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Geometrical Structure of Solvated Electrons in Ethanol Glass Determined from Electron Spin Echo Modulation Analyses

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Abstract: Two-pulse and three-pulse electron spin echo deuterium modulation patterns have been analyzed for radiation-produced solvated electrons in the following specifically deuterated ethanol glasses: CH_3CH_2OD, CH_3CD_2OH, and CD_3CH_2OH. The analyses are all consistent with four first-solvation-shell molecules around the electron with the CD_3 deuterons at 0.38 nm, the CD_2 deuterons at 0.33 nm, and the OD deuteron at 0.22 nm from the electron. The distances are compatible only with a *molecular dipole* orientation of the ethanol molecules with the bisector of the COD bond angle approximately oriented toward the electron. This contrasts with the OD *bond dipole* orientation found for solvated electrons in aqueous matrices.

Solvated electrons were probably first produced in the middle 1800s by dissolving sodium in liquid ammonia to generate a beautiful blue color; however, this spectrum was not assigned to solvated electrons as such until the early 1900s.[1] Optical and magnetic resonance spectroscopy has been applied extensively to solvated electrons in liquid ammonia, and together with a variety of other physical measurements and extensive theoretical calculations many facets of these solvated electrons have been deduced. However, their detailed geometrical structure still awaits concrete experimental definition. In 1962 a solvated electron in water was discovered as a transient optical spectrum produced by pulse radiolysis.[2] Since that time transient solvated electrons have been discovered in a variety of other polar and nonpolar liquids and have also been found to be stabilized in a variety of polar and nonpolar aqueous and organic glasses.[3] A variety of spectral, theoretical, and kinetic characteristics of solvated electrons in both liquid and glassy matrices have been intensively studied over the past 15 years,[3] but it is only in the last several years that striking advances have been made in deducing the detailed geometrical structure of solvated electrons in both aqueous and organic matrices.[4]

These advances in the determination of solvation geometry have been made possible by the development of new methods of analysis of electron magnetic resonance spectra to obtain very weak hyperfine interactions characteristic of the solvated molecules around a paramagnetic species in disordered solids. The most important of these methods has been the analysis of electron spin echo modulation patterns.[5-9] Supporting information has come from the analysis of electron spin resonance second moment line shapes[10-12] and forbidden proton spin flip transitions,[13,14] specifically for paramagnetic species in disordered solids. The use of specifically deuterated solvent molecules has been crucial in these studies to give not only the numbers of first-solvation-shell molecules and their distances from the solvated electron but also their orientation with respect to the solvated electron.

It has been deduced that solvated electrons in aqueous systems have a solvation shell of six water molecules octahedrally arranged with one OH bond of each water oriented toward the electron and an electron-to-nearest proton distance of 0.21 nm.[10,15,16] It is particularly interesting that one OH bond dipole of water *rather than* the molecular dipole of water is oriented toward the electron in aqueous systems.

The other solvated electron system that has been studied in great structural detail is electron solvation in a relatively large cyclic ether, 2-methyltetrahydrofuran (MTHF).[6] Here, the electron to nearest proton distance is significantly larger, 0.34 nm. There are three MTHF molecules in the first solvation shell arranged trigonally around the solvated electron with the ring carbon plane of MTHF perpendicular to a line toward the electron. Because of the methyl group in MTHF, there are two orientations of the MTHF ring carbon plane with respect to the electron; the data show that the solvated electron has a statistical distribution of these two orientations.

In this investigation we extend the study of the geometrical structure of solvated electrons to an important solvent, intermediary between the highly polar aqueous solvent molecules and the relatively nonpolar ether solvent molecules. We have studied the detailed geometrical structure of solvated electrons in ethanol and have been able to deduce not only the number and distance of solvating molecules but also their orientation by using specifically deuterated ethanols and electron spin echo modulation analyses. A preliminary communication on this work has been published[17] which dealt only with two-pulse electron spin echo results. Here we give a more definitive analysis of the structure based on both two-pulse and three-pulse electron spin echo modulation analyses.

The geometrical structure deduced here is in agreement with the qualitative conclusions reached earlier from semicontinuum model theoretical calculations[18] and from pulse radiolysis studies.[19] Of particular interest in this study is the unambiguous determination that the molecular dipole of the first-solvation-shell ethanol molecules is oriented toward the electron.

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(1) (a) W. Weyl, *Pogg. Ann.*, **121**, 601 (1864); (b) C. A. Kraus, *J. Am. Chem. Soc.*, **30**, 1323 (1908).

(2) E. J. Hart and M. Anbar, "The Hydrated Electron", Wiley-Interscience, New York, 1970.

(3) L. Kevan and B. C. Webster, Eds., "Electron–Solvent and Anion–Solvent Interactions", Elsevier, Amsterdam, 1976.

(4) L. Kevan, *J. Phys. Chem.*, **84**, 1232 (1980).

(5) L. Kevan in "Time Domain Electron Spin Resonance", L. Kevan and R. N. Schwartz, Eds., Wiley-Interscience, New York, 1979, Chapter 8.

(6) T. Ichikawa, L. Kevan, M. K. Bowman, S. A. Dikanov, and Yu. D. Tsvetkov, *J. Chem. Phys.*, **71**, 1167 (1979).

(7) L. Kevan, M. K. Bowman, P. A. Narayana, R. K. Boeckman, V. F. Yudanov, and Yu. D. Tsvetkov, *J. Chem. Phys.*, **63**, 409 (1975).

(8) W. B. Mims and J. L. Davis, *J. Chem. Phys.*, **64**, 4836 (1976).

(9) P. A. Narayana and L. Kevan, *J. Chem. Phys.*, **65**, 3379 (1976).

(10) B. L. Bales, J. Helbert, and L. Kevan, *J. Phys. Chem.*, **78**, 221 (1974).

(11) L. Kevan, M. K. Bowman, P. A. Narayana, R. K. Boeckman, V. F. Yudanov, and Yu. D. Tsvetkov, *J. Chem. Phys.*, **63**, 409 (1975).

(12) B. L. Bales, M. K. Bowman, L. Kevan, and R. N. Schwartz, *J. Chem. Phys.*, **63**, 3008 (1975).

(13) M. Bowman, L. Kevan, and R. N. Schwartz, *Chem. Phys. Lett.*, **30**, 208 (1975).

(14) B. L. Bales and E. Lesin, *J. Chem. Phys.*, **65**, 1299 (1976).

(15) P. A. Narayana, M. K. Bowman, L. Kevan, V. F. Yudanov, and Yu. D. Tsvetkov, *J. Chem. Phys.*, **63**, 3365 (1975).

(16) S. Schlick, P. A. Narayana, and L. Kevan, *J. Chem. Phys.*, **64**, 3135 (1976).

(17) M. Narayana and L. Kevan, *J. Chem. Phys.*, **72**, 2891 (1980).

(18) D. F. Feng and L. Kevan, *Chem. Rev.*, **80**, 1 (1980).

(19) L. Kevan, *J. Phys. Chem.*, **83**, 3378 (1979).

0002-7863/81/1503-1618$01.25/0 © 1981 American Chemical Society

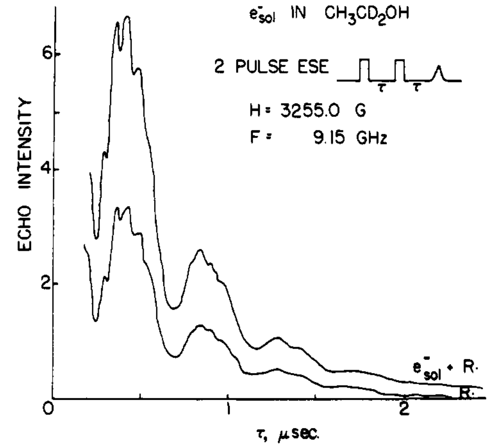

Figure 1. Two-pulse electron spin echo spectrum of the solvated electron in CH_3CD_2OH. The spectrum due to the radical CH_3CHOH after photobleaching the trapped electron is also shown. Both proton and deuterium modulation can be seen.

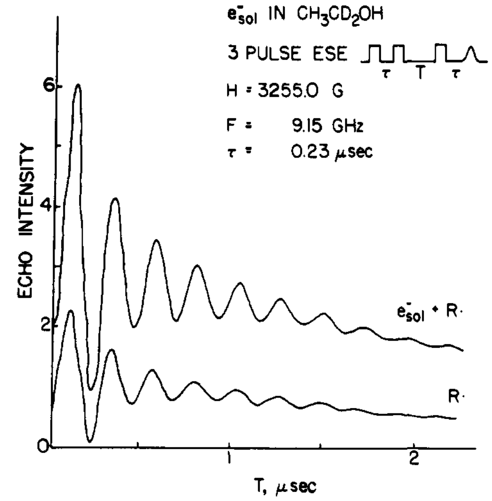

Figure 2. Three-pulse electron spin echo spectrum of the solvated electron in CH_3CD_2OH and that of the radical after photobleaching the electron. The pulse width was so chosen as to suppress the proton modulation.

Experimental Section

The deuterated compounds, CH_3CH_2OD, CD_3CH_2OH, and C_2D_5OD were obtained from Stohler Isotope Chemicals and CH_3CD_2OH was obtained from Dr. Yu. D. Tsvetkov. All samples were vacuum distilled into 3-mm od spectrosil quartz tubes and irradiated at 77 K with a cobalt-60 γ source to a typical dose of 0.5 Mrad.

Electron spin echo spectra were recorded at 77 K on a home-built spectrometer.[20] It is important to note that the spectrometer can be operated so as to generate modulation only from deuterons and not protons weakly coupled to the paramagnetic species. Generation of the modulation requires simultaneous excitation of both allowed and forbidden transitions associated with the weak nuclear coupling. With use of long (~100-ns), low amplitude pulses, both allowed and forbidden transitions can be excited for weakly coupled deuterons but not for weakly coupled protons.[5] This occurs because the deuteron nuclear coupling is smaller than the proton nuclear coupling. The advantage of being able to look selectively at deuteron interactions in the presence of protons allows one to use specifically deuterated molecules to determine explicit molecular orientations of the first-solvation-shell molecules with respect to the paramagnetic species, in this case the solvated electron. Some experiments were also carried out for solvated electrons in C_2H_5OH in which case 20-ns pulses were used to generate proton modulation.

Results

The electron spin echo decay data consist of contributions from both the solvated electrons and the CH_3CHOH radicals or the specifically deuterated radical analogue. The solvated electrons can be removed by optical bleaching with visible light to give a spin echo decay curve due to the background radical only. In this bleaching process the radical yield increases by twofold so correction is made for this increase when the radical background decay curve is subtracted from the total decay curve of solvated electrons plus radical. Figures 1 and 2 show two-pulse and three-pulse electron spin echo decay curves for the solvated electron plus radical and for the radical alone after optical bleaching in CH_3CD_2OH. In the two-pulse data shown in Figure 1 the radical contribution before bleaching is approximately one-fourth of the total response from the solvated electron plus the radical. Thus, the radical background can be subtracted to give a significant signal due only to the solvated electron. In the case of the three-pulse spin echo data shown in Figure 2 the radical background before bleaching is only about one-sixth of the total response due to both the solvated electron plus the radical. The apparent smaller radical background in the three-pulse spectrum is partially due to the slower time scale of decay for the three-pulse echo as compared to the two-pulse echo. Both two-pulse and three-pulse results have been analyzed for the variously deuterated ethanols, but the three-pulse data are considered to be somewhat more accurate in this system.

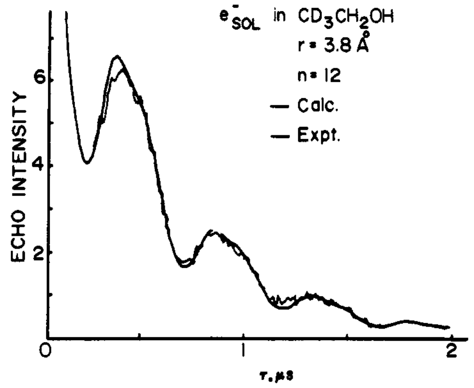

Figure 3. The calculated and experimental two-pulse electron spin echo spectra of the solvated electron in CD_3CH_2OH. The decay function used was $\exp(2.72 - 1.94\tau - 0.13\tau^2 + 0.04\tau^3)$.

Table I. Geometrical Parameters *n*, *r* and *a* (see text) from Two-Pulse and Three-Pulse Electron Spin Echo Data for Solvated Electrons in Ethanol Glass

	two-pulse echo			three-pulse echo		
matrix	*n*	*r*, nm	*a*, MHz	*n*	*r*, nm	*a*, MHz
CH_3CH_2OD	4	0.22	0.7	4	0.24	0.7
CH_3CD_2OH	8	0.33	0.1	8	0.34	0.1
CD_3CH_2OH	12	0.38	0.0	12	0.39	0.0

The spin echo decay data have been analyzed by a ratio analysis method already described.[6] An example of the fit of the simulated decay data to the experimental decay data is shown for solvated electrons in CD_3CH_2OH in Figure 3. Here the simulated data fit the experimental data quite well for 12 equivalently interacting deuterons at a distance of 0.38 nm. Since there are three deuterons per molecule in this specifically deuterated ethanol, these data correspond to four approximately equivalent ethanols in the first solvation shell of the solvated electron. A similar analysis of the solvated electron data in the CH_3CD_2OH gives eight approximately equivalent interacting deuterons at a distance of 0.34 nm with an isotropic coupling constant of 0.1 MHz. Again, this number is consistent with four first-solvation-shell ethanol molecules around the solvated electron. Similarly, analysis of the data in CH_3CH_2OD gives four equivalent interacting deuterons at 0.22 nm with an isotropic coupling of 0.7 MHz. These parameters for the various specifically deuterated ethanols are summarized in Table I.

Figure 4 shows the electron spin echo decay envelope for solvated electrons in C_2H_5OH where a larger pulse energy has

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[20] T. Ichikawa, P. A. Narayana, and L. Kevan, *J. Phys. Chem.*, **83**, 3378 (1979).

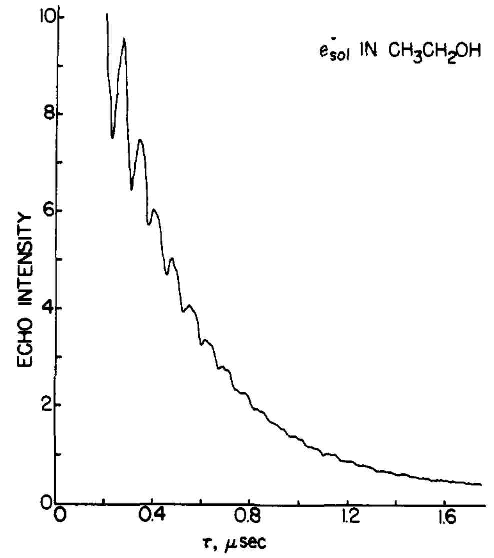

Figure 4. Two-pulse electron spin echo spectrum of the solvated electron in CH_3CH_2OH after correcting for the radical contribution. The modulation seen is from protons.

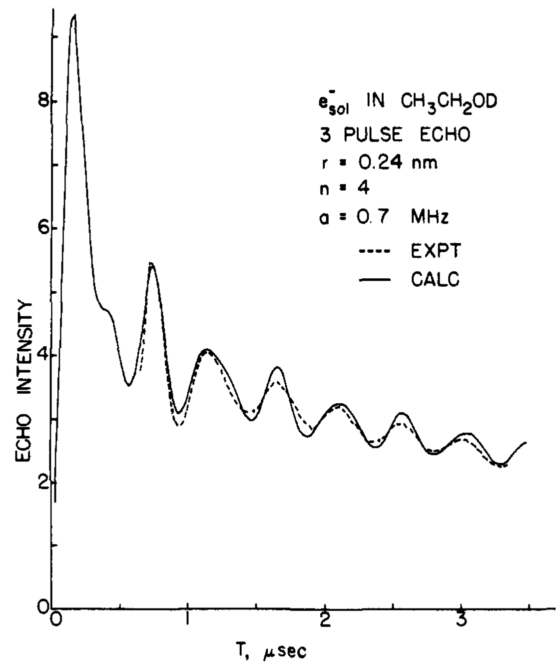

Figure 5. The calculated and experimental three-pulse electron spin echo spectra of the solvated electron in CH_3CH_2OD. The loss of symmetry in the periods is due to the strong isotropic coupling. The decay function used was $\exp(3.5 - 0.471\tau + 0.11\tau^2 - 0.012\tau^3)$.

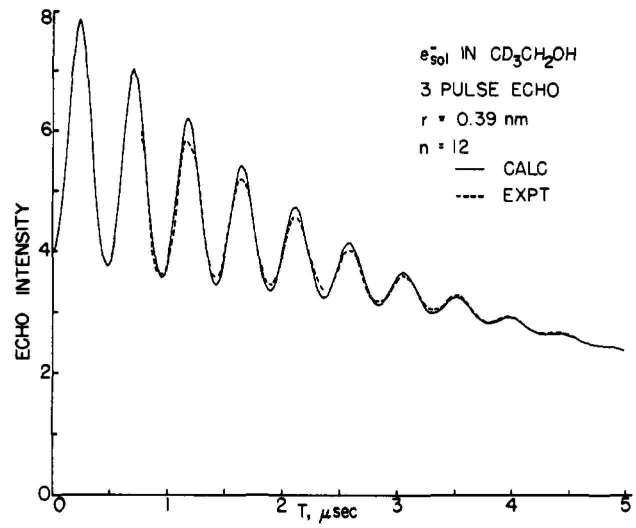

Figure 6. The calculated and experimental three-pulse electron spin echo spectra of the solvated electron in CD_3CH_2OH. The decay function used was $\exp(2.11 - 0.18\tau)$.

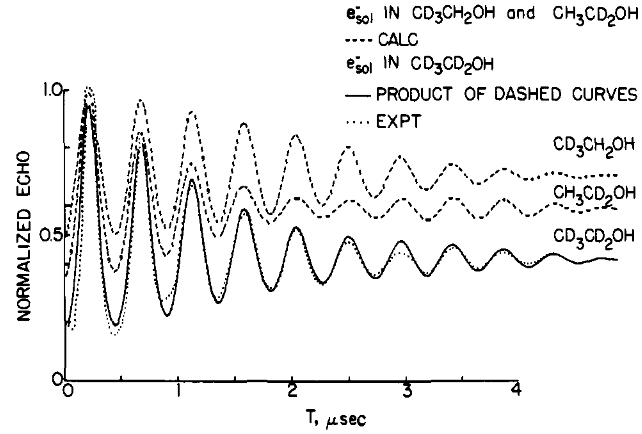

Figure 7. The calculated, normalized three-pulse electron spin echo spectra of the solvated electron in CD_3CH_2OH and CH_3CD_2OH using the parameters from Table I. The product of these two spectra and the normalized, experimental three-pulse electron spin echo spectra of the solvated electron in CD_3CD_2OH is shown at the bottom. This figure demonstrates the validity of a two-shell simulation model.

been used to reveal the proton modulation. It can be seen that the proton modulation depth is not as great as is the deuterium modulation depth. This follows since the modulation depth for weakly coupled nuclei is greater for larger nuclear spins.[5,8] Thus, simulation of the proton modulation data is not as precise and does not give a unique set of parameters as does simulation of the deuterium modulation data. Furthermore, since the various protons are at different distances, a multishell model would be needed to simulate the proton modulation data. A simulation can be made which fits fairly well on the basis of the parameters determined from the specifically deuterated ethanols, but several sets of parameters also give similarly acceptable fits. So the uniqueness of the parameter determination from a fit to the proton modulation data is not as great as it is for analysis of the deuterium modulation data.

Figures 5 and 6 show the three-pulse modulation data with associated simulations for solvated electrons in C_2H_5OD and in CD_3CH_2OH, respectively. The parameters deduced from these fits as well as from the analysis of solvated electrons in CH_3CD_2OH shown in Figure 2 are summarized in Table I. The agreement of the parameters determined from the two-pulse data and the three-pulse data shown in Table I is excellent and lends credence to the uniqueness of the solvation-shell structure for electrons in ethanol glass that we will deduce. Note that for each of the three specifically deuterated ethanols the number of equivalent interacting deuterons is consistent with a first-solvation-shell number of molecules equal to four. This is determined redundantly from each of the specifically deuterated ethanols for both the two-pulse data and the three-pulse data.

As another check of the data analysis Figure 7 shows the experimental results for the electron spin echo decay associated with solvated electrons in CD_3CD_2OH compared with the product of the simulation generated from the parameters deduced for solvated electrons in CH_3CD_2OH and in CD_3CH_2OH. The good fit serves as a cross check of the analysis procedure and independently supports the uniqueness of the parameters determined for these two specifically deuterated ethanols.

Discussion

The data in Table I clearly show that there are four approximately equivalent first solvation shell ethanol molecules around the solvated electron. Using the three distances to the OD, CD_2,

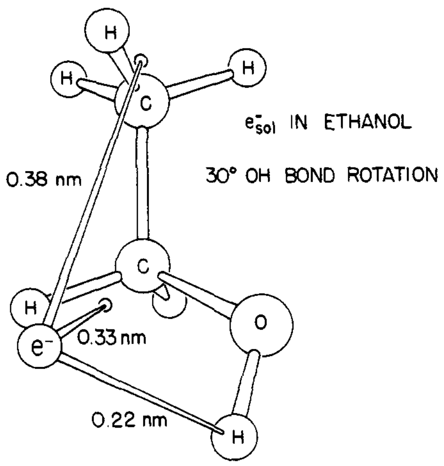

Figure 8. Suggested orientation of an individual first-solvation-shell molecule with respect to the solvated electron in ethanol with the OH bond rotated 30° around the OC bond away from the CCO plane. The distances are average distances to the OH, CH$_2$, and CH$_3$ protons. The entire solvation shell includes four ethanol molecules so oriented and arranged tetrahedrally around the electron. The molecular dipole of ethanol approximately bisects the COH angle and can be seen to be oriented approximately toward the electron.

and CD$_3$ deuteron groups in the specifically deuterated ethanol molecules and the known molecular structure of ethanol, we are able to obtain the orientation of the ethanol molecule with respect to the solvated electron. Although the electron-to-OD deuteron distance of 0.22 nm is the shortest, it is quite clear that the OD bond is not oriented toward the electron. If it were, the distances to the CD$_3$ and CD$_2$ groups would be much greater than are found experimentally. Using the CCO plane as a reference, we find that the three distance constraints can be met by rotating the OD bond around the OC bond away from the CCO plane through an angle of 30–60°. Thus the orientation of a first-solvation-shell ethanol molecule around the solvated electron is determined to this precision by the spin echo data. Perspective drawings of the OD bond rotated 30° to 60° are shown in Figures 8 and 9. In both limiting cases and for different rotational angles between 30° and 60° the electron is located approximately on the bisector of the COH angle of a first-solvated-shell ethanol. The main structural parameter that varies between these two limiting geometries is the electron-to-oxygen distance which varies from 0.25 nm for a OD rotation of 30° to 0.28 nm for an OD rotation of 60°. The 30° rotation should have less steric hindrance within the ethanol molecule and is favored on this basis.

The location of the solvated electron near the bisector of the COH angle of the solvating ethanol molecule is, in fact, the direction of the molecular dipole of ethanol. From microwave spectroscopic studies on methanol[21] it is known that the molecular dipole moment is not oriented along the OH bond but instead is oriented approximately along the bisector of the COH angle. It is certainly reasonable to assume that the molecular dipole orientation in ethanol is similarly oriented. Thus the orientations shown in Figures 8 and 9 for the solvated electron in ethanol assume a special significance in that they represent a molecular dipole oriented solvation shell with four ethanol molecules tetrahedrally arranged around the electron. The tetrahedral arrangement is not deduced unambiguously but is deduced indirectly from the requirement that the four solvating molecules in the first solvation shell are approximately equivalent.

We have now determined the solvated electron geometrical structure in three rather different solvating media, namely, water,[16] ethanol in this paper, and methyltetrahydrofuran.[6] In each case the geometry is somewhat different, but we think that we can qualitatively understand the interactions that generate these differing geometries. In aqueous systems we find an OH-bond-oriented solvation shell with six first-solvation-shell molecules. This geometry is indicative of dominating chemical bonding or chemical exchange interactions which determine the structure of the first solvation shell. This we propose is characteristic of small, strongly solvating molecules. In the case of ethanol we have a molecular-dipole-oriented solvation shell with only four first-solvation-shell molecules. This can be understood qualitatively in terms of simple electron charge–molecular dipole interactions which have been the mainstay of the theoretical semicontinuum potential model for solvated electron structure.[18] Finally, in the case of the larger and considerably less polar solvating molecule, methyltetrahydrofuran, we find that the CH groups are oriented toward the electron in contrast to orientation of the relatively weak molecular dipole moment. This suggests the dominance of electron charge–molecular polarizability interactions for determining the solvation-shell geometry in less polar and nonhydroxyllic media. These types of interactions also have been emphasized in a nonpolar version of the theoretical semicontinuum potential model for solvated electron structure.[22] It is interesting to note that a rather indirect analysis of the number of first-solvation-shell ethanol molecules around the solvated electron deduced from pulse radiolysis data on mixed water–ethanol glasses also came up with an average number of four first-solvation-shell molecules.[23]

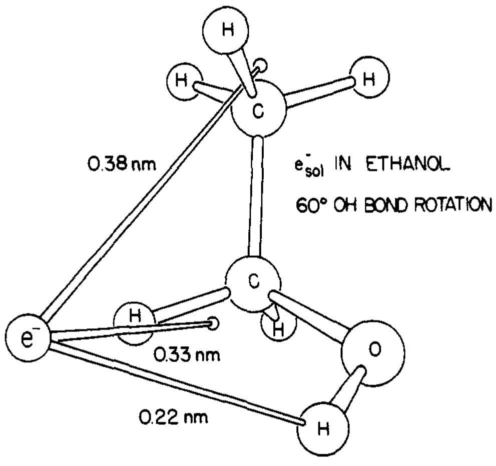

Figure 9. Suggested orientation of an individual first-solvation-shell molecule with respect to the solvated electron in ethanol with the OH bond rotated 60° around the OC bond away from the CCO plane. The distances are average distances to the OH, CH$_2$, and CH$_3$ protons. The entire solvation shell includes four ethanol molecules so oriented and arranged tetrahedrally around the electron. The molecular dipole of ethanol approximately bisects the COH angle and can be seen to be oriented approximately toward the electron.

It would be very interesting to deduce the explicit solvation-shell geometry for methanol around solvated electrons since it occupies a somewhat intermediate situation between water solvation and ethanol solvation, which have strikingly different geometries. We have made a number of attempts to deduce the structure of the solvated electron in methanol by electron spin echo studies. However, the phase memory time from the echoes is much shorter, so, thus far, we could not obtain any definitive data. We also attempted to eliminate the effect of the background radical contribution by using carbon-13-enriched methanol so as to split away the radical background signal from the center of the spectrum where the electron absorbs. Apparently the carbon-13 anisotropy is such to still give a significant radical contribution in the center of the spectrum so this idea was thwarted.

The best structural information we have obtained in the case of methanol is from an analysis of forbidden proton spin flips at 70 GHz.[24] We obtain a fairly unambiguous distance of 0.23 nm between the solvated electron and the nearest OH protons in the first solvation shell and a probable number of four first-solvation-shell methanol molecules. However, the orientation of the

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(21) E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **21**, 1804 (1979).

(22) T. Kimura, K. Fueki, P. A. Narayana, and L. Kevan, *Can. J. Chem.*, **55**, 1940 (1977).

(23) L. Kevan, *J. Phys. Chem.*, **79**, 2846 (1975).

(24) L. Kevan, *Chem. Phys. Lett.*, **66**, 578 (1979).

methanol molecule is not determined by this experiment. The distance to the OH proton is quite compatible with the present values for solvated electrons found in ethanol. We originally[24] suggested that the solvated electron in methanol would have an OH bond orientation, but we are now inclined to the view that it would have a molecular dipole orientation. A clear-cut resolution to this problem awaits new experimental approaches.

In summary, a general outline of the electron solvation geometry in both polar and nonpolar solvents is beginning to emerge. To some extent the current theory based on semicontinuum model potentials can semiquantitatively account for the experimental geometries for solvated electrons in ethanol and in methyltetrahydrofuran solvents, that is, for the case of large, polar solvating molecules and large, nonhydroxyllic, less polar solvating molecules.[18] For example, the electron-to-molecular-point-dipole distance for the first solvation shell in ethanol calculated on the basis of the semicontinuum model is 0.24 nm. One would presumably locate the point dipole near the oxygen in ethanol, so this theoretical distance correlates with the experimental distance range of 0.25–0.28 nm for the electron-to-oxygen distance determined here. However, for small, polar solvating molecules, as exemplified by water, the semicontinuum potential theoretical model, even in its ab initio incarnation,[25] does not satisfactorily explain the experimental geometry found.

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(25) M. Newton, *J. Phys. Chem.*, **79**, 2795 (1975).

Semiconductor Electrodes. 32. n- and p-GaAs, n- and p-Si, and n-TiO_2 in Liquid Ammonia

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Abstract: The behavior of several n- and p-type semiconductors in liquid ammonia with 0.1 M KI as supporting electrolyte was investigated. The flat-band potentials were estimated from Schottky–Mott plots, and the current–potential curves with several redox couples (e.g., benzophenone, naphthalene, nitrobenzene) in the dark and under illumination were obtained. Photoinjection of solvated electrons at p-GaAs and p-Si was demonstrated, and the results with these materials were shown to be consistent with those from the Fermi level pinning model. Solvated electron photovoltaic cells with these semiconductors were also constructed.

Introduction

The behavior of semiconductor electrodes in nonaqueous solvents such as acetonitrile (MeCN) is often very different than that observed in aqueous solutions.[1–6] The smaller interaction of the solvent with the electrode material and its oxidation products frequently results in higher stability of the semiconductor under irradiation, which is important in the design of photoelectrochemical (PEC) cells. Moreover, the wide potential range over which the solvent is stable allows the investigation of redox processes not observable in aqueous systems. There have been a number of electrochemical studies at metal electrodes in liquid ammonia.[7,8] Because the background limit of NH_3 is very negative and NH_3 has a low acidity, highly reduced species (e.g., radical anions, dianions) and solvated electrons are stable in this medium. In a recent study from this laboratory on the photoelectrochemical properties of p-GaAs in NH_3[9] we demonstrated that the photoinjection of solvated electrons at potentials ~0.9 V positive of the reversible potential for solvated electron production at a Pt electrode [−2.74 V vs. Ag/Ag^+ (0.1 M)[8,10]] could be accomplished. Such photoinjection suggested either that the conduction band edge of GaAs was situated at very negative potentials compared to the location found in other solvents or that the photopotential originated from specific surface effects.

Table I. Semiconductor Materials

semiconductor	source	contact	etchant
n-GaAs	Monsanto	In/Au[a]	(1) 3/1/1 mixture of $H_2SO_4/H_2O/30\%\ H_2O_2$ for 5 s (2) 6 M HCl for 25 s
p-GaAs	Atomergic	Au	as n-GaAs
n-Si	Monsanto	In/Ga	5/3/3 as mixture of $HNO_3/HF/CH_3CO_2H$ for 10 s
p-Si	Monsanto	Au	as n-Si
n-TiO_2	Fuji Titanium	In/Ga	5/3/3 mixture of $HNO_3/HF/CH_3CO_2H$ + 1 drop Br_2 per 100 cm^3 for 15 s

[a] Heated in H_2 to 400 °C for 2 h.

Recently, however, results from our group with p-GaAs[2,11] as well as by Wrighton and co-workers for p-Si[12] have led to our proposing that with these materials in aqueous and MeCN solutions, Fermi level pinning[13] occurs. This refers to the condition when the surface state density is sufficiently high that the accumulation of surface charge causes a shift in the location of the band edges; i.e., changes in the potential drop across the Helmholtz layer. More recent experiments have also suggested Fermi level

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(1) Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 747.

(2) Kohl, P. A.; Bard, A. J. *J. Electrochem. Soc.* **1979**, *126*, 59.

(3) Legg, K. D.; Ellis, A. B.; Bolts, J. M.; Wrighton, M. S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 4116.

(4) Yeh, L-S. R.; Hackerman, N. *J. Phys. Chem.* **1978**, *82*, 2719.

(5) Nakatani, K.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 783.

(6) Frank, S. N.; Laser, D.; Hardee, K. L.; Bard, A. J. *Proc.—Electrochem. Soc.* **1977**, *77-3*, p 149.

(7) Smith, W. H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 5203, and references therein.

(8) Teherani, T.; Itaya, K.; Bard, A. J. *Nouv. J. Chim.* **1978**, *2*, 481.

(9) Malpas, R. E.; Itaya, K.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 2535.

(10) Bard, A. J.; Itaya, K.; Malpas, R. E.; Teherani, T. *J. Phys. Chem.* **1980**, *84*, 1262.

(11) Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3677.

(12) Bocarsly, A. B.; Bookbinder, D. C.; Dominey, R. N.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3683.

(13) Bard, A. J.; Bocarsly, A. B.; Fan, F.-R. F.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3671.

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