weight average. [b] V vs. SCE. [c] D_0 calculated from equation $c/M^{0.55}$, cm^2 s^{-1}.[14] [d] Obtained from diffusion current of polarogram by Ilkovic equation.[13] [e] Number of electrons involved in electron transfer process. [f] Degree of polymerization. [g] Slope of plot of E vs. log $[(i_d − i)/i]$.

N-dimethylformamide (DMF) and THF solutions and provide evidence for multielectron transfer into noninteracting groups on these molecules. A brief study of the electrogenerated chemiluminescence[10,11] of systems containing these species is also described.

Experimental Section

The purification of solvents, TBAP, and tetra-n-butylammonium fluoborate (TBAF) and the general apparatus and procedures have been described in previous papers from this laboratory.[11] PVA was prepared by free-radical polymerization of 9-vinylanthracene.[12] PVN was prepared by bulk or solution thermal polymerization of 2-vinylnaphthalene. The average molecular weight (M) of the polymers was determined by viscometric measurements in benzene. All solutions were prepared and studied either on a vacuum line or in a glove box (Vacuum Atmospheres Corp., Hawthorne, Calif.).

Results

Voltammetry. The cyclic voltammogram of PVN (N = 20K) at platinum in 0.1 M TBAF–THF exhibits one reduction wave occurring at potentials close to background reduction ($E_{1/2}$ = −2.77 V vs. SCE) (Figure 1a). For this wave $i_{pc}/v^{1/2}C$ (i_{pc} is the cathodic peak current, v is the scan rate, and C the concentration) is constant with scan rate, E_{pc}, the cathodic peak potential is independent of v, and i_{pa}/i_{pc} (i_{pa} is the anodic peak current) is essentially unity. The peak potential separation ($E_{pa} - E_{pc}$) is about 60 mV. Thus the wave has the characteristics of a Nernstian one-electron reduction to form a stable product. The same features are observed for the waves of the reduction of PVN of higher molecular weight (100K and 300K). The dc polarograms obtained at a dropping mercury electrode similarly show reversible waves with $E_{1/2}$ independent of molecular weight and near that for naphthalene (Table I). The cyclic voltammogram of PVA (3.1K) in 0.1 M TBAP–DMF shows two reduction waves at −1.79 and −2.3 V (Figure 1b). The first wave again has characteristics of a reversible process and both waves occur at potentials near those for anthracene.

It is of interest to estimate the number of electrons associated with the reduction of the polymer, n_p. This can be obtained from the dc polarograms by applying the Ilkovic equation[13]

$$(i_d)_p = \text{constant} \times n_p D_p^{1/2} C_p \qquad (1)$$

where D_p and C_p are the diffusion coefficient and concentration of the polymer, respectively, and the constant is determined by the drop time and drop mass. Theoretical studies and experimental data for macromolecules show that D_p varies as $M^{-0.55}$ for good solvents, assuming the polymer is randomly coiled and can be treated as a sphere.[14] Thus D_p for PVN can be estimated from that
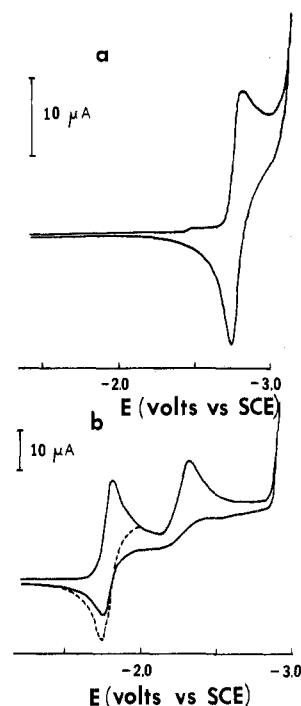

Figure 1. Cyclic voltammograms of (a) 0.021 mM PVN (20K) in 0.1 M TBAF–THF; (b) 0.3 mM PVA (3K) in 0.1 M TBAP–DMF at Pt electrode; scan rate, 200 mV/s.

of naphthalene (D_n) determined from the dc polarogram of this species in THF (taking n = 1) by the equation

$$D_p = D_n(128/M)^{0.55} \qquad (2)$$

Values for n_p for PVN of different molecular weights and degrees of polymerization (DP) are given in Table I. In a similar way n_p for PVA in DMF was estimated from the dc polarographic results for PVA and anthracene. In all cases n_p is surprisingly large, with DP/n_p lying between 1 and 2, i.e., the waves involve the transfer of large numbers of electrons (at least 1200 for 300K PVN), although the wave shape is characteristic of a one-electron transfer reaction. The electron transfer reactions can be written

$$(M)_m + ne \rightleftharpoons (M)_m^{n-} \qquad (3)$$

where m is the degree of polymerization; from the evidence here, $n \approx m$.

Coulometry. To obtain evidence for multielectron transfers into the polymer molecules without the requirement of estimating relative diffusion coefficients, Coulometric reduction of the PVA sample in DMF–0.1 M TBAP at a platinum electrode maintained at −2.1 V was carried out. A 1 h electrolysis yielded n_{app} = 18 (n_{app} is the number of Faradays passed per mole of PVA), in very good agreement with the estimate from voltammetric measurements. The reduced product in solution was blue.
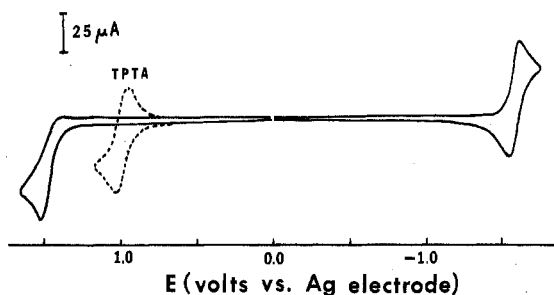
Figure 2. Cyclic voltammograms of 0.3 mM PVA and 5 mM TPTA in DMF at a Pt electrode with 0.1 M TABP. Scan rate 200 mV/s.

TABLE II: Cyclic Voltammetry Results from PVA, PVN, and TPTA in DMF with 0.1 M TBAP[a]

| Compound (R)	R/R^+		R/R^-	
	E_{pa}	E_{pc}	E_{pa}	E_{pc}
PVA	1.52		−1.54	−1.62
PVN			−2.38	−2.53
TPTA	1.04	0.97		

[a] Potentials in V vs. Ag wire reference electrode; solutions contained 0.1 M TBAP.

Coulometric oxidation of this solution at −1.5 V yielded an $n_{app} = 8$.

Electrogenerated Chemiluminescence. The emission of light which results from the electron transfer reactions of electrogenerated radical ions or other reduced and oxidized species, called electrogenerated chemiluminescence (ecl), has been the subject of rather intensive study.[10] In these reactions electron transfers which involve large enthalpies of reaction will frequently produce electronically excited states (singlets or triplets) which emit light, i.e.

$$A^{\cdot-} + D^{\cdot+} \rightarrow A^* + D \qquad (4)$$
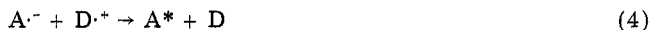
Since ecl studies of anthracene have been carried out earlier,[15–17] we thought it of interest to investigate ecl for the PVA system. The cyclic voltammetric behavior of PVA in 0.1 M TBAP–DMF solutions in the absence and presence of tri-*p*-tolylamine (TPTA) are shown in Figure 2. The peak potentials for the different processes are given in Table II. The reduction process is the same as that described previously. The oxidations represent the irreversible oxidation of PVA, again in a multielectron step (by comparison of the anodic wave height to that of the cathodic one), and the oxidation of TPTA to the radical cation (TPTA·+). When the potential of a platinum electrode immersed in a 0.1 M TBAP–DMF solution containing 0.3 mM PVA is cycled at 0.5 Hz between potentials for PVA reduction and oxidation, ecl emission is observed (Figure 3a). The ecl spectrum, with an emission maximum at 440 nm, is very similar to the fluorescence spectrum of PVA obtained by us (Figure 3b) and reported by Skorokhodov et al.[12] The emission can be ascribed to the reaction of radical cationic and anionic anthracene groups, which apparently behave as noninteracting centers on the polymer molecules, to produce excited state emitting centers. This can be schematically represented as

$$\text{WW}(A^{\cdot-}) + \text{WW}(A^+) \rightarrow \text{WW}(A)^* + \text{WW}(A) \qquad (5)$$
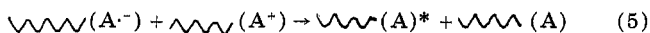
It is possible that the chains upon which the excited center forms still contain charged centers, or even that the oxidized and reduced centers are formed on a single polymer chain (although this seems unlikely for the low molecular weight PVA employed here) but this type of information is not available from the results. The enthalpy of reaction 5 (obtained from $E_{pa} - E_{pc}$ and corrected for the entropy factor[10]) appears marginally sufficient to populate the
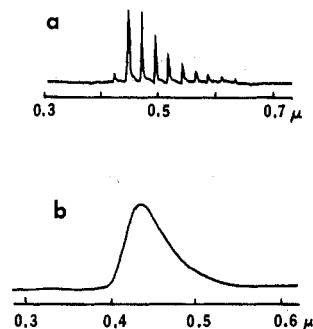

Figure 3. (a) Ecl emission spectrum of 0.3 mM PVA in DMF using a cyclic square wave at 0.5 Hz between +1.70 and −1.75 V vs. Ag reference electrode. (b) Fluorescence emission spectrum of 0.3 mM PVA in DMF with excitation at 380 nm.

excited singlet state of the reacting anthracene center. Note that no longer wavelength emission was observed in the ecl of the PVA system as contrasted with the ecl of the anthracene system.[15–17] In the latter case decomposition of the anthracene radical cation occurs and produces anthranol. This species can then be excited by energy transfer from singlet anthracene producing emission at longer wavelengths. For PVA, even with the oxidized PVA being unstable (as is clear from the irreversible cyclic voltammetric anodic waves), no emission from a decay product appears. Moreover, no emission which could be assigned to excimeric species resulting from interaction of an excited anthracene center with another anthracene center[5,6] is observed. Thus, the geometry within PVA appears unfavorable for overlap between the substituent anthracenes.

We could also observe weak emission with a similar spectral distribution for solutions containing both PVA and TPTA and cycling at 0.5 Hz between PVA reduction and TPTA oxidation. In this case the reaction enthalpy for the electron transfer between reduced PVA and TPTA·+, ca 2.5 eV, is insufficient to populate the singlet state of PVA directly, so that the reaction probably occurs by formation of a triplet followed by triplet–triplet annihilation (tta) to form the emitting singlet:

$$\text{WWW}A^{\cdot-} + TPTA^{\cdot+} \rightarrow \text{WWW}\,^3A + TPTA \qquad (6)$$

$$\text{WW}\,^3A + \text{WWW}\,^3A \rightarrow \text{WWW}\,^1A^* + \text{WWW}\,A \qquad (7)$$

While it is possible that both triplets are formed on the same polymeric chain and intramolecular tta occurs, as has been previously reported in delayed fluorescence studies of polymers,[4] the rapid quenching of triplets by radical ions[18,19] would suggest that this could only occur in PVA molecules which were nearly completely oxidized, with no or few remaining A·− centers.

Ecl emission was also observed with mixtures of PVN (20K) and TPTA in THF solutions. In this case the ecl spectrum showed emission peaks at 340 and 450 nm. This differs from the fluorescence spectrum of PVN obtained by us and reported by Vala et al.[5] for 1,2-dichloroethane solutions, where in addition to the fluorescence emission peak at 342 nm a structureless emission at 410 nm (attributed to polymer excimer states) is found. The ecl emission at 450 nm could be caused by exciplex states between excited naphthalene centers on the chain and TPTA which form directly during the annihilation process. Similar emission has been observed during ecl studies of the naphthalene–TPTA system.[20]

Discussion

The results presented here provide strong evidence that the substituent groups on the polymer chain behave as

noninteracting centers with the reduction potentials of the polymers being close to those of the substituents themselves. The fact that multielectron waves occur with the shape of one-electron reductions is further evidence of noninteraction of the substituent groups. Ammar and Savéant[21] have shown that for molecules with two identical noninteracting centers the $E°$ values of the successive electron transfers are governed by statistical considerations, and the difference between them (RT/F) ln 4 (or 36 mV at 25 °C), is such that the Nernstian voltammetric wave shape is identical with that of a Nernstian one-electron transfer reaction. Experimental evidence has appeared for such two-electron systems (nitro compounds[21] and 9,10-anthrylbis(styryl) ketone[22]). Recent calculations by Flanagan[23,24] have extended this to multielectron systems and have demonstrated that the spacings for reversible successive electron transfers in molecules with many noninteracting groups will be such as to yield voltammetric waves with the one-electron wave shape. Details of the calculations and further experimental evidence for this behavior in poly(vinyl ferrocenes) (PVF) will appear elsewhere.[24] In the study of Smith et al.[3] of PVF, evidence of multiple electron transfers to the polymer molecules was also obtained. In that study the authors felt that there was some interaction between neighboring ferrocene residues so that values of DP/n_p for the higher molecular weights of 3 to 4 were estimated. Recent voltammetric and Coulometric studies[24] of PVF however place DP/n close to one. Further evidence for weak interaction of the centers in these kinds of polymers is the fact that the absorption spectra of the polymers are very similar to those of the monomeric chromophores, so that the chromophores appear to act independently of one another in absorbing radiation.[5]

The voltammetric behavior of the PVA allows us to make some comments about its structure. There has been some discussion of the structure of PVA and both vinyl (or 1,2 type, II) and "across-the-ring" (or 1,6 type, III) polymerization has been reported.[25] The evidence from the electrochemical studies suggests that the PVA investigated here is of the vinyl (structure II) form. This is inferred from the fact that the reduction potential of PVA and its general voltammetric behavior is very similar to that of anthracene and very different than that of the monomeric form related to structure III, 1,1-diphenylethylene, which is reduced at potentials about 0.5 V more negative than anthracene. Moreover, the ecl characteristics of PVA resemble that of anthracene. An electrochemical study of PVA prepared by different methods would be of interest. However, even the preliminary results reported here are evidence of the potential utility of electrochemical techniques in the characterization of polymers (i.e., determination of concentration, structure, DP, diffusion coefficient).

A question might be raised about the rate of electron transfer between centers on the same polymer chain and how these affect the electrochemical behavior. Szwarc and co-workers[7-9] studied the ESR behavior of radical anions of two naphthyl moieties linked by a chain of j CH_2 groups (i.e., $N-(CH_2)_j-N\cdot^-$), and determined the frequency of intramolecular electron transfer (P) as a function of chain length. The results showed that P decreased as j increased from 3 to 20 (e.g., in hexamethylphosphoric triamide (HMPA) solutions from 6.7×10^9 to 7.4×10^6 s^{-1}). Note that for $j = 2$ intramolecular collisions were not expected because of steric constraints.[8] Thus in PVN some intramolecular electron transfer is expected between nonneighboring centers, although the rate of this process will probably be much slower in the bulkier polymeric chain than in the $N-(CH_2)_j-N$ system. Moreover the studies in HMPA probably involved dissociated anions, while the studies of PVN in THF almost certainly involved ion pairs between the naphthyl radical anion centers and tetra-n-butylammonium cations. Such ion pairing is known to slow electron transfer and probably also slows conformational changes in the polymeric chain. Thus the results suggest that in the absence of near neighbor interactions intramolecular electron transfer would not affect the voltammetric behavior under the conditions of these studies.

Finally, the work here suggests several applications of the electrochemistry of polymers. The reduced (or oxidized) polymers should undergo chemical reactions similar to those of the corresponding monomeric forms, e.g., radical anions (or cations). Thus attack by electrophilic (or nucleophilic) agents, internal dimerizations, further reduction (or oxidation) should occur. The rates of these processes can be studied using electroanalytical techniques and electrochemical methods may provide a useful method of polymer modification. In fact the voltammetric behavior of PVA upon oxidation and upon reduction of the substituent centers to the dianionic forms indicates further reaction and hence modification of the PVA. If the reactions of the substituents follow those of free anthracene, this would involve addition of hydroxyl (upon oxidation) and saturation of the rings at the 9 and 10 positions (upon reduction). Moreover the adsorption or precipitation of polymers or their reduced or oxidized forms on an electrode surface may be a useful technique for providing a modified electrode surface. Such behavior for proteins adsorbed on mercury has already been observed.[26,27] These applications as well as further studies on these materials and other polymers and copolymers are currently under investigation in these laboratories.

References and Notes

(1) B. L. Funt and J. Tanner in "Technique of Electroorganic Synthesis", Vol. V, Part II, N. L. Weinberg, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter XI.
(2) G. Parravano in "Organic Electrochemistry", M. M. Balzer, Ed., Marcel Dekker, New York, N.Y., 1973, Chapter XXIX.
(3) T. W. Smith, J. E. Kuder, and D. Wychick, *J. Polym. Sci.*, **14**, 2433 (1976), and references therein.
(4) N. F. Pasch and S. E. Webber, *Chem. Phys.*, **16**, 361 (1976), and references therein.
(5) M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).
(6) L. A. Harrah, *J. Chem. Phys.*, **56**, 385 (1972).
(7) K. Shimada, G. Moshuk, H. D. Connor, P. Caluwe, and M. Szwarc, *Chem. Phys. Lett.*, **14**, 396 (1972).
(8) H. D. Connor, K. Shimada, and M. Szwarc, *Macromolecules*, **5**, 801 (1972).
(9) K. Shimada and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 3321 (1975).
(10) L. R. Faulkner and A. J. Bard in "Electroanalytical Chemistry", Vol. 10, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1977.
(11) T. Saji and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 2235 (1977), and references therein.
(12) S. S. Skorokhodov, M. G. Krakovjak, E. V. Anufrieva, and N. S. Shelekhov, *J. Polym. Sci., Symp.*, **No. 42**, 1229 (1973).
(13) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience, New York, N.Y., 1952.
(14) C. Tanford, "The Physical Chemistry of Macromolecules", Wiley, New York, N.Y., 1961, p 362.
(15) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964).
(16) L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **90**, 6284 (1968).
(17) T. C. Werner, J. Chang, and D. M. Hercules, *J. Am. Chem. Soc.*, **92**, 763 (1970).
(18) L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **91**, 6497 (1969).
(19) H. Tachikawa and A. J. Bard, *Chem. Phys. Lett.*, **26**, 10 (1974).
(20) S. M. Park and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 2978 (1975).

(21) F. Ammar and J. M. Savéant, *J. Electroanal. Chem.*, **47**, 115 (1973).
(22) T. Teherani, L. A. Tinker, and A. J. Bard, *J. Electroanal. Chem.*, in press.
(23) J. B. Flanagan, Ph.D. Dissertation, California Institute of Technology, 1978.
(24) J. B. Flanagan, S. Margel, A. J. Bard, and F. C. Anson, *J. Am. Chem.*

Soc., in press.
(25) A. Rembaum and A. Eisenberg, *Macromol. Rev.*, **1**, 57 (1966).
(26) K. S. V. Santhanam, N. Jespersen, and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 274 (1977).
(27) M. T. Stankovich and A. J. Bard, *J. Electroanal. Chem.*, **85**, 173 (1977).

Molecular and Magnetic Structure of the Paramagnetic Ion Pair Bis(tetraglyme)potassium Biphenyl

J. H. Noordik, J. Schreurs, R. O. Gould, J. J. Mooij, and E. de Boer*

Research Institute for Materials (RIM), University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands (Received July 5, 1977)

Publication costs assisted by the University of Nijmegen

The crystal structure of K^+ $[CH_3O(CH_2CH_2O)_4CH_3]_2C_{12}H_{10}^-$ has been determined by x-ray diffraction at 120 K. The crystal data are as follows: space group Cc or $C2/c$, $a = 9.654(3)$, $b = 16.803(9)$, $c = 21.845(7)$ Å, $\beta = 96.03(2)°$, $Z = 4$, and $d_x = 1.03$ g cm^{-3}. The ten oxygen atoms of the two tetraglyme molecules spherically surround each K^+ ion, such as to give a solvent-separated ion pair structure. Susceptibility measurements point to a ferromagnetic coupling between the spins. The ESR spectrum consists of a single exchange narrowed line with a line width depending on the orientation of the magnetic field with respect to the crystal. The molecular **g** tensor of the biphenyl anion has been determined. The **g** tensor calculated using Stone's theory agreed well with the experimental **g** tensor. A satisfactory explanation for the angular dependent line width could not be given.

Introduction

The concept of an ion pair was introduced in 1926 by Bjerrum.[1] That different types of ion pairs could exist in solution was suggested in 1954 by Fuoss[2] and Winstein.[3] Szwarc[4] referred to these distinct ion pairs as loose and tight ion pairs. In loose ion pairs the partners of the pair are separated by solvent molecules (solvent-separated ion pairs), in tight ion pairs the partners are in close contact and solvated only on the outside (contact ion pairs). In numerous papers, Szwarc and his co-workers,[4] using various techniques, shed much light on the structure of these ion pairs in solution, so that by now the concept of an ion pair is well established.

Recently we reported on the structure and magnetic properties of ion pairs in the solid state.[5] Examples were found both of contact[5b,c] and of solvent-separated ion pairs.[5a] In this paper we report the crystal structure and the magnetic properties of bis(tetraglyme)potassium biphenyl (KBp·2Ttg). As in the rubidium analogue[5a] the ions occur in the crystals as solvent-separated ion pairs. Despite the correspondence in chemical composition the compounds are not isomorphous. The unit cell of KBp·2Ttg is half that of RbBp·2Ttg.

The large concentration of electron spins in the crystals causes a strong exchange interaction between these spins. Under these circumstances the spin Hamiltonian for these crystals in a magnetic field is

$$\mathcal{H} = \beta \sum_j^N \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}_j - \sum_{j>k}^N 2J_{jk} \mathbf{S}_j \cdot \mathbf{S}_k + \sum_{j>k}^N \mathbf{S}_j \cdot \mathbf{D}_{jk} \cdot \mathbf{S}_k \qquad (1)$$

where the three terms represent the Zeeman, the exchange, and the dipolar interactions, respectively. The summation indices j and k run over all pairs of spins in the crystal. The crystals under investigation contain two magnetically nonequivalent sites in the unit cell. Because of the exchange, only a single exchange-narrowed ESR line is observed, its g value corresponds to the average value of the g values of the two sites. The exchange interaction is isotropic since no orbital angular momentum is associated with the ground states of the interacting molecules. The magnetic dipole–dipole interaction has to be included in the Hamiltonian when the electron spins are not largely separated. The components of the traceless symmetric dipolar tensor $\mathbf{D}_{jk}$ are given by

$$D_{pq}{}^{jk} = g^2 \beta^2 \frac{\psi | r_{jk}^2 \delta_{pq} - 3p_{jk}q_{jk} | \psi}{r_{jk}^5} \qquad (2)$$

$$p, q = x, y, z$$

where $\mathbf{r}_{jk}$ is the vector between the two relevant electrons, j and k, and ψ is the electron wave function.

The average g values have been measured in three planes normal to the crystallographic axes. Utilizing the crystal structure, the molecular **g** tensor has been derived. These values have been compared with the theoretical g values, calculated with the theory of Stone.[6]

The ESR line width depends on the orientation of the magnetic field with respect to the crystal axes. Using the theory of Anderson and Weiss[7] and van Vleck,[8] an explanation for this was sought. Susceptibility measurements revealed a ferromagnetic coupling in the crystals, contrary to antiferromagnetic coupling observed for the crystals of RbBp·2Ttg.[5a]

Experimental Section

Preparation of the Crystals. A solution of KBp in Ttg was prepared under high vacuum using standard techniques.[9] From this solution, single crystals were obtained by slowly cooling the solution to about 10 °C, 1 °C/h. Since the crystals are very sensitive to air and moisture, they had to be mounted in thin glass capillaries under a He atmosphere in a glove box. These manipulations had to be carried out at a temperature of about −20 °C because of the low melting point of the KBp·2Ttg crystals (about 40 °C). The crystals used for the x-ray data collection at