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Ionic liquid induced surface exclusion and anomalous first-order phase transition in Laponite dispersions

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ABSTRACT

Spontaneous liquid–liquid phase separation occurring in Laponite dispersions of ionic liquid (IL) solutions was observed at room temperature driven by surface exclusion of clay platelets at the water–air interface. The water–air interface dependent demixing behavior followed anomalous first-order phase transition kinetics described by a partition reaction $CS \overset{K}{\leftrightarrow} S + C$ with a demixing partition coefficient $K = [S] / [C]$ where the initial homogeneous dispersion [CS] phase separated into a Laponite-poor [S] and Laponite-rich [C] state. The colloidal aggregates were found to be fractal structures with a mass fractal dimension $1.35 < d_f < 1.75$. The demixing process could be described by a droplet splitting model. The settling dynamics was induced by ionic liquids due to their charge specific interaction with clay platelets, and the surface exclusion of clay particles at the liquid–air interface governed the rate of demixing. Interestingly, the time-constant of first-order dynamics was found to be invariant of IL concentration.

1. Introduction

Liquid–liquid phase separation leading to demixing of a homogeneous polymer solution or a colloidal dispersion into two distinct liquid phases, one polymer/colloid-rich and another polymer/colloid-poor has been observed in a wide variety of systems [1–5]. At equilibrium there is a discernible interface between these two liquid states and these two phases maintain liquid–liquid phase equilibria as far as their thermodynamic compatibility is concerned. Aqueous two-phase demixing has been investigated in detail over the past many decades and some fundamental thermodynamic understanding of this phenomenon is available in the literature.

Phase demixing studies in aqueous polymer solutions have yielded valuable information that has been extensively utilized for the recovery and purification of various biomolecules like proteins, enzymes and antibodies according to their charge, size, hydrophobicity etc. [6–11]. Nagaraja and Iyyaswami [11], and Asenjo and Andrews [12] have reported the phase demixing kinetics in aqueous two phase systems consisting of polyethylene glycol and sodium citrate. Kaul et al. [13] have provided a general understanding of these systems and observed that a characteristic change in the phase inversion time, where the separated phase reenters the continuous phase or vice versa, could be observed at phase inversion point. In general, in the conventional aqueous two-phase systems, the normal strategy is to cause demixing induced by addition of PEG or certain salts like potassium phosphate or sodium citrate, above their critical concentration. These classical procedures are routinely adopted in chemical and pharmaceutical industries particularly for purification and separation of proteins and polypeptides [6–12].

The phase separation was induced using IL which caused change in interface properties. By introducing IL in Laponite dispersions we induced the shift in interface plane that caused the formation of two phases. This process can be driven by the addition of one of the components present in the system that introduces instability and causes change in the interfacial properties, thereby, forcing the interface to shift to a new equilibrium position [14,15]. As a consequence, the dispersion separates along a new tie-line to give rise to two distinct phases in the demixing curve which is in equilibrium. The inherent advantage of this process lies in the fact that the rate limiting process is regulated by an underlying phase transition mechanism. Further, it must be realized that the two phase separated components are in their equilibrium composition states. Not much is known about the phase formation kinetics of the aforementioned systems.

Herein, we report a systematic and comprehensive study of the liquid–liquid phase equilibria and partition kinetics observed in anisotropic colloidal dispersions (Laponite nanoclay platelets) where the necessary provocation for phase transition was provided by ionic liquids (ILs). Laponite is an entirely synthetic layered silicate that is widely used as a rheology modifier in industrial applications such as paints, varnishes, cosmetics and polymer nanocomposites [16,17]. Laponite platelets have an aspect ratio of 25 (diameter 25 nm and thickness 1 nm) and the faces are negatively charged whereas the rim is positively charged

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[18]. The structural anisotropy associated with the clay particles, combined with the presence of attractive and repulsive terms in their interparticle interactions, causes the complexity observed in the phase diagram of such colloidal systems [19]. A large number of studies have taken place earlier in liquid–liquid phase separation of homogeneous polymer solutions mainly to proteins but in literature there are very few studies concerning colloidal dispersions. This work was undertaken to qualitatively discuss phase separation in colloidal dispersions inspired by ionic liquid. Here, we specifically study the concentration range of ILs which led to phase separation in Laponite dispersions.

Ionic liquids comprise of organic ions and are associated with negligible vapor pressure, high thermal, chemical and electrochemical stability that enable these to be called as green solvents [20,21]. As far as the interactions are concerned, the presence of ionic liquids in solutions introduces mobile ions (in the form of anions and cations), hydrophobicity (alkyl chain length) and hydrogen bonding (N–H bonding) simultaneously into the continuous phase. Due to their characteristic hydrophobic–hydrophilic balance, these are widely used as surface active agents to study their micellization behavior in water [22–24]. In this work, we have used two ILs, 1-ethyl-3-methylimidazolium chloride [C2mim][Cl] and 1-octyl-3-methylimidazolium chloride [C8mim][Cl] having different hydrophobicities, but same anions and explore their control on the phase separation kinetics.

2. Materials and methods

Laponite RD clay was purchased from Southern Clay Products, USA. 1-Ethyl-3-methyl imidazolium chloride ([C2mim][Cl]) in solid and 1-octyl-3-methyl imidazolium chloride ([C8mim][Cl]) in immensely viscous form were bought from Sigma-Aldrich. The concentrated stock solutions of both the ILs were prepared by dissolving required amount of ILs in deionized water followed by mixing with a magnetic stirrer at 80 °C for 30 min. The temperature of the samples was then brought down to room temperature and used after 15 min of equilibration time. Laponite dispersions were prepared by dissolving Laponite powder in deionized water at room temperature and mixing them vigorously for 2 h. After the Laponite dispersion preparation we get a homogeneous and transparent solution and required amount of ILs (0.1–0.3% (w/v)) from the concentrated stock solutions were added to those dispersions and the solutions were further stirred for 5 min. All the experiments were performed at room temperature 25 °C and the relative humidity was less than 50%. The concentration of Laponite was fixed at 2% (w/v) and concentration of both the ILs used was varied from 0.1–0.3% (w/v).

Measurement of viscosity was done using a Sine-wave Vibro Viscometer (model — SV10, A and D company, Japan). The instrument uses a matched pair of gold plated flat plates which are driven with at the same frequency. When the plates are vibrated with a uniform frequency of 30 Hz, the amplitude of less than 1 mm varies in response to the amount of frictional force produced by the viscidity between the sensor plates and the sample. The driving electric current which is the origin of exciting force, will be detected as the magnitude of the viscidity between the sensors plates and the sample fluids. The Vibro Viscometer measures electric current, and then viscosity is given by the positive correlation between driving electric current and the viscosity.

Raman spectra of these Laponite–IL suspensions were performed using FT-IR spectrometer attached with a microscope (Varian 7000 FT-Raman and Varian 600 UMA). Raman spectroscopy was done to investigate the structure of water in Laponite–IL dispersions because vibrational spectra are very sensitive to the molecular environment. In the Raman spectrum one can see different peaks showing different functional groups. The spectral curve was fitted to multiple peak Lorentzian functions in a fixed spectral wave-number width to obtain peak area fraction for each peak. This peak area gives information about the quantity of a particular group present in system.

Average particle sizing and its distribution were done by using a JEOL 2100F, TEM (Digital TEM) with image analysis system at a maximum magnification of 1, 50,000× operating at a voltage 200 kV. The aqueous dispersions of Laponite–IL particles were drop-cast onto a carbon coated copper grid, and the grid was air dried at room temperature before loading onto the microscope. To calculate the fractal dimension, a software known as fractal analysis system was used. The software uses box counting method for fractal dimension estimation. The box counting method was used because it is easy, automatically computable, and applicable for patterns with or without self-similarity.

The suspensions after preparation were poured into measuring cylinders. As the formation of two coexisting phases started, we systematically measured the variation in the height of lower phase using a scale as function of time to map the demixing kinetics.

3. Results and discussion

As stated earlier, the phase separation yielded a supernatant phase [S] and a colloid-rich phase [C]. The supernatant phase was examined by viscometry methods which indicated that this phase was mostly solvent-like. Thus, the bottom phase comprising of colloid-rich dispersion was subjected to further probing.

3.1. Phase separation kinetics

Fig. 1 illustrates a spontaneous liquid–liquid phase separation equilibria occurring in the dispersions of 2% (w/v) Laponite platelets in 0.15% (w/v) [C2mim][Cl] IL solutions at room temperature. More specifically, at time $t = 0$, the air–liquid meniscus was located at a height ($h_0 = 50$ mm). During the passage of time a clear visible liquid–liquid meniscus developed, which shifted further downwards into the bulk and after $t = 432{,}000$ s (~4 days), it attained an equilibrium height = 25 mm ($\approx h_0/2$). Thus, a free-energy driven liquid–liquid phase separation was observed in nanoclay dispersions in IL solutions. Interestingly, no such phase separation was noticed at this Laponite concentration when the dispersions were prepared in water only. On the contrary a phase separation was observed in pure Laponite suspensions for lower weight concentrations $C_w \leq 1\%$ on the time scale of the order of years [38]. This dynamics caused the top colloid-poor region to remain in thermodynamic equilibrium with the colloid-rich bottom phase. The pH of the solution over the entire process is 8.9. The time-dependent shift of the meniscus is shown in Fig. 2a for phase separations occurring in aqueous Laponite dispersions at 2% (w/v) for 0.15, 0.20, 0.25 and 0.30% (w/v) [C8mim][Cl] solutions. Similar, data for [C2mim][Cl] solutions is presented in Fig. 2b. Similar data for surface covered with hexanol samples is presented in Fig. S1a and b (Supplementary material).

The spontaneous two phase separation can be modeled using the following simplistic mechanism. Phase separation can be visualized as the result of two phenomena: droplet ascent or descent, and their coalescence. Thus, for simplicity, when a single droplet is considered, the aforesaid processes can occur in sequence. A droplet ascends/descends to the liquid–liquid interface and there it coalesces with the compatible phase. In such a model, the density difference between the two liquid phases drives the motion of the droplet and the surface tension governs its coalescence behavior.

We assume that the homogeneous dispersion at $t = 0$ comprises of hydrated unstable aggregates of platelets (droplets) which spontaneously split into smaller stable structures. Of course this splitting will be governed by various factors like, size of the droplets, the interfacial tension, and medium viscosity to name a few. Let a droplet of a certain size have a concentration $n_1(t)$ at a given point of time. This splits