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Mobility Of Solvent Molecules In A Nonaqueous Lyotropic Liquid Crystal

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induced fluorescence. The buildup of triplet fluorescence intensity was measured as a function of the time separation between the excitation and the probe pulses, and allowed analysis of the appearance of ^{3}DPC. The value of k_{ST} measured by this method was found to be $(9.1 \pm 1) \times 10^9$ s^{-1}.

Combining the value of k_{ST} with that for k_{ST}/k_q^1 (measured from Figure 1) allows evaluation of $k_q^1 = (3.5 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}. The latter is very close to the value for diffusion-controlled reaction in acetonitrile. From knowledge of k_{ST} and k_{TS}, the equilibrium constant for the process ^{1}DPC $\rightleftarrows$ ^{3}DPC is computed to be $(5.4 \pm 1) \times 10^3$, with an associated free-energy difference of 5.1 ± 1 kcal/mol at 25 °C.

These values may be compared to the estimates of Closs and Rabinow,[3] who, with the assumption of a diffusional quenching constant of 5×10^9 M^{-1} s^{-1} of ^{1}DPC by methanol in benzene, computed an equilibrium constant of 5×10^2. The difference between our direct experimental value and the indirect measurement of Closs and Rabinow[3] may reflect a small solvent effect on the equilibrium constant.[11] Our steady-state data for the quantity $k_{ST}/(k_q^1 k_{TS})$ was found to be 1.6×10^{-7} Ms in acetonitrile, and we compute a value of 1.0×10^{-7} Ms for this quantity from published data.[3]

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(11) **Note Added in Proof**: Equation 1 may be inverted to yield an expression for $^1\phi/^3\phi$ which is a linear function of 1/[IP] at constant methanol concentration. Evaluation of the rate constants of Scheme I by fitting this expression leads to values which are in even closer agreement to the estimates of Closs and Rabinow[3] than the values achieved employing eq 1.

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Mobility of Solvent Molecules in a Nonaqueous Lyotropic Liquid Crystal

Sir:

The binary system composed of phosphatidylcholines (lecithins) and water is known to exhibit several phases,[1] and this system has been studied by a variety of techniques,[2] including NMR.[3] Recently, we have found[4] that the important aqueous lyotropic liquid crystalline phase, exhibited by lechithins, has a nonaqueous counterpart, and we are currently undertaking a research program to delineate and characterize this new phase.

Deuterium NMR quadrupole splittings and spin–lattice relaxation times have been found to be very useful for characterizing the aqueous lecithin phases,[5] and we have made preliminary ^{2}H NMR studies on the lamellar liquid crystalline phase formed by dilinoleyllecithin (L) and ethylene glycol-d_4 (EG) at 20 °C. The ^{2}H NMR parameters are presented in Table I for sample compositions that span the range of stability of the phase. The results

Table I. Deuterium NMR Parameters[a] for Lecithin/Ethylene Glycol-d_4 Liquid Crystalline Phase

wt percentage L:EG	mol of EG/ mol of L	quadrupole[b] splitting, Hz	T_1,[c] ms
90:10	1.32	1750	6.2
80:20	2.97	928	14.7
70:30	5.04	630	24.0
60:40	7.91	461	33.3

[a] Parameters refer to methylene deuterons. [b] Experimental uncertainty ±3%. [c] Experimental uncertainty ±10%.

Table II. Parameters for "Bound" and "Free" Sites in Lecithin/Ethylene Glycol-d_4 Liquid Crystalline Phase

quadrupole splitting, Hz		relaxation time, ms	
bound	free	bound	free
2240	230	5.1	140

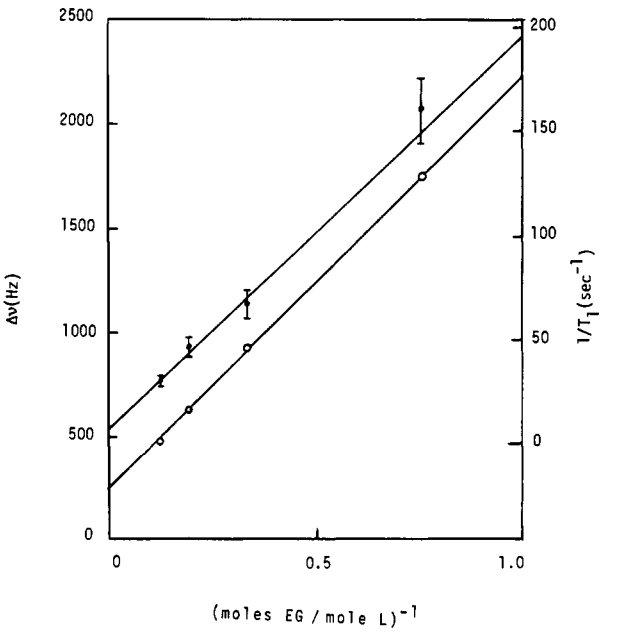

Figure 1. Deuterium NMR quadrupole splittings ($\Delta\nu$) (O) and spin–lattice relaxation rates ($1/T_1$) (·) vs. fraction bound for lecithin/ethylene glycol-d_4 liquid crystalline phase at 20 °C.

shown in Table I are indicative of increased motion, on the average, with increased EG content. However, we wish to analyze both the concentration dependence and the magnitude of the splittings in terms of models. It is of interest that a very simple model appears to account for the concentration dependence of the splittings in Table I. Consider EG interacting with the L head group to form a 1:1 complex, in which all L sites are filled, and the remaining EG exists in a "free" state. Rapid exchange between "bound" and "free" EG is assumed so that NMR parameters are weighted averages over the two sites. The splittings in bound and free sites are $\Delta\nu_B$ and $\Delta\nu_F$, respectively, and the fraction of bound EG is p_B = [mol of EG/mol of L]$^{-1}$. The observed splitting $\Delta\nu$ is given by eq 1. If both $\Delta\nu_B$ and $\Delta\nu_F$ are concentration independent, then a plot of $\Delta\nu$ vs. p_B will be linear. Such a plot is shown in Figure 1, wherein it can be seen that the plot is linear within experimental error. An analogous treatment for spin–lattice relaxation predicts eq 2, and the appropriate plot is also shown in Figure 1. It can be seen that this plot is linear within experimental error. The parameters characterizing bound and free sites are obtained from the intercepts in Figure 1, and these are shown in Table II.

$$\Delta\nu = p_B(\Delta\nu_B - \Delta\nu_F) + \Delta\nu_F \quad (1)$$

$$1/T_1 = p_B(1/T_{1B} - 1/T_{1F}) + 1/T_{1F} \quad (2)$$

There are several interesting results that are obtained within the context of this simple model. First, $\Delta\nu_B$ and $\Delta\nu_F$ are inde-

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pendent of sample composition. Since these splittings are unaffected by "slow" motions and are reduced by "rapid" motions, the observation is equivalent to the statement that no motion changes from the slow limit to the rapid limit as a function of sample composition. Second, T_{1B} and T_{1F} are also independent of sample composition. This result places a further restriction on the system that the correlation times for motions controlling relaxation in both bound and free sites are independent of sample composition.[6] Third, a nonzero splitting is obtained for the free site, and this is indicative of restricted motion.[7]

Interpretation of T_{1B} and T_{1F} values can be done only in terms of the specific motion controlling each relaxation; a procedure similar to that used for D_2O relaxation in lecithin/D_2O systems might be used.[8] Our interpretation of the quadrupole splittings (see below) suggests that there are several rapid motions that could contribute to spin-lattice relaxation in this system which will make interpretation of T_1 values difficult.

The magnitude of $\Delta\nu_B$ can be explained in a straightforward manner, using an approach similar to that used for aqueous lecithin phases.[9] If the binding site for EG is taken to be the phosphate group on L, then local rotation of EG while bound to L could result in the P-O bond axis becoming a symmetry axis. Rapid reorientation of L around an axis parallel to the long chain is also expected.[10,11] We assume tetrahedral geometry for EG and nonbonding orbitals on O, and an O-P-O bond angle[13] of 121.6°; from these values, assuming the motions above, we calculate a splitting of 2.0 kHz, which agrees with the $\Delta\nu_B$ value given in Table II.

This preliminary study indicates that the EG/L nonaqueous system lends itself to a more straightforward interpretation than does the H_2O/L system. This is due partly to the fact that in the aqueous system, solvation of the L head group apparently involves at least five water molecules.[9] We are continuing these studies by investigating other features of the nonaqueous lecithin liquid crystalline phase, including proton relaxation, translational diffusion, and the effect of varying the diol chain length.

(6) Spin-lattice relaxation times are usually given in terms of spectral density functions, which are developed in terms of correlation times. See: A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, Oxford, 1961, Chapter 8.
(7) The concept of restricted motion has been discussed in C. H. A. Seiter and S. I. Chan, *J. Am. Chem. Soc.*, **95**, 7541 (1973).
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Theory versus Experiment: The Case of Glycine

Sir:

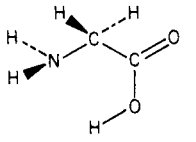
Some time ago, the microwave spectrum of glycine was recorded independently by Brown et al.[1] and by Suenram and Lovas.[2]

Table I. 4-21G ab Initio Optimized Structural Parameters of Glycine[a]

	I	II	III
r(N-H)	1.001	1.000	1.001
r(N-C)	1.457	1.474	1.457
r(C-H)	1.081	1.081	1.081
r(C-C)	1.514	1.535	1.522
r(C=O)	1.203	1.202	1.204
r(C-O)	1.364	1.345	1.365
r(O-H)	0.966	0.975	0.966
θ(NCC)	113.28	110.19	115.92
θ(CC=O)	126.41	122.32	125.42
θ(CC-O)	110.62	113.82	112.18
θ(CO-H)	112.28	108.44	111.49
θ(CNH)	113.27	114.49	112.58
θ(CCH)	107.87	107.67	107.14
θ(HNH)	110.29	111.36	109.79
θ(HCH)	107.04	107.37	106.61
θ(NCH)	110.27	111.87	109.80
τ(NCC=O)	0.0	180.0	180.0
τ(NCCO)	180.0	0.0	0.0
τ(CCOH)	180.0	0.0	180.0
τ(CCNH)	63.29	114.83	62.38
τ(O-CCH)	57.65	122.25	122.96
E(tot)	-282.15805	-282.15460	-282.15497
E(rel)	0.0	2.2	1.9
μ	1.10	6.54	1.76
F(res)	<0.007	<0.004	0.005

[a] Bond lengths, r, in Å; bond angles, θ, and torsional angles, τ, in deg; total energies, E(tot), in au; relative energies, E(rel) in kcal/mol; dipole moments, μ, in D; largest residual force, F(res), in mdyn. Pulay's FORCE program with the 4-21G basis[6] was used in connection with the normal coordinate force relaxation procedure of Sellers et al.[7] to generate the optimized parameters.

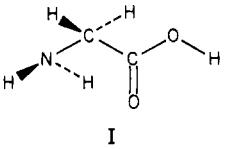
From the experimental evidence, both groups concluded that the particular conformer observed was II. Since no isotopic sub-



II

stitutions were performed, however, quantitative structural information regarding precise bond lengths and angles could not be obtained. In parallel with the microwave work, Sellers and Schäfer carried out a completely relaxed ab initio equilibrium structure on two low-energy forms of glycine.[3]

These calculations confirmed the results of earlier less sophisticated calculations[4] in that they predict II to be less stable than I by approximately 1-2 kcal/mol. The striking fact here,



I

however, is that the refined ab initio calculations for II yielded a structure that reproduced the microwave rotational constants with an amazing degree of accuracy. Although it is possible that the excellent agreement was simply fortuitous, it was also possible that the calculations were providing a reasonable estimate of the structure and relative energy. In view of this, two interpretations were possible. Brown et al.[1] concluded that II was "the most likely conformation of glycine in the vapor state", even though they could not exclude the possibility that the vapor contained one or more other, undetected species. Suenram and Lovas[2] and Sellers and Schäfer[3] concluded that the exclusive observation of II did not

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