

affect the quality of a semiconductor in a liquid junction solar cell. Since "prompt" carrier separation is essential, and since carriers are separated more rapidly by the field associated with the depletion region than by mere diffusion, it is essential to exclude high concentrations of impurities which increase the concentration of the majority carrier and thus shrink the depletion layer to below the absorption length. Impurities which do not change the carrier concentration must be avoided only if they trap one of the carriers, substantially reducing its mobility. Thus, we believe that not all impurities in semiconductors are damaging to the performance of semiconductor liquid junction solar cells.

The "laser off" experiments of Figures 2-4 correspond to a level of irradiance,  $I_1$  (Figure 6), at which there is no saturation. Consequently, a change in irradiance ( $\Delta I$ ) produces a similar change in current ( $\Delta i$ ) in both the imperfect semiconductor with a high recombination rate and in the one with the better material having a low recombination rate. The photocurrent spectra of the unetched and etched materials are thus not greatly different. Once the irradiance is increased to  $I_2$  ("laser on") a change in irradiance ( $\Delta I$ ) produces no change in the photocurrent ( $\Delta i$ ) in the unetched material but continues to produce in the etched sample a current increment ( $\Delta i$ ) identical with the earlier one. Consequently, the invariance of the photocurrent spectrum with irradiance at or above solar levels is an excellent indicator of the adequacy of the quality of a semiconductor in semiconductor liquid junction cell applications.

Using this criterion, we succeeded in attaining solar to electrical conversion efficiencies of 8-9% in several semiconductor liquid junction solar cells (Table I). The approximate short circuit current ("quantum") efficiencies range from 65 to 80% and would be closer to 100% if corrected for interface reflection and for solution absorption losses. Typical current-voltage curves for the unimproved ("unetched") and improved ("etched") CdSe cells are shown in Figure 7 of ref 7. At a typical solar irradiance (75 mW/cm<sup>2</sup>) a 40-fold improvement in efficiency is observed between the two samples.

## Experimental Section

The crystals used, the electrical contacts, the electrode structures, the auxiliary electrodes, the solutions, the light sources, the spectroscopic equipment, the electrochemical instrumentation, and the experimental method of measuring efficiencies are given in ref 7 except for the following. Cubic n-CdTe crystals cleaved in the (100) plane were purchased from Cleveland Crystals Inc., Cleveland, Ohio. The conductivities of the crystals were at least  $0.1 \Omega^{-1} \text{ cm}^{-1}$ . Ohmic contacts were formed to the back of CdTe plates with indium amalgams. Sn and Si doped (100) and (111) cleaved GaAs crystals were used. The contacts to these were made with successively evaporated tin, palladium, and gold layers. The active crystal face was brought to  $1 \pm 0.5 \text{ mm}$  of the window to minimize solution light absorption. In the CdTe and GaAs experiments the solution was 1 M K<sub>2</sub>Se-0.1 M Se-1 M KOH. A 1-mm thick layer of this solution cuts off 50% of the light near 500 nm. CdTe crystals were etched for 30 s in a 1:1:1 solution of concentrated HCl, concentrated HNO<sub>3</sub>, and saturated K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. GaAs was etched in a 1:1:4 solution of 30% H<sub>2</sub>O<sub>2</sub>, water, and concentrated H<sub>2</sub>SO<sub>4</sub> for 30 s. The initial spectra and voltammetric characteristics of all crystals as supplied could be changed by etching and restored by polishing with Linde A (0.3  $\mu$  alumina).

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## Anisotropic Motion inside a Micelle

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**Abstract:** Carbon-13 spin-lattice relaxation times have been determined for monomeric and micellar  $\omega$ -phenylalkanoic acids in aqueous base. Micellization decreases  $T_1$ 's markedly for the aromatic carbons, e.g.,  $T_1(\text{para}) = 2.9$  and 0.39 for monomeric and micellar  $\omega$ -phenyldecanoic acid, respectively. Moreover, micellization increases  $R = T_1(\text{ortho})/T_1(\text{para})$ , a parameter indicative of anisotropic motion by the aromatic system. Thus,  $R = 3.6$  for micellar  $\omega$ -phenyldecanoate (compared, for example, with a value of only 1.8 for biphenyl). The results are interpreted in terms of an 11-fold faster rotation about the carbon-carbon bond linking the benzene ring with the chain relative to rotations about axes perpendicular to this bond. Diluting the phenyl-substituted surfactants with simple straight-chain surfactants (SDS and DTAB) does not suppress values of  $R$  significantly; hence, anisotropic motion within a micelle cannot be ascribed solely to phenyl/phenyl interactions. Anisotropic motion inside a micelle is shown to depend on the depth of the phenyl ring, the pH, and the presence of additives. A comparison of the micellar  $T_1$  values with those in glycerol solutions of different viscosity demonstrates that the micelle interior is relatively fluid.

Problems of organization are intimately involved in living systems where thousands of reactions occur simultaneously. Because of the close relationship between life and molecular

order, more and more attention is being focused on organized assemblages such as the micelle. Micelles and related aggregates provide information not available from the usual studies

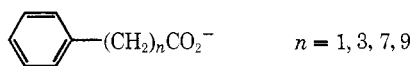
**Table I.**  $^{13}\text{C}$  Spin-Lattice Relaxation Times and Anisotropy Parameters for  $\omega$ -Phenylalkanoic Acids,  $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{COOH}$ , at 37.8 °C

<i>n</i>	Concn, M	Solvent	pD <sup>a</sup>	Additive	<i>T</i> <sub>1</sub> (ortho)	<i>T</i> <sub>1</sub> (para)	<i>R</i> <sup>b</sup>
7	0.50	CH <sub>3</sub> CN <sup>c</sup>			7.4	3.5	2.1
9	0.50	CH <sub>3</sub> CN <sup>c</sup>			6.1	2.9	2.1
1	0.50	29.5% glycerol/D <sub>2</sub> O <sup>d</sup>			2.5	1.4	1.8
1	0.50	68.1% glycerol/D <sub>2</sub> O <sup>e</sup>			0.49	0.27	1.8
1	0.50	D <sub>2</sub> O	12.7		5.3	3.1	1.7
3	0.50	D <sub>2</sub> O	12.7		3.5	2.0	1.8
7	0.50 <sup>f</sup>	D <sub>2</sub> O	12.7		1.6	0.59	2.7
9	0.50 <sup>g</sup>	D <sub>2</sub> O <sup>h</sup>	12.7		1.4	0.39	3.6
9	0.50	D <sub>2</sub> O	12.7	0.50 M NaCl	1.2	0.38	3.2
9	0.50	D <sub>2</sub> O	12.7	4.0 M urea	1.2	0.43	2.8
9	0.50	D <sub>2</sub> O	12.7	0.10 M DTAB <sup>i</sup>	1.1	0.34	3.2
9	0.50	D <sub>2</sub> O	12.7	25% EtOH	1.8	0.74	2.4
9	0.10	D <sub>2</sub> O	9.6	0.40 M SDS <sup>j</sup>	1.4	0.42	3.3
3	0.10	D <sub>2</sub> O	9.9	0.40 M SDS	2.8	1.5	1.9
9	0.50	D <sub>2</sub> O	9.5		1.1	0.44	2.5

<sup>a</sup> pD = meter reading + 0.4. <sup>b</sup>  $R = T_1(\text{ortho})/T_1(\text{para})$ . <sup>c</sup> Contained 5% D<sub>2</sub>O (v/v). <sup>d</sup> Viscosity = 4.334 cP at 37.8 °C. <sup>e</sup> Viscosity = 28.41 cP at 37.8 °C. <sup>f</sup> Cmc = 0.055 M at 25 °C. <sup>g</sup> Cmc = 0.013 M at 25 °C. <sup>h</sup> Viscosity = 3.429 cP at 37.8 °C. <sup>i</sup> Dodecyltrimethylammonium bromide. <sup>j</sup> Sodium dodecyl sulfate.

of sequestered chemical processes in solution. The transition from single molecule to aggregate has not been easy; virtually every aspect of micellar chemistry is now under debate. Consider, for example, the subject of this paper: molecular motion and viscosity inside a micelle. In a recent review it is written, "The micelle interior is viscous, as illustrated by the polarization of fluorescence of probe molecules dissolved in the micelle. Microviscosities approaching 100 cP have been measured".<sup>1</sup> Yet in a concurrent article one reads, "The intuitive view is that the interior of the micelle is like a liquid hydrocarbon droplet. Comparisons of the mobilities of fluorescence and ESR probe molecules solubilized in micelles and dissolved in organic solvents have shown that this is largely true ...".<sup>2</sup>

We describe herein an examination of micellar systems by means of carbon-13 spin-lattice relaxation times ( $T_1$ ).  $T_1$  values have been widely used to explore the vagaries of molecular motion: anisotropic reorientations, flexibility differences along carbon chains, effects of intermolecular association on mobility.<sup>3,4</sup> Previous scrutiny of micelles by the  $T_1$  method has been based primarily on the concept of "segmental motion".<sup>5-11</sup> Thus, in 1973 Cordes et al.<sup>11</sup> showed that aggregation of *n*-octyltrimethylammonium bromide in water restricts the movement of the octyl carbons near the polar head more than those near the other end of the chain. Our own  $T_1$  experiments rely not so much on the idea of segmental motion as on the observation that anisotropic motion relaxes unequally the ortho and para carbons of many monosubstituted benzenes.<sup>12</sup> Preferred rotation around the  $C_2$  symmetry axis changes the direction of the ortho C-H bond (but not the para C-H bond) relative to the applied field. As a result, the  $^{13}\text{C}$ - $^1\text{H}$  dipole-dipole interactions relax the para carbon more efficiently than the ortho carbon ( $T_1^o > T_1^p$ ).<sup>13</sup> We have investigated anisotropic motion inside a micelle by means of  $T_1^o/T_1^p$  ratios ("R" values) for monomeric and micellar  $\omega$ -phenylalkanoic acids in aqueous base.



## Results and Discussion

Molecular motion in surfactant aggregates is best analyzed using the monomeric state as a basis for comparison. There are three simple ways of achieving nonaggregated systems: operate below the critical micelle concentration of the surfactant; use an organic solvent in which micelles do not form; shorten the chain length of the surfactant to a point where the compound

loses its surfactant properties under the experimental conditions. The first of these is in principle the most satisfactory because neither the surfactant nor the solvent is perturbed. Unfortunately, sensitivity problems preclude  $T_1$  measurements below most cmc values; several weeks of machine time would have been required for a single  $T_1$  experiment on  $\omega$ -phenyldecanoate below its cmc. We therefore relied on a combination of the "organic solvent" and "shortened chain" methods to evaluate monomeric  $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{COOH}$ . One sees from Table I that long-chain acids ( $n = 7$  and 9) in CH<sub>3</sub>CN and short-chain acid anions ( $n = 1$  and 3) in D<sub>2</sub>O give equivalent results characteristic of the monomeric state: large  $T_1$ 's for the ortho and para carbons (2.0–7.4 s) and small  $R$  values (1.7–2.1).

$\omega$ -Phenyldecanoate ( $n = 7$ ) and  $\omega$ -phenyldecanoate ( $n = 9$ ) in D<sub>2</sub>O exist predominantly as micelles at 0.50 M (the concentration of most of the  $T_1$  runs). Critical micelle concentrations, determined by the dye method with pinacyanol chloride,<sup>14</sup> were found to be 0.055 M for  $n = 7$  and 0.013 M for  $n = 9$  at pD 12.7. Presumably, the structure of the  $\omega$ -phenylalkanoate aggregates does not deviate too radically from the conventional picture of micelles<sup>15</sup> because the phenyl group is hydrophobic and known to be equivalent to 3.4 methylenes in lowering cmc values.<sup>16,17</sup> Our cmc values are normal when compared to fatty acids of equivalent chain length.<sup>18</sup> Diluting  $\omega$ -phenyldecanoate with more prosaic surfactants (e.g., sodium dodecyl sulfate) does *not* change the  $T_1$  parameters (Table I). Whatever the precise micellar structure, it is obvious that aggregation has a drastic effect on the absolute  $T_1$  values of both the ortho and para carbons. For example,  $T_1^p$  decreases from 2.9 s to 0.39 s upon micellization of  $\omega$ -phenyldecanoate. In addition, the anisotropy parameter  $R$  displays a marked increase from approximately 2 for the monomer to as high as 3.6 for the micelle.

Although the  $T_1$ 's for the micellar systems represent weighted averages of  $T_1$ 's from monomeric and aggregated surfactant, a correction to obtain "true" micellar values is unnecessary for  $\omega$ -phenyldecanoate; the percentage of monomer under the experimental conditions is insignificant (2%). We did make a minor correction on the  $\omega$ -phenyldecanoate data using eq 1 ( $T_1$ ,  $T_{1f}$ , and  $T_{1m}$  are the observed, monomeric, and micellar relaxation times, respectively;  $\chi_f$  and  $\chi_m$  are the corresponding mole fractions).<sup>11</sup>

$$1/T_1 = \chi_f/T_{1f} + \chi_m/T_{1m} \quad (1)$$

Since exchange between micelle and monomer is rapid relative to  $1/T_1$ , the observed  $1/T_1$  is a weighted average of the com-

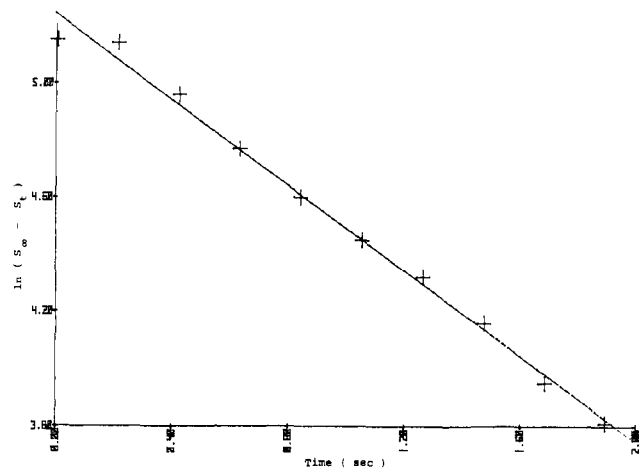


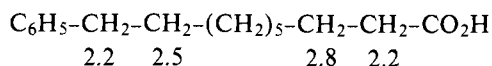
Figure 1. Inversion-recovery plot for  $T_1$  determination (peak height  $S$  in arbitrary units); ortho carbon of  $\omega$ -phenyldecanoate (0.50 M) at pD 12.7 and 37.8 °C.

ponent  $1/T_1$  values. In accordance with the "phase separation" theory of micelles,<sup>19</sup> we used the cmc to approximate the monomer concentration.

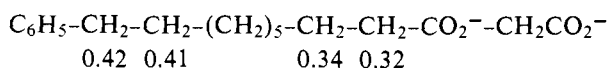
Absolute  $T_1^\circ$  values in Table I can be used to gauge the microviscosity of the micelle interior. Monomeric  $\omega$ -phenylacetic acid has a  $T_1^\circ$  which decreases from 5.3 s in  $D_2O$  to 2.5 s in a glycerol solution of viscosity 4.33 cP and to 0.49 s in a glycerol solution of viscosity 28.4 cP. In contrast,  $T_1^\circ = 1.4$  s for micellized  $\omega$ -phenyldecanoate (with the macroscopic viscosity of the solution equaling 3.43 cP). If one assumes a linear relationship between  $T_1^\circ$  and the reciprocal of the viscosity,<sup>8</sup> then a  $T_1$  of 1.4 corresponds to a micellar viscosity of 8.3 cP. By way of comparison, 8.3 cP is *less* than the value for neat dodecane at 23 °C (12.6 cP). Our  $T_1^\circ$  data point clearly to a fluid micelle interior. This is consistent with work of others<sup>19,20</sup> but not with the claim of a 100-cP microviscosity or the existence of a paraffin-like micelle core.<sup>21</sup> No doubt the disparate opinions with regard to micellar viscosity originate in part from the nature of the specific experimental technique. For example, a large fluorescent probe molecule adsorbed into a micelle would likely experience mobility problems different from those of a small benzene ring.

Segmental motion in micellar *n*-octyltrimethylammonium bromide has been shown to cause a monotonic increase in the methylene  $T_1$ 's from 0.9 s at the head to 2.9 s at the tail.<sup>11</sup> The ionic head of the surfactant anchors the proximal carbons. The question arose as to how the phenyl group in the interior of the  $\omega$ -phenyldecanoate micelles affects the mobility of the methylene chain. Thus a series of runs was performed with monomeric and micellar  $\omega$ -phenyldecanoate in  $CH_3CN$  and  $D_2O$ , respectively, to determine  $T_1$  values of the chain carbons  $\alpha$  and  $\beta$  to the phenyl and carboxyl groups. The data are presented below.

monomeric



micellar



Both monomer and micelle have interior methylenes with  $T_1$  values similar to those of methylenes adjacent to the carboxylate. The phenyl group impedes segmental motion of the nearby methylenes, but the effect is no greater in the micelle than in the free state. This substantiates our conclusion that

the aromatic moiety is embedded in a relatively low-viscosity region inside the micelle.

We now turn to the issue of anisotropic motion within a micelle as determined by  $R = T_1^\circ/T_1^p$ . Since  $R$  is a ratio of relaxation times, the parameter is less sensitive to micellization than absolute  $T_1$  values. For example,  $R$  for  $\omega$ -phenyldecanoate increases from 2.1 as a monomer to 3.6 as a micelle. In order to prove that this change is in fact exceptionally large and significant, we must first discuss briefly data accuracy.<sup>22</sup> The matter of data accuracy is covered in the Experimental Section, but it should be emphasized again that we evaluated one  $T_1$  at a time under optimum settings (determined in a trial run) taking ten points between 0 and 75% recovery (Figure 1). This contrasts with the more usual procedure of measuring several widely different  $T_1$ 's in a single experiment, under less than optimum settings, and then using only three to five points per  $T_1$ .<sup>23</sup> As a result of our precautions, the experimental error in  $R$  is  $\pm 10\%$ .

Anisotropy parameters never assume large values. Diphenylacetylene, a classical example of a rigid tubular molecule which rotates preferentially about its long axis, has an  $R$  of only 2.9. An  $R = 3.6$  for micellar  $\omega$ -phenyldecanoate (among the largest ever measured) cannot be reasonably explained either by isotropic tumbling of the entire aggregate or by rotation of the surfactant molecule as a whole about its long axis.<sup>24-26</sup> Anisotropic motion of the occluded phenyl group most likely relates to a favored spinning mode about the C-C bond joining the benzene ring and methylene chain.<sup>27</sup> An  $R = 3.6$  corresponds to a rotation around this bond which is 11-fold faster than rotation about axes perpendicular to the bond.<sup>12</sup> A smaller rotational preference is observed for  $\omega$ -phenyloctanoate ( $R = 2.7$ ) perhaps because the shorter chain results in a less compacted aggregate.<sup>28,29</sup>

Adding 0.40 M cosurfactant (either sodium dodecyl sulfate or dodecyltrimethylammonium bromide) to 0.10 M  $\omega$ -phenyldecanoate in  $D_2O$  dilutes the phenyl groups within the micelles. Yet the large  $R$  value for  $\omega$ -phenyldecanoate persists in the mixed micelle systems (Table I). Accordingly, anisotropic motion cannot be ascribed solely to phenyl/phenyl interactions within the aggregate core. This experiment is important in relation to the lingering question of whether or not the micelles of  $\omega$ -phenyl surfactants are "normal". A short-chain analogue, 4-phenylbutyrate, has relatively large  $T_1$  values and an  $R$  of only 1.9 when adsorbed into sodium dodecyl sulfate micelles (Table I). Motional freedom thus depends on how *deep* the aromatic ring penetrates the micelle. This conclusion emphasizes the difficulties in generalizing from experiments involving large environmental probes (e.g., fluorescence depolarization probes) incorporated into micellar aggregates. A probe molecule measures a property at only one point (or a weighted average from several points) in what seems to be a continuum of environments.

Urea (4.0 M) and ethanol (25% v/v) both reduce the  $R$  value for 0.50 M  $\omega$ -phenyldecanoate at pD 12.7 (Table I). Surprisingly, lowering the pD from 12.7 to 9.6 (just above the precipitation point) decreases  $R$  from 3.6 to 2.5. One might have expected partial production of the anionic head groups to have contracted the Stern layer and increased the value of  $R$ . Since just the opposite was observed, the aggregates probably *lose* compactness near precipitation conditions, causing a diminished rotational preference. Previous workers have also recorded peculiar behavior of fatty acids in less basic solutions.<sup>30</sup>

Peripheral spin-lattice relaxation experiments were carried out on mixtures of 0.50 M  $\omega$ -phenyldecanoate and 0.50 M ethanol ( $D_2O$ , pH 12.7, 37.8 °C). The methylene of *ethanol* was found to have a  $T_1$  value of 6.6 s (compared to 14.2 s in  $D_2O$  without surfactant). Much smaller changes in the  $T_1$  of this methylene occur when 0.50 M ethanol is mixed in  $D_2O$

Table II. Reproducibility of  $T_1$  Data for 4-Phenylbutyric Acid

Run	Ortho	Para	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
1	3.51				
2	3.56				
3		1.93	1.82	1.81	1.91
4		2.10	1.70	1.85	1.97

with 0.50 M phenylacetate (13.4 s), 7.5% w/v  $\gamma$ -globulin (13.6 s), and 10% w/v Carbowax 6000 (12.6 s). We have for the first time provided direct evidence that low levels of ethanol are in fact adsorbed by micelles.<sup>31</sup>

### Experimental Section

**Materials.** Pfaltz and Bauer  $\omega$ -phenyloctanoic acid and  $\omega$ -phenyldecanoic acid were found sufficiently pure to use as purchased. Other surfactants were crystallized prior to the experiments. Certified viscosity standards were obtained from Cannon Instrument Co.

**$T_1$  Measurements.** Spin-lattice relaxation time measurements on a Varian CFT-20 spectrometer were first conducted on compounds with known  $T_1$  values (ethylbenzene, camphor, dioxane, and phenol) using inversion-recovery pulse sequences. Only after convincing ourselves of the reliability of the methodology did we begin  $T_1$  determinations with the surfactant systems. The following two precautions were considered especially important in minimizing experimental error: (1) Initial trial runs were carried out to select optimal pulse delays "PD" and increments "LI" and "LT" for each carbon. (2) Spin-lattice relaxation times were then determined for a single carbon at a time using the optimal settings for that particular carbon. We also kept the surfactant concentration as low as possible ( $\leq 0.5$  M) because micelle size and shape are known to change at high concentrations. The combination of dilute solutions, repeat runs, and single-carbon  $T_1$ 's required substantial amounts of machine time (often 1 week per  $T_1$ ). Typical conditions: pulse width = 23  $\mu$ s (calibrated), pulse delay  $\geq 4T_1$ , 10 points per run, 500 accumulations per point. The constancy of the equilibrium signal intensity was always checked over the entire time span of the run. Probe temperature was measured periodically ( $37.8 \pm 0.2$  °C). Table II illustrates the degree of reproducibility commonly achieved with our system. On the basis of such repeat runs we believe that reported  $R$  values are accurate to  $\pm 10\%$ .

The C-13 chemical shift of the ortho carbon appeared downfield from the para carbon in all systems. Assignments of the chain carbons  $\alpha$  and  $\beta$  to the phenyl and carboxyl groups were made with the aid of reference compounds (pentanoic acid and 1-phenyldecane) along with literature data.<sup>32</sup>

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