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Structure-Transport Relationship in Organized Soft Matter Systems by Diffusion NMR

Sergey Vasenkov

University of Florida, Department of Chemical Engineering, 423 ChE Bldg., Gainesville,
FL 32611, USA, E-Mail: svasenkov@che.ufl.edu

1. Introduction

Room temperature ionic liquids show great promise as a media for organic synthesis, catalytic reactions, separation processes, and extraction. Formation of a unique and well-defined nanostructure including polar and unpolar domains is believed to be responsible for many useful properties of these “green” solvents. Aggregation of molecules into various types of domains also determines many properties of other types of soft matter systems such as multicomponent lipid bilayers. In particular, translational diffusion can be drastically altered by the formation of domains and aggregates. Fundamental knowledge of an influence of domain formation and aggregation on transport properties can be obtained by using a pulsed field gradient (PFG) NMR technique that combines advantages of high field (17.6 T) NMR and high magnetic field gradients (up to 30 T/m). This technique has been recently introduced at the University of Florida in collaboration with the National Magnet Lab. High field and high gradient PFG NMR was used to perform diffusion studies of several imidazoluim-based ionic liquids and their mixtures with carbon dioxide and water as well as of multicomponent lipid bilayers with and without membrane domains. In addition to a more conventional ^{1}H PFG NMR, also ^{13}C PFG NMR was used.

2. Experimental

^{1}H and ^{13}C PFG NMR diffusion studies were carried out using a wide bore 17.6 T Bruker Biospin Spectrometer. Magnetic field gradients were generated using diff60 diffusion probe (Bruker Biospin) and Great60 gradient amplifier (Bruker Biospin). In most cases diffusion studies were performed by using the standard PFG NMR stimulated echo pulse sequence. Diffusion data were obtained from PFG NMR attenuation curves, viz. dependencies of the intensity of the PFG NMR signal on the amplitude of the magnetic field gradients. The signal intensity was determined by either integrating the area under selected line(s) of the NMR spectra or by measuring the amplitudes of these lines. Different lines in NMR spectra can correspond to different species. Hence, diffusion data for a chosen type of species in a sample can be obtained by selecting an appropriate line in the spectrum for data processing.

PFG NMR samples for studies of ionic liquids (IL) and lipid bilayers were prepared as discussed in Refs. [1, 2]. Briefly, IL samples were prepared by filling 5 mm NMR tube with a chosen IL. In all cases the sample height in a vertically-oriented tube was around 15 mm or smaller to prevent disturbing influence of convection effects on the data measured at elevated temperatures. The samples were dried by heating under high vacuum for at least 1 day. Ionic liquids were loaded with CO_2 using a custom-made vacuum system by exposing a dry liquid to CO_2 gas at a fixed pressure for at least 4 hours.

PFG NMR diffusion studies of lipid bilayer samples were performed with multibilayer stacks supported on thin glass plates. The bilayer stacks were prepared from ternary lipid mixtures of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), and cholesterol (CHOL). Formation of multibilayer stacks was confirmed using proton and ^{31}P NMR.

3. Results and Discussion

^{1}H and ^{13}C PFG NMR was used to investigate influence of water and carbon dioxide dissolved in the ILs on the ion diffusion. In addition, diffusion of water and CO_2 in the mixtures of ILs with water or CO_2 was also studied. It was found that an addition of water to ILs can change the relationship between the diffusivities of the cations and the anions. While in the water-free samples the diffusivity of a larger cation was observed to be larger than that of a smaller anion, this anomalous relationship between the size and diffusivity of the diffusing species was found to gradually disappear with an addition of water to the ILs. This behaviour is attributed to the existence of well-defined local structures in RTILs resulting in a cooperative character of ion diffusion and even in an appearance of diffusion anisotropy for the cation diffusion. With increasing water concentration these structures could become progressively less defined leading to a change towards “normal” relationship between the size and diffusivity of diffusing species. In contrast to water, the absorption of carbon dioxide into ILs did not result in any significant changes of the ion diffusion in the studied samples. The CO_2 diffusivity was found to be approximately an order of magnitude larger than that of ions.

It was demonstrated that ^{1}H PFG NMR can be used to directly monitor the exchange of lipids between membrane domains and their surroundings in ternary lipid bilayers. Comparison of the experimental results and the corresponding results of dynamic Monte Carlo simulations allowed estimating permeability of the interfaces between the domains and their surroundings as well as the domain sizes.

4. Conclusion

Application of high field and high gradient PFG NMR in combination with dynamic Monte Carlo simulations can allow obtaining a deep insight into the transport-structure relationship in nanostructured soft matter systems.

References

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