A novel liquid crystalline system for partial alignment of polar organic molecules

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Abstract

A new system for partial alignment of polar organic molecules to measure residual dipolar couplings in NMR consists of a 1:1 or a 2:1 mixture of water and DMSO including 3–13% n-alkylpentaethylene glycol as the surfactant. Temperature and concentration dependence of the alignment system are investigated and, as examples, the $^{13}C,^1H$ residual dipolar couplings for the amino acid methionine **1** and for an α-methylene-γ-butyrolactone **2** have been obtained and are compared with those obtained from the alignment media consisting of n-alkylpentaethylene glycol, n-alkyl alcohol and water.
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Keywords: NMR; Partial alignment; Liquid crystal; Residual dipolar couplings; Organic molecules

1. Introduction

Traditionally, the structure determination of relatively small organic compounds in solution is based on both one- and two-dimensional NMR spectroscopy such as COSY, HMQC, and HMBC [1]. Stereochemical questions are most often addressed with NOESY [2] which allow the determination of the distances between magnetic nuclei up to 5 Å. Increasing the number of atoms in a molecule and hence their distances results in NMR spectra, where *J* couplings and NOE values often are not more sufficient to adequately describe the conformation between separated parts of the molecules.

For this reason, a new approach for the structure determination of macromolecules has been worked out [3–5]. By partial alignment of the molecule in question in a lyotropic liquid crystalline medium, residual dipolar couplings (RDCs) between magnetic nuclei can be observed, where the actual values are taken from the difference between molecules dissolved in an isotropic and in the anisotropic medium.

The expression for the residual dipolar coupling $D_{IJ(\theta\varphi)}$ between two directly coupled nuclei can be simplified to the form [4]:

$$D_{IJ}(\theta, \varphi) = D_a^{IJ}\left\{A_a(3\cos^2\theta - 1) + \frac{3}{2}A_r\sin^2\theta\cos 2\varphi\right\}, \quad (1)$$

where

$$D_a^{IJ} = -\frac{\mu_0 h}{16\pi} S \frac{\gamma_I \gamma_J}{r_{IJ}^3}. \quad (2)$$

Here $A_a = \frac{1}{3}\left(A_{zz} - \frac{A_{xx}+A_{yy}}{2}\right)$ is the axial component of the molecular alignment tensor **A** characterizing the preferential orientation of the molecule relative to the static field direction; $A_r = 1/3(A_{xx} - A_{yy})$ is the rhombic component of **A**; A_{xx}, A_{yy}, and A_{zz} are the principal axes of **A**; θ and φ define the polar coordinates of the internuclear vector (between I and J) with respect to the static magnetic field direction; S is the generalized order parameter describing