

## Liquid–Liquid Phase Separation of Viologen Bistriflimide/Benzene Mixtures: Role of the Dual Ionic and Organic Nature of Ionic Liquids

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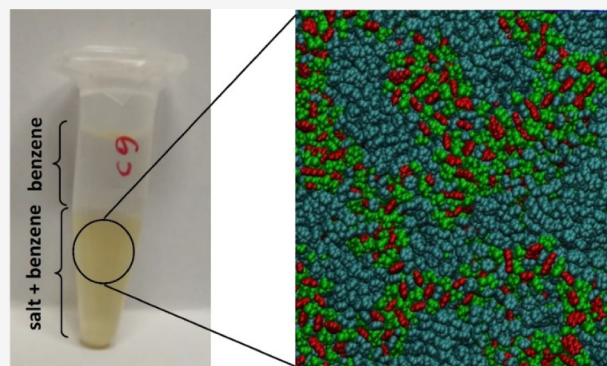
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**ABSTRACT:** Liquid–liquid phase separation occurs at room temperature when mixing an excess of benzene with solid viologen bistriflimide salts with various alkyl side-chain lengths. A liquid phase composed of (almost) pure benzene is above the other sponge-like liquid phase with salt absorbed in benzene. Nuclear magnetic resonance experiments indicate that the mole ratio of benzene/salt in the sponge-like phase remains unchanged upon varying the amounts of (nonexcessive) salt or benzene. Moreover, the benzene/viologen salt mole ratio in the sponge-like phase increases linearly with respect to the side-chain length of the cation. Similarly, when an excess of viologen salt is added in benzene, a sponge-like liquid phase composed of salt absorbed by benzene is observed in equilibrium with some solid viologen salt neither dissolved nor absorbed by the solvent. The mole ratio of the sponge-like liquid phase again increases linearly with side-chain length, while it remains independent of the relative amount of benzene and viologen salt as long as the latter is in excess. Finally, when appropriate amounts of benzene and viologen salt are mixed, a single sponge-like liquid phase is observed at an intermediate composition between the lower and upper limits. Molecular dynamics simulations reveal that because of their dual ionic and organic nature, when absorbed in benzene, the studied salts form nanoscale segregated liquid structures, akin ionic liquids, with a continuous polar network composed of anions and cationic charged groups, along with nonpolar domains composed of alkyl cationic side chains. Benzene molecules are preferentially absorbed inside the nonpolar region, which effectively expands the nonpolar region to be sponge-like and consequently liquidizes the viologen salt. The linearity of the benzene/salt ratio in the upper and lower phase boundaries comes from the fact that the effective volume of the nonpolar region for accommodating benzene molecules grows linearly with cationic alkyl side-chain length. The occurrence of the above phenomena is attributed to the nonpolar feature of benzene molecules, and there is no evidence of  $\pi$ – $\pi$  or ion– $\pi$  interaction between the ions and benzene molecules. Moreover, the diffusion of benzene in the sponge-like phase is found to be close to that in *n*-alkanes, supporting the idea of nanoscale segregation of polar and nonpolar regions in the sponge-like phase. The revealed mechanism is anticipated to be general for understanding liquid–liquid phase separation observed in mixtures of organic salts (ionic liquids) having relatively long alkyl chains with small organic molecules.

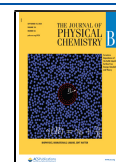


## 1. INTRODUCTION

Liquid–liquid phase separation is of great importance in many fields of chemistry, chemical engineering, biology, physics, and materials science. For instance, liquid–liquid phase separation can be used for membrane preparation,<sup>1,2</sup> liquid catalysis,<sup>3</sup> and providing separated environment for complex bio–chemical interactions in cell.<sup>4,5</sup> Liquid–liquid phase separation of organic salts (ionic liquids) mixing with small organic molecules is also of great importance, especially in catalysis<sup>6,7</sup> and separation.<sup>8,9</sup> For instance, the biocatalytic synthesis of 16 flavor esters<sup>10</sup> or monoacylglycerides<sup>11</sup> can be carried out in specific ionic liquids and separated through liquid–liquid phase separation. Similar procedures were also found when mixing ionic liquids with other small organic molecules such as neryl acetate<sup>12</sup> and immobilized lipase.<sup>13</sup> Ionic liquids are also a good liquid environment for biodiesel production.<sup>14</sup>

The liquid–liquid phase separation phenomena of organic salts (ionic liquids) mixed with small organic compounds have drawn researchers' attention for less than 2 decades. In 2003, Holbrey et al.<sup>15</sup> found that liquid–liquid phase separation, that is, two well-separated liquid phases with different physiochemical properties, appeared when mixing ionic liquids and aromatic solvents, and ionic clathrates were assumed to form in these mixtures. Further studies<sup>16–18</sup> have concluded that the

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electrostatic interactions between solutes and the ionic species of the solvent are very important in determining the local liquid structure. In 2006, Łachwa et al.<sup>19</sup> reported the phase diagram of the binary mixture of [emim][Tf<sub>2</sub>N] and benzene at different temperatures, and a similar phase diagram was reported for imidazolium-based ILs ([C<sub>8</sub>Mim][Tf<sub>2</sub>N] and [C<sub>8</sub>Mim][BF<sub>4</sub>]) mixing with benzene.<sup>20</sup> Both studies have ended with the hypothesis that the liquid–liquid phase separation is attributed to the cation– $\pi$  interaction between cations and benzene molecules.

None of the hypotheses proposed by the above studies have been actually inspected in detail, and thus, the mechanism of liquid–liquid phase separation and the molecular structure of the sponge-like phase are still unclear. In particular, liquid–liquid phase separation does not always occur when ionic liquids, or organic salts closely related to them in terms of molecular structure, are mixed with low-polar or nonpolar small organic compounds. For instance, viologen-based salts aggregate when dissolved in either acetonitrile or chloroform, but no liquid–liquid phase separation is observed.<sup>21</sup> Therefore, it is an interesting question when and how liquid–liquid phase separation occurs when organic salts or ionic liquids are mixed with small organic molecules.

In this work, nuclear magnetic resonance (NMR) spectroscopy and molecular dynamics (MD) simulations are combined together to investigate the liquid–liquid phase separation mechanism as well as the molecular structures and dynamic properties of the sponge-like liquid phase composed of benzene and viologen bistriflimide salts [C<sub>m</sub>bpC<sub>n</sub>][Tf<sub>2</sub>N]<sub>2</sub> (denoted as C<sub>m</sub>bpC<sub>n</sub>) with *m* and *n* being the numbers of carbon atoms on the two side chains. The formula for the Tf<sub>2</sub>N anion is (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>−</sup>. Although the viologen salts are solid at room temperature, they have ionic liquid crystalline and ionic liquid phases at higher temperatures exhibiting the same structural features of common ionic liquids. Our experiments indicate that the salts mix with benzene to form a new sponge-like phase resulting from the absorption of benzene into the nanosegregated ionic liquid-like structure. When benzene is excessive, the sponge-like phase coexists with liquid benzene, while it coexists with solid viologen salt when the salt is in excess. Both coexistence phase boundaries show a linear dependence of the mole ratio with alkyl chain length. Our MD simulations reveal that because of the ionic and organic nature of the viologen salt, akin common ionic liquids,<sup>22</sup> when benzene is absorbed, the salt transforms from a crystalline solid into a nanoscale segregated liquid (NSL):<sup>23,24</sup> the continuous polar network formed by anions and cationic head groups surrounds the nonpolar domains formed by cationic alkyl side chains. A certain amount of benzene molecules are dissolved in the nonpolar domains, and we do not find any evidence of  $\pi$ – $\pi$  or ion– $\pi$  interaction between ions and benzene molecules proposed in the previous studies.<sup>19,20</sup> In contrast, our results suggest that, for the studied salts having relatively long alkyl chains, the nonpolar feature of benzene molecules allows them to accommodate and diffuse freely in the nonpolar domains of the salt, and the continuous polar network ensures that the topology of the NSL structure is retained after the expansion caused by the insertion of benzene molecules.

## 2. METHODS

**2.1. Synthesis.** The synthetic protocol has been reported already in our previous work<sup>25</sup> and closely follows the work of ref 26. The identity and purity of all compounds have been

determined by electrospray ionization mass spectrometry, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. Details are reported in the [Supporting Information](#). Samples are prepared in a conic vial by adding the appropriate amount of viologen salt (300–800 mg) and benzene (1–2 mL). After vigorous shaking and sonication, the samples are left to rest overnight to allow a complete phase separation. All operations are carefully conducted under fume hood.

**2.2. NMR Spectroscopy.** Solution-state NMR spectra were collected at 25 °C on a Bruker AVANCE III 500 (500.13 MHz <sup>1</sup>H) equipped with a 5 mm z-gradient broad band inverse probe (53 G/cm max gradient strength). The delay time was set to 20 s in order to obtain reliable integrals. For diffusion-ordered spectroscopy, 32 transient spectra were collected by means of a standard stimulated spin echo-longitudinal eddy current delay-bipolar pulse (STE-LED-BPP) pulse scheme. The typical employed parameters were 3–4 ms for the encoding gradient length ( $\delta$ ), ca. 250 ms for the diffusion delay ( $\Delta$ ). Experiments were run at 298 K in a coaxial capillary NMR tube, containing the sample to investigate, inserted in a 5 mm tube with external D<sub>2</sub>O for the lock. The capillary tube was filled with the sponge-like phase for about 5 cm in length. This includes completely the active volume for the NMR experiments. The almost pure benzene phase, which remains on top of the sponge-like phase, is therefore totally outside the active volume and neither contributes to, nor perturbs in any ways, the NMR experiment.

**2.3. MD Simulation.** MD simulations were conducted for C<sub>8</sub>bpC<sub>8</sub> and C<sub>12</sub>bpC<sub>12</sub> systems, respectively, mixed with benzene. The force fields and partial charges for [C<sub>8</sub>bpC<sub>8</sub>]<sup>2+</sup>, [C<sub>12</sub>bpC<sub>12</sub>]<sup>2+</sup>, and [Tf<sub>2</sub>N]<sup>−</sup> are taken from ref 21. The force-field parameters of benzene were taken from the AMBER force field,<sup>27,28</sup> and the partial charges were determined by using the restrained electrostatic potential method.<sup>29</sup> The periodic boundary conditions were applied to all three dimensions of the cubic simulation box, and the particle mesh Ewald method<sup>30</sup> was used to handle the long-range electrostatic interactions. The cutoff distance for the short-range interactions was 1.2 nm, and the time step was 1 fs. The simulation temperature was kept constant by the Nosé–Hoover thermostat,<sup>31</sup> and the pressure for an NPT simulation was controlled by the Parrinello–Rahman barostat.<sup>32</sup>

Two systems with fewer ions were prepared and simulated by MD simulation to see initially whether liquid–liquid phase separation occurs: benzene/C<sub>8</sub>bpC<sub>8</sub> mixture with a mole ratio of 20:1 (10,000 benzene molecules vs 500 ion pairs, which hereafter refers to the neutral 1:2 combination of one cation and two anions, given the stoichiometry [C<sub>n</sub>bpC<sub>n</sub>][Tf<sub>2</sub>N]<sub>2</sub> of the salts), and benzene/C<sub>12</sub>bpC<sub>12</sub> mixture with a mole ratio of 30:1 (9000 benzene molecules vs 300 ion pairs). The large amount of benzene molecules in these two boxes is needed to guarantee that, if phase separation is observed, it is not an artifact induced by the small number of solvent molecules. However, because a larger number of viologen ion pairs are necessary to have a better statistics, other two systems with more ions were also prepared and simulated for sampling and data analysis: benzene/C<sub>8</sub>bpC<sub>8</sub> mixture with a mole ratio of 12:1 (9600 benzene molecules vs 800 ion pairs) and benzene/C<sub>12</sub>bpC<sub>12</sub> mixture with a mole ratio of 17:1 (10,200 benzene molecules vs 600 ion pairs).

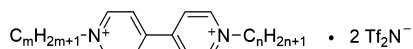
A 4 ns NVT MD simulation at *T* = 1200 K in a large box was conducted to fully mix the two species. An annealing process was followed to cool down the system from 1200 to 900 K

with a temperature interval of 100 K. An 8 ns NPT MD simulation at  $T = 900$  K and  $P = 1$  atm was then performed to sample the average box size. Another annealing process further cools down the system from 900 to 300 K with a temperature interval of 100 K. At each temperature, a constant NVT MD simulation was run for 4 ns. Then, an 8 ns NPT MD simulation at  $T = 300$  K was run to get the appropriate box size. Finally, another 8 ns NVT MD simulation at  $T = 300$  K was run for data collection with a sampling interval of 4 ps. The GROMACS software package<sup>33</sup> was employed to run all the MD simulations.

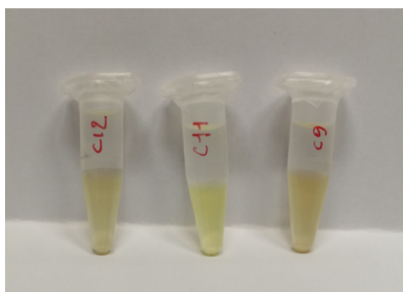
### 3. RESULTS AND DISCUSSION

**3.1. NMR Experiments.** As shown in Scheme 1, viologen cations are typical amphiphilic molecules with both ionic and

**Scheme 1. Molecular Formula of Viologen-Based Salts  $[C_m\text{bp}C_n][\text{Tf}_2\text{N}]_2$  Investigated in the NMR Experiments, with  $m$  and  $n$  Being the Lengths of Two Side Chains, Including Symmetric Cations  $m = n = 4, 7, 8, 9, 11, 12, 14, 16$  and Nonsymmetric Cations  $(m, n) = (7, 9), (7, 10), (7, 11), (8, 16), (10, 16)$**



organic features. Viologen bistriflimide salts are solid at room temperature, an ionic liquid crystal phase of smectic type is often found upon heating, and the isotropic phase is obtained at relatively high temperatures depending on the alkyl chain length and symmetry.<sup>34,35</sup> For example, highly nonsymmetric viologen bistriflimide salts, such as  $\text{C}_2\text{bpC}_8$ ,  $\text{C}_3\text{bpC}_{11}$ , and  $\text{C}_4\text{bpC}_{11}$ , exhibit a crystal-to-isotropic transition below 100 °C to become ionic liquids.<sup>25,36</sup> More symmetric systems have much higher melting points, for example,  $\text{C}_{14}\text{bpC}_{14}$  forms an isotropic ionic liquid only above 200 °C.<sup>25</sup> As reported in our previous study, the viologen bistriflimide salts are poorly soluble in weakly polar solvents such as chloroform and dichloromethane.<sup>21</sup> However, when mixed with an excess of benzene, a dissolution of the solid viologen salt and a liquid–liquid phase separation occurs with two liquid phases macroscopically distinguished, see Figure 1. Both phases are transparent and homogeneous and the upper phase has no color, while the lower phase is pale yellow. The system quickly recovers the separated phases even after vigorous shaking and sonication. Furthermore, adding in more salt results in an increased volume of the lower phase and a decreased volume of the upper phase. The only exception among our samples is



**Figure 1.** Samples containing the two liquid phases in equilibrium obtained after adding an excess of benzene to the viologen salts  $[C_m\text{bp}C_n][\text{Tf}_2\text{N}]_2$ ,  $m = n = 9, 11, 12$ .

$\text{C}_4\text{bpC}_4$ : for this salt, we observed that the solid viologen simply did not dissolve in benzene, even after stirring and sonication. The solid phase remained on the bottom of the vial for several days without forming any additional liquid phase.

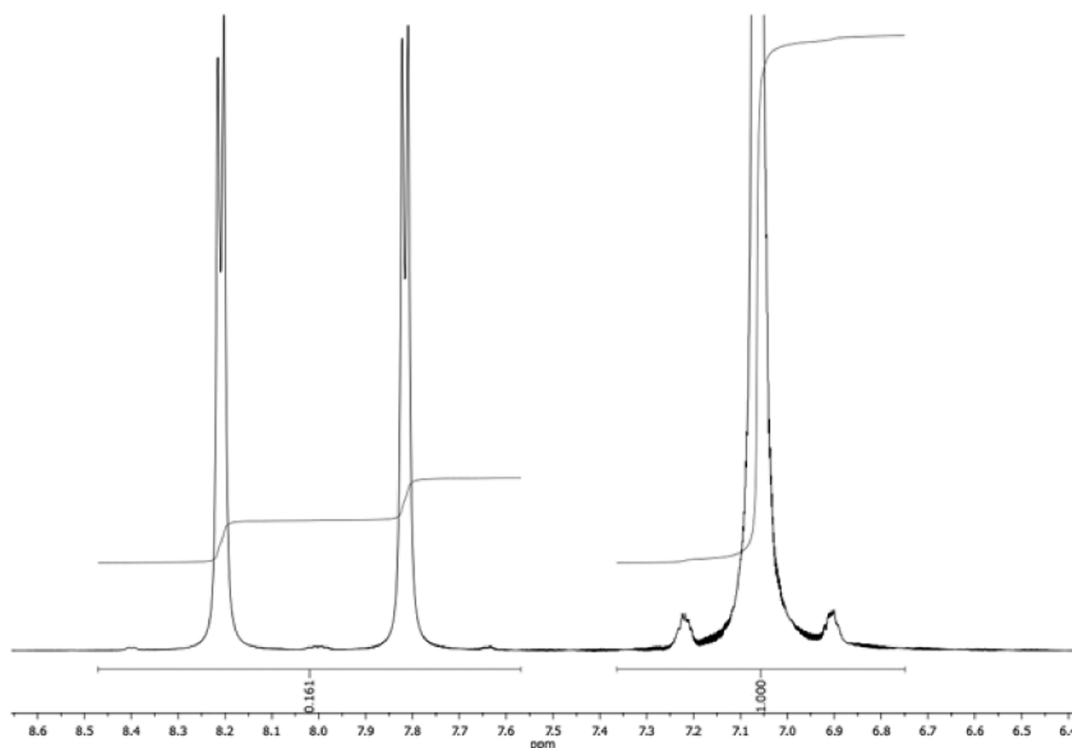
The upper phase is essentially constituted by liquid benzene, with an extremely low concentration of salt dissolved in it, as investigated in a previous report.<sup>37</sup> The lower phase of viologen salts absorbed in benzene, the sponge-like liquid phase, has been experimentally investigated by  $^1\text{H}$  NMR and diffusion ordered spectroscopy (DOSY). We focus our attention on the aromatic region of the  $^1\text{H}$  NMR spectrum where the signal of the viologen core (ortho and meta proton resonances at about 8.2 and 7.8 ppm, respectively) and the solvent resonance, just above 7.0 ppm, can be found.

In Figure 2, we show the proton NMR spectrum of the lower phase obtained by mixing  $[\text{C}_9\text{bpC}_9][\text{Tf}_2\text{N}]_2$  with an excess of benzene. The homogeneity of the magnetic field is rather good because the proton resonances are quite sharp and we can clearly distinguish the doublet-like pattern of the viologen aromatic resonances (though the spin system is a complex multiplet of AA'BB' type for parasubstituted aromatic rings with different substituents), indicating a macroscopically homogeneous solution. Therefore, we can easily measure the integrals of the aromatic resonances of the viologen cation as well as the benzene solvent. The mole ratios for all systems investigated, after being normalized by the number of protons under each resonance, are reported in Table S1 of the Supporting Information and shown in Figure 3. The NMR data show that the lower phase is an isotropic liquid phase composed by a certain mole ratio of viologen salt and benzene. The mole ratio is fixed for a given type of viologen salt as far as the added benzene is in excess, and adding more salt to the two-phase samples with excess benzene does produce an increase of the volume of the lower sponge-like liquid phase because more benzene is required to absorb the extra viologen.

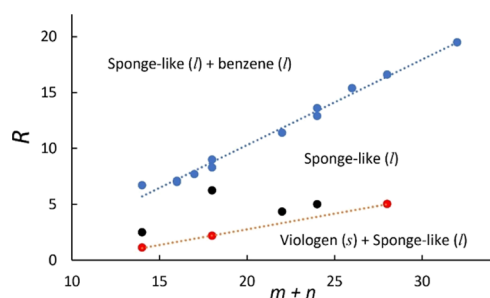
On the other hand, when an excess of viologen salt is added to benzene, the sponge-like liquid phase and the viologen solid phase coexist. The sponge-like liquid phase in equilibrium with solid viologen is now more viscous since it contains the minimum amount of benzene that is necessary for its formation. It has been difficult to fill the NMR capillary tubes due to the high viscosity, so only a few systems are reported in Table S1. The experiments indicate that the relative amount of benzene in the sponge-like liquid phase in equilibrium with solid viologen again increases linearly with the total alkyl chain length.

Figure 3 shows the mole ratio  $R = N_{\text{benzene}}/N_{\text{viologen}}$  obtained from the integrals of the resonances of the two components in the sponge-like liquid phase versus  $m + n$ , which represents the total number of carbon atoms in the alkyl chains of viologen cations. The blue dots are the experimentally determined upper bound of the ratio  $R_{\text{max}}$ , corresponding to the coexistence of sponge-like phase and liquid benzene, which shows a quite good linear relation with  $m + n$ . The red dots are the lower bound of the ratio  $R_{\text{min}}$ , corresponding to the coexistence line between sponge-like phase and solid viologen, which also shows a very good linear relation with  $m + n$ . The black dots represent monophasic systems obtained by mixing viologen salts and benzene with an intermediate mole ratio so that benzene can be completely absorbed by the viologen (or equivalently, the viologen can be completely dissolved in benzene).





**Figure 2.**  $^1\text{H}$  NMR spectrum of the lower phase (see Figure 1) of the biphasic system of  $[\text{C}_9\text{bpC}_9][\text{TF}_2\text{N}]_2$  with benzene. From the aromatic integrals, we can obtain the mole ratio  $N_{\text{benzene}}/N_{\text{viologen}}$  after dividing each integral by the number of protons, which is 6 for benzene and 8 for the viologen, respectively.



**Figure 3.** Phase diagram of the mole ratio  $R = N_{\text{benzene}}/N_{\text{viologen}}$  vs  $m + n$ , the total number of carbon groups in the cationic alkyl chains. The blue symbols represent the coexistence line between liquid benzene and sponge-like liquid phase (fitting line:  $0.79(m + n) - 5.44$ ), the red symbols represent the coexistence line between solid viologen salt and sponge-like liquid phase (fitting line:  $0.28(m + n) - 2.83$ ), and the black symbols represent intermediate state points with only the sponge-like liquid phase present.

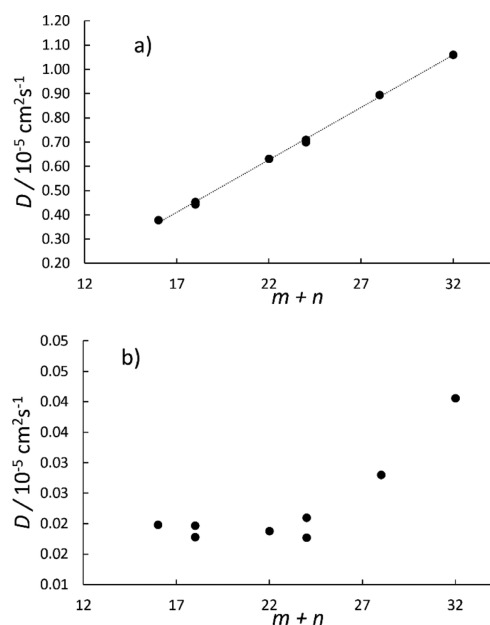
Because alkyl side chains of viologen cations and benzene molecules are both nonpolar, it seems reasonable to assume that benzene molecules are absorbed by the nonpolar region of the viologen salt. It is well known that, in the solid state,<sup>38</sup> as well as in the liquid-crystalline and isotropic states,<sup>25,39</sup> viologen bistriflimide salts exhibit strong nanosegregation of the ionic parts from the nonpolar alkyl chain regions. This is responsible for the lamellar structures of both the solid and the liquid crystal phases and for the NSL phase as normally observed in many ionic liquids.<sup>23,24,40,41</sup> Therefore, longer side chains, resulting in larger volumes of the nonpolar regions, will accommodate more benzene molecules, so  $R_{\text{max}}$  increases with the side-chain length. On the other hand, more benzene molecules are needed to balance stronger van der Waals

(vdW) interactions of longer side chains to form the sponge-like liquid phase, which results in the increase of  $R_{\text{min}}$  with respect to side-chain length.

Because the sponge-like phase with the largest amount of benzene is the least viscous, its diffusion can be measured by NMR DOSY spectroscopy. Diffusion coefficients of viologen cations and benzene molecules in the sponge-like liquid phase using the samples obtained from the sponge-like/benzene biphasic systems are listed in Table S2 in the Supporting Information and plotted in Figure 4.

It can be seen from Figure 4 that the diffusion coefficient of benzene molecules in the sponge-like phase is about 1 or 2 orders of magnitude larger than the diffusion coefficient of viologen cations and increases linearly (Figure 4a) with the total number of carbon atoms on the side chains. In Figure 4b, we can see that the diffusion coefficient of the viologen salt is roughly a constant when the total number of carbon atoms is less than 24 and then gradually increases.

The above dynamic behavior can be qualitatively understood as follows. The increase of the number of carbon atoms in the alkyl side chain leads to a growth of the nonpolar domains in the sponge-like liquid phase, and a larger nonpolar domain can accommodate more benzene molecules, which makes the diffusion of benzene molecules easier, corresponding to a larger diffusion coefficient. In contrast, because of the strong electrostatic interactions between the charged groups of viologen cations and anions, the diffusion of viologen cations is slower than that of benzene molecules and is weakly influenced by nonpolar side-chain length, except for very long alkyl side chains when the vdW interactions between side chains become significant, which counterbalance the electrostatic interactions and thus facilitate the diffusion of cations.

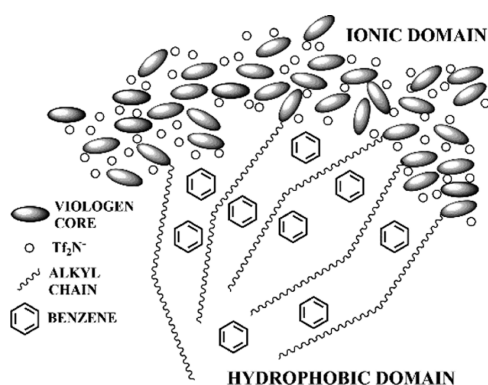


**Figure 4.** Diffusion coefficients of benzene (a) and viologen cations (b) with respect to total side-chain length of viologen salt. Data are obtained from the sponge-like liquid phase along the coexistence line SP (I) + B (I). The fitting line in (a) is  $D = 0.0432(m + n) - 0.3249$ . The diffusion coefficient of benzene in *n*-alkanes around room temperature (see main text) varies from  $2.75 \times 10^{-5} \text{ cm}^2/\text{s}$  in *n*-nonane to  $1.06 \times 10^{-5} \text{ cm}^2/\text{s}$  in *n*-pentadecane.<sup>42</sup>

It is quite interesting to make a comparison with reported values of the diffusion coefficients of benzene in *n*-alkanes at similar temperatures. In ref 42, Kowert and Register have reported the diffusion coefficients of benzene in *n*-nonane, *n*-decane, *n*-dodecane, and *n*-pentadecane obtained at slightly different temperatures, from 293 to 297 K. The experimental data range from  $D_{\text{benzene}} = 2.75 \times 10^{-5} \text{ cm}^2/\text{s}$  in *n*-nonane down to  $D_{\text{benzene}} = 1.06 \times 10^{-5} \text{ cm}^2/\text{s}$  in the more viscous *n*-pentadecane. The values we have measured in the sponge-like phase at  $T = 298 \text{ K}$  are rather close to the values found in pure alkanes, suggesting that benzene molecules in the sponge-like liquid phase experience an environment and a microviscosity very similar to a liquid alkane, which, in turn, supports the microscopic view of a nanosegregated ionic and nonpolar regions in the sponge-like liquid phase. A schematic representation is shown in Figure 5.

**3.2. MD Simulations.** MD simulations have been conducted to understand the microscopic structure of the sponge-like liquid phase as well as the associated mechanism. Two systems with large benzene/viologen mole ratios are first simulated in order to observe liquid–liquid phase separation: the first system contains 10,000 benzene molecules and 500  $[\text{C}_8\text{bpC}_8][\text{Tf}_2\text{N}]_2$  ion pairs (mole ratio of 20:1), and the second one contains 9000 benzene molecules and 300  $[\text{C}_{12}\text{bpC}_{12}][\text{Tf}_2\text{N}]_2$  ion pairs (mole ratio of 30:1). The very large excess of benzene is intended to make sure that phase separation observed in the simulation box is not attributed to some artifacts related to a small amount of solvent molecules.

It can be seen from the equilibrated snapshots in Figure 6 that the liquid–liquid phase separation indeed takes place for both systems. Figure 6a,d shows that ions aggregate together to form the viologen domain, and Figure 6b,e indicates that some benzene molecules are accommodated in the viologen domain. The other phase composed of pure benzene (see Figure 6c,f)



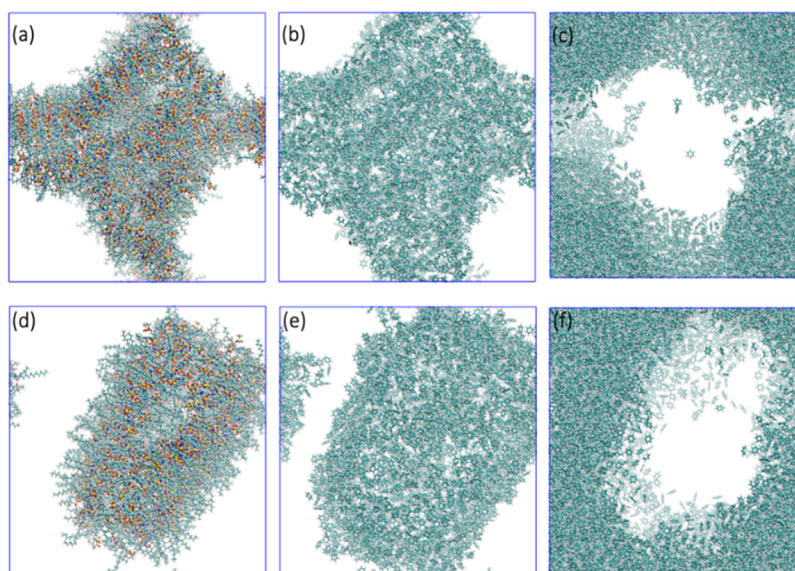
**Figure 5.** Schematic representation of the sponge-like phase. The typical nanoscale segregation normally observed in ionic liquids between the polar network and the alkyl chains is reproduced in the sponge-like phase after adsorption of benzene in the hydrophobic regions. For the sake of clarity, only few alkyl chains are schematically drawn.

has almost no ions inside. Both of the simulated systems do spontaneously separate into a pure benzene phase plus a sponge-like phase composed of benzene molecules and ions.

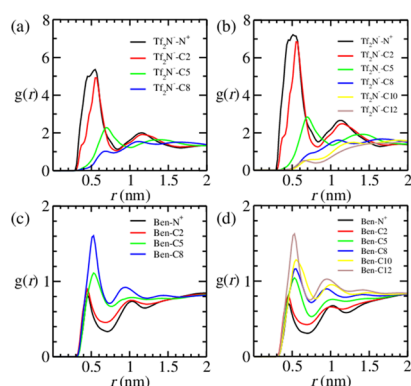
Because the numbers of ion pairs in the above two systems are inadequate for a good statistics, two additional systems with more viologen molecules and lower benzene/salt mole ratios have also been simulated to study the microscopic structure of the sponge-like liquid phase: the first system contains 9600 benzene molecules and 800  $[\text{C}_8\text{bpC}_8][\text{Tf}_2\text{N}]_2$  ion pairs (ratio of 12:1), and the second system contains 10,200 benzene molecules and 600  $[\text{C}_{12}\text{bpC}_{12}][\text{Tf}_2\text{N}]_2$  ion pairs (ratio of 17:1). The radial distribution functions (RDFs) calculated from the simulation data are shown in Figure 7. The RDFs in Figure 7a,b indicate that, as expected, the anions stay close to the charged groups of the cations, that is, the bipyridinium core, and do not have significant contacts with the terminal methylene groups of alkyl side chains. In contrast, as shown in Figure 7c,d, benzene molecules locate around the nonpolar cationic side chains and aggregate with the terminal methylene groups of the side chains.

In Figure 8a,b, we show the snapshots of the ionic domains of the benzene/ $[\text{C}_8\text{bpC}_8][\text{Tf}_2\text{N}]_2$  (mole ratio of 12:1) and benzene/ $[\text{C}_{12}\text{bpC}_{12}][\text{Tf}_2\text{N}]_2$  (mole ratio of 17:1) mixtures, respectively. Because of dual ionic and organic nature of viologen salts, anions and charged groups of cations form a continuous polar network through electrostatic interaction, while alkyl cationic side chains aggregate to form nanoscale nonpolar domains, exactly as the NSL state observed in the isotropic phase of ionic liquids,<sup>23,24,40,41</sup> in which a large amount of benzene molecules are accommodated. In other words, the amphiphilic feature of viologen bistriflimide salts allows them to form a sponge-like liquid structure when being mixed with benzene, which can expand and accommodate benzene molecules into its nonpolar domains. The accommodation of benzene molecules enlarges the effective volume of the sponge-like structure but cannot destroy its topology, so there is an upper limit for the accommodation and extra benzene molecules form an almost pure liquid phase above the mixture.

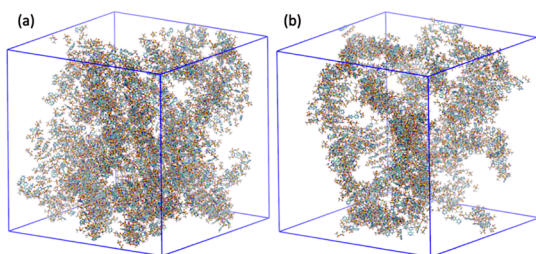
The mole ratios of benzene/salt in the sponge-like phase by MD simulation can be calculated to compare with experimental results. A benzene molecule is considered to be in a nonpolar domain of salt if the distance between the



**Figure 6.** Snapshots of benzene/ $C_8\text{bp}C_8$  (a–c) and benzene/ $C_{12}\text{bp}C_{12}$  (d–f) mixtures. (a,d) Viologen cations and anions in the sponge-like phase. (b,e) Benzene molecules inside the viologen domain. (c,f) Benzene molecules in the pure benzene phase. Additional snapshots, with a different color scheme to highlight the nanosegregation, can be found in [Supporting Information](#), Figures S4–S6.



**Figure 7.** RDFs between the geometric centers of anions and different atoms on  $C_8\text{bp}C_8$  (a) and  $C_{12}\text{bp}C_{12}$  (b) and the RDFs between the geometric centers of benzene molecules (labeled as Ben) and different atoms on  $C_8\text{bp}C_8$  (c) and  $C_{12}\text{bp}C_{12}$  (d).  $N^+$  represents the charged nitrogen on viologen cation and  $C_x$  ( $x = 2, 5, 8, 10, 12$ ) represents different carbon atoms on alkyl side chain away from  $N^+$  with the distance of  $x$ . The full RDFs up to 6 nm can be found in Figure S2 in the [Supporting Information](#). Also, in [Supporting Information](#), Figure S3, we report the RDF of the distance between benzene and the pyridinium carbons, averaged over all ring's carbons, and the coordination numbers obtained by integrating the RDF up to the first minimum.



**Figure 8.** Snapshots of benzene/ $C_8\text{bp}C_8$  mixture with a mole ratio of 12:1 (a) and benzene/ $C_{12}\text{bp}C_{12}$  mixture with a mole ratio of 17:1 (b). Only anions and charged groups of cations are shown.

geometric center of the aromatic ring and any atom (except hydrogen atoms) of any viologen cation is smaller than 0.72 nm for  $C_8\text{bp}C_8$  or 0.74 nm for  $C_{12}\text{bp}C_{12}$ . This choice of distances comes from the first valley of the RDFs in [Figure 7c,d](#). Applying this rule to all simulated benzene molecules, we can determine that the simulated mole ratio for  $C_8\text{bp}C_8$  is  $6.80 \pm 0.03$  and  $11.2 \pm 0.7$  for  $C_{12}\text{bp}C_{12}$ , in very good agreement with the NMR experimental measurements of 7.0 for  $C_8\text{bp}C_8$  and 12.9 for  $C_{12}\text{bp}C_{12}$ .

The self-diffusion coefficients  $D$  of viologen cations as well as benzene molecules in the sponge-like liquid phase were determined by a linear fit of the simulated mean square displacements  $\langle \Delta r(t)^2 \rangle$  using the Einstein relation  $\langle \Delta r(t)^2 \rangle = 6Dt$ , where  $t$  is the time interval. From [Table 1](#), we can see that,

**Table 1. Simulated Self-Diffusion Coefficients of Viologen Cations and Benzene Molecules in the Sponge-like Liquid Phase<sup>a</sup>**

$D$ ( $10^{-5}$ cm <sup>2</sup> /s)	benzene	viologen
$C_8\text{bp}C_8$	$8.95 \times 10^{-1}$ ( $3.79 \times 10^{-1}$ )	$2.80 \times 10^{-2}$ ( $1.98 \times 10^{-2}$ )
$C_{12}\text{bp}C_{12}$	$1.06 \times 10^0$ ( $7.00 \times 10^{-1}$ )	$4.06 \times 10^{-2}$ ( $1.77 \times 10^{-2}$ )

<sup>a</sup>The experimental values for the two simulated systems are in parentheses (see also [Figure 4](#) and [Table S2](#) in [Supporting Information](#)).

in accordance with the experiments, the self-diffusion coefficients of benzene also increase with total side-chain length. Meanwhile, the self-diffusion coefficients of benzene molecules in the sponge-like liquid phase are about 2 orders of magnitude larger than that of the viologen cations, which is also in agreement with the NMR experiments. A qualitative interpretation is that, as the nonpolar domains grow in size, the relative weight of strong electrostatic interaction versus weak vdW interaction decreases, namely, vdW becomes relatively more important, so the system becomes more and more fluid, and thus, benzene molecules can move more freely, leading to faster diffusion.



#### 4. DISCUSSION AND CONCLUSIONS

In this study, NMR experiments and MD simulations are combined together to investigate the structural and dynamic properties of the sponge-like liquid phase obtained by mixing solid viologen salts and liquid benzene at room temperature, as well as the associated mechanisms for both liquid–liquid and liquid–solid phase separations that occur when mixing benzene with viologen bistriflimide salts with different cationic side-chain lengths. Liquid–liquid phase separation is observed when mixing an excess of benzene with viologen bistriflimide salt. The upper liquid phase is essentially (almost) pure benzene. In the lower liquid phase, because of dual ionic and organic nature of viologen salts, anions and charged groups of viologen cations form a continuous polar network, while alkyl side chains aggregate to form nonpolar domains. Benzene molecules are easily accommodated in the nonpolar domains, and the whole system forms a sponge-like structure. Because the absorption of benzene molecules cannot destroy the topology of the sponge-like structure, the benzene/salt mole ratio has an upper limit, which increases linearly with the total number of carbon atoms on the alkyl side chain and thus the volume of the hydrophobic domains. For such a sponge-like phase with the maximum amount of benzene absorbed, the diffusivities of cations and benzene molecules in the sponge-like phase increase with the number of carbon atoms because longer side chains have a stronger vdW interaction which effectively weakens the restraint from the strong electrostatic interaction of the continuous polar network.

The sponge-like phase can form even with a very small amount of benzene absorbed. Because a minimum amount of benzene is required to liquidize the salt, a lower limit of benzene/salt mole ratio in the sponge-like liquid phase exists, which again grows linearly with the side-chain length because of the fact that the effective vdW interaction and thus the amount of benzene required to liquidize salt are proportional to the side-chain length. Mixing benzene and salt can form a single sponge-like liquid phase without phase separations when the mole ratio is between the upper and lower bounds for liquid–liquid and liquid–solid phase separations, respectively. The diffusion coefficients of benzene molecules in the sponge-like phase are close to the values found in pure alkanes, supporting the microscopic physical picture that benzene molecules essentially move inside the nonpolar region rather than the ionic region of the sponge-like liquid phase.

Previous works<sup>15,19</sup> have proposed that  $\pi$ – $\pi$  or ion– $\pi$  interactions between benzene molecules and ions play an important role in liquid–liquid phase separation. In fact, liquid clathrates between benzene and short-chain imidazolium salts have been crystallized and the X-ray structure clearly reveals the aromatic moiety being sandwiched between two imidazolium rings.<sup>15,19</sup> We stress here that these observations are referred to short-chain imidazolium salts. However, the data analysis of our MD simulation results have found no meaningful number of  $\pi$ – $\pi$  or ion– $\pi$  structures, and thus the liquid–liquid or liquid–solid phase separation for our studied systems is only attributed to the nonpolar feature of benzene molecules and the relatively long alkyl chains of the viologens.

The mechanism shown in this work, though focused on the mixture of solid viologens bistriflimide with benzene, may be anticipated to serve as a general theoretical framework for understanding liquid–liquid phase separations observed in mixtures of organic salts (ionic liquids) having relatively long

alkyl chains with small organic compounds.<sup>10–14,16,17</sup> This applies, in particular, to the ionic liquid phases reported by Lozano and co-workers obtained by mixing long-chain (e.g., C<sub>16</sub> or C<sub>18</sub>) imidazolium bistriflimide salts with aromatic solvents and/or organic small molecules.<sup>10,11,14</sup> It appears, therefore, that one of the key ingredients necessary for observing this behavior from organic ionic salts, whether liquid or solid at room temperature, is the presence of relatively long alkyl chains. In fact, no matter if in the solid or liquid state at room temperature, both organic salts and ionic liquids with relatively long alkyl chains have dual ionic and organic nature, which is the structural feature responsible for the formation of the sponge-like NSL structure accommodating small organic molecules. This mechanism is expected to be helpful for the wide applications of liquid–liquid phase separations of organic salts and ionic liquids in many fields of chemistry, chemical engineering, biology, physics, and materials science and to be enlightening for understanding various biological phase separation phenomena.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.0c03207>.

Experimentally determined sponge-like phase composition and diffusion coefficients, materials characterization, and <sup>1</sup>H and <sup>13</sup>C NMR (PDF)

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##### Notes

The authors declare no competing financial interest.

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