

## Hydrodynamic effect on chemically induced dynamic spin polarization\*

J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 23 April 1973)

Chemically induced dynamic nuclear and electron polarization, CIDNP and CIDEF, respectively, refer to the anomalous NMR or ESR spectra that arise from free-radical reactions in solution. Recently Pedersen and Freed<sup>1-3</sup> have shown how Kubo's stochastic Liouville method<sup>4</sup> for the spin density matrix  $\rho(\mathbf{r}, t)$  may be employed to obtain a systematic analysis of these phenomena. A closely related approach has been reported by Evans, Flemming, and Lawler.<sup>5</sup> The analysis of the CIDNP and CIDEF phenomena rely on the adoption of a particular model for the motion of a radical pair in solution. Accordingly, as we have emphasized,<sup>6</sup> these measurements present an attractive tool for the study of radical recombination. The purpose of this Note is to draw attention to a mechanism, the hydrodynamic interaction, that influences the relative diffusive motion of the radical pair. This hydrodynamic mechanism, which has not previously been considered in CIDNP and CIDEF studies, leads to a model for diffusion that is substantially different from prior models.

The stochastic Liouville equation is

$$\partial\rho(\mathbf{r}, t)/\partial t = -i[H(\mathbf{r}), \rho(\mathbf{r}, t)] + L(\mathbf{r})\rho(\mathbf{r}, t), \quad (1)$$

where  $H(\mathbf{r})$  is the appropriate spin Hamiltonian for the radical pair which depends on the distance between radicals  $\mathbf{r}$  through the exchange interaction  $J(\mathbf{r})$ . The operator  $L(\mathbf{r})$  describes the stochastic relative motion of the radical pair. Early treatments<sup>1,2,5,6</sup> adopted a model of independent diffusion for the relative motion of the radicals. Thus  $L_D(\mathbf{r}) = D\nabla^2$  where  $D = (D_A + D_B)$  is the diffusion coefficient for the relative motion between the two radicals A and B. More recently, Pedersen and Freed<sup>4</sup> have adopted a more realistic model that includes the effects (perhaps spin dependent) of attraction or repulsion through a potential energy  $U(r)$  between the radicals. They adopt the Smoluchowski form of the diffusion operator appropriate to the diffusive motion of a particle in a potential field,  $L_U(\mathbf{r}) = D\{\nabla^2 + (kT)^{-1}\nabla \cdot [\nabla U(r)]\}$ . For various cases of interest Pedersen and Freed find significant effects in their numerical results from the presence of the interaction  $U(r)$ .

There is, however, an important *hydrodynamic* effect that is not included in the Smoluchowski diffusion operator model. This effect, which is well known in polymer theory, arises from the systematic flow pattern created in an incompressible fluid as a pair of particles diffuse under the influence of an interaction potential. For spherical Brownian particles at large separation, this hydrodynamic effect can be included within the framework of the diffusion theory.<sup>7</sup> For this model the appropriate diffusion operator<sup>7,8</sup> is

$$L_H(\mathbf{r}) = \nabla \cdot [D\mathbf{I} - 2(kT)\mathbf{T}(\mathbf{r})] \cdot \{\nabla + (kT)^{-1}[\nabla U(r)]\}, \quad (2)$$

where  $\mathbf{I}$  is the unit tensor and  $\mathbf{T}(\mathbf{r})$  is Oseen's tensor given by  $\mathbf{T}(\mathbf{r}) = (8\pi\eta r)^{-1}[1 + \mathbf{r}\mathbf{r}(r^{-2})]$  with  $\eta$  the solvent viscosity.<sup>9</sup> The presence of Oseen's tensor in  $L_H(\mathbf{r})$  approximately takes into account the hydrodynamic effect on the diffusive motion of the radicals. The effect is known to be of importance. For example the steady-state rate of diffusion-controlled radical recombination reactions may be reduced by as much as 50% compared to the Smoluchowski-Debye model where the hydrodynamic effect is not considered.<sup>8</sup>

For systems where spherical symmetry can be assumed, the three alternative diffusion operators take the form  $L_D(r) = Dr^{-2}(\partial/\partial r)(r^2)(\partial/\partial r)$ ;  $L_U(r) = Dr^{-2}(\partial/\partial r)(r^2)[(\partial/\partial r) + (kT)^{-1}U'(r)]$  and

$$L_H(r) = r^{-2}(\partial/\partial r)(r^2)[D - (kT/2\pi\eta r)] \times [(\partial/\partial r) + (kT)^{-1}U'(r)]. \quad (3)$$

This operator formally corresponds to diffusion in a potential field with a space-dependent diffusion coefficient. We have not been able to find an exact solution for this problem. Accordingly for solution of the stochastic Liouville equation Eq. (1) with  $L(\mathbf{r}) = L_H(r)$  one must resort to a finite difference numerical technique such as that employed by Pedersen and Freed<sup>1-3</sup> for the case of  $L = L_D$  and  $L = L_U$ . For some cases of interest, depending on the values of the relevant parameters substantial differences may be anticipated, even for the case  $U=0$ . A very crude estimate of the effect may be obtained by approximating  $L_H(r)$  by  $L_U(r)$  with a

smaller, effective diffusion coefficient,  $D_{\text{eff}} = [D - (kT/2\pi\eta\bar{r})]$  where  $\bar{r}$  is an "average" separation. Use of Stokes' law and the assumption that  $\bar{r}$  is  $f$  times the radical diameter ( $f > 1$ ) leads to the conclusion that  $(D_{\text{eff}}/D) = [1 - (\frac{3}{4}f)]$ . From the reported numerical results<sup>2,3</sup> one sees that this difference can cause a substantial change in observed polarizations. Of course a complete appreciation of the impact of the effect of the hydrodynamic interaction on the observed quantities requires a numerical analysis that properly includes the perturbation of the hydrodynamic interaction on the diffusion trajectories. Such an analysis would be most welcome.

Introduction of the hydrodynamic model presented here serves to emphasize once again the desirability of extensive CIDNP and CIDEP experimental

studies that may distinguish between the various models of radical motion in solution.

\*Supported in part by the National Science Foundation.

<sup>1</sup>J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* **57**, 1004 (1972).

<sup>2</sup>J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* **58**, 2746 (1973).

<sup>3</sup>J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* (to be published).

<sup>4</sup>R. Kubo, *Adv. Chem. Phys.* **15**, 101 (1969); *J. Phys. Soc. Jap. Suppl.* **26**, 1 (1969).

<sup>5</sup>G. T. Evans, P. D. Flemming, and R. G. Lawler, *J. Chem. Phys.* **58**, 2071 (1973).

<sup>6</sup>J. M. Deutch, *J. Chem. Phys.* **56**, 6076 (1972).

<sup>7</sup>R. Zwanzig, *Adv. Chem. Phys.* **15**, 325 (1969).

<sup>8</sup>J. M. Deutch and B. U. Felderhof, *J. Chem. Phys.* **58**, 1669 (1973).

<sup>9</sup>If desired the analysis may be performed with Oseen's tensor replaced by Stokes' tensor  $\mathbf{A}(\mathbf{r}) = \zeta\mathbf{T} + (a^3/4r^3)[\mathbf{I} - 3\hat{r}\hat{r}]$  where  $\zeta = (kT/D)$  is the friction coefficient.