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Binary Systems of a Hydrophobic Aprotic Ionic Liquid and Water as Catalysts for Michael Addition Reaction

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Abstract: Binary systems of an Aprotic Ionic Liquid (AIL), 8-hexyl-1,8-diazabicyclo[5.4.0]-undec-7-ene-8-iumhydroxide ([C_6DBU]OH) and water were prepared at molar ratio, X^{AIL} ranging from 0 to 1.0. Physicochemical properties of the pure and binary systems of the AIL have been studied in detail by viscosity, Fourier Transform Infrared (FTIR) spectroscopy, and dynamic light scattering measurements and thermogravimetric analysis. The negative deviation of excess viscosity at $X^{AIL} < 0.4$ indicated the formation of micelle like aggregation and the positive deviation of excess viscosity at $X^{AIL} > 0.4$ indicated the formation of reverse micelle like aggregation due to the surfactant-like behavior of the long alkyl chain in [C_6DBU]OH. The spectral and the particle size analyses show the presence of the confined water at $X^{AIL} > 0.4$ in the cored structure of the reverse micellar aggregates. The variation of the microstructures in water-rich and ionic liquid (IL)-rich region significantly influenced the kinetics of Michael addition reaction between acetylacetone and 2-cyclohexene-1-one in absence of organic solvents while using [C_6DBU]OH and its binary systems with water as catalysts. The reaction was studied by using thin layer chromatographic technique using aluminum plates coated with silica gel as the stationary phase and mixture of chloroform and n-hexane (1:1 by volume) as the eluent. The progress of the addition reaction was monitored by observing the development of spots in the chromatographic plate. The kinetic investigations in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), NaOH, and a DBU based protic IL, [HDBU]OH have also been made and the catalytic performances have been compared. Finally, the role of the [C_6DBU]OH and its binary systems with water as catalysts in the mechanism of the Michael addition reaction has been explained in terms of different molecular interactions.

Keywords: Aprotic ionic liquid, Average reaction rate, Catalyst, Micelle, Reverse Micelle, Michael addition reaction, 1, 8-diazabicyclo[5.4.0]-undec-7-ene (DBU).

I. Introduction

Ionic liquids (ILs) are salts in the liquid state which comprise liquids exclusively ions and the structure of the cation or the anion may be widely varied to have series of ILs most of which are liquid at ambient temperature [1-4]. Physicochemical properties of ILs can therefore, be easily tuned simply by changing the structure of the component ions and varying the nature from aprotic to protic. However, due to high viscosity, ILs, in many instances, are found not to be suitable for practical applications [5]. The combination of an IL with molecular solvents can resolve the issue [6-7]. This makes studies on binary mixtures containing ILs interesting. Since the ionic state and ionic mobility influence the physicochemical properties directly, it is crucial to understand the molecular interactions such as, solute-solute, solute-solvent, and solvent-solvent interactions between ILs and solvents in binary systems of ILs. Systematic investigation of ILs and their binary systems can help optimizing properties by varying the structure and compositions for a specific task [8]. For instance, specific reaction media with controlled reaction dynamics may be designed by tuning the polarity of aprotic ionic liquid (AIL)-based binary systems by suitable choice of solvents and their compositions [9, 10]. Quite reasonably, there has been surge of interest to find new ILs and their binary systems, which can be better and practical substitute of traditional catalysts and serve as reaction media for organic synthesis.

Michael addition reaction is one of the most useful routes for the formation of C-C bonds in organic synthesis. The reaction is generally catalyzed by bases and sometimes acids, but requires large volume of organic solvents as reaction medium, high temperature, and long reaction time. The product is separated from the reaction mixture by solvent extraction using volatile organic solvent or mixture of solvents. The separation of product is not easy as it contains some other undesirable byproducts. ILs have been found to be promising and attracted extensive

interest as excellent alternatives to organic solvents for Michael reaction [11]. Research to date includes various attempts to study the kinetics of Michael addition reaction catalyzed by pure ILs. A basic IL, 1-butyl-3-methylimidazolium hydroxide, [BMIm]OH was reported to catalyze Michael addition reaction without the use of any other catalyst and solvent [12, 13]. The [BMIm]OH-catalyzed reaction showed remarkable advantages, such as operational simplicity, short reaction time, high yields of products, and greenness of procedure avoiding hazardous organic solvents and toxic catalysts. Despite the promise, the use of ILs for Michael addition reaction is still in the rudimentary stage and the potential of binary systems with molecular solvents is yet to be explored.

In this regard, the use of a superbase, like 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) or its derivative to enhance the catalytic efficiency or for use as a medium for Michael addition reaction appears to be interesting. DBU can accept proton even from a weak acid to give rise to a positively charged species and form protic ionic liquid (PIL) with an anion (conjugated base of the acid). If the acid is weak, the conjugate base or the anion will become a strong base. Therefore, DBU has the potential for use as a precursor for preparation of a new class of task-specific ILs, PILs and AILs and use as a catalyst for Michael addition reaction. The advantages of DBU are associated with properties such as its large size, low cation symmetry and strong charge delocalization on the N–C=N structure [14]. We have recently prepared a PIL, [HDBU]OH based on DBU, and studied physicochemical properties of the IL and its binary system with water and reported that the kinetics of Michael addition reaction is catalyzed by [HDBU]OH and [HDBU] OH-water binary systems [15]. The research on the preparation of new AILs based on DBU is however, very limited [6-17] and extensive research on this area is demanding with focus on their application for study of the title reaction. It would be interesting to introduce long alkyl groups with different chain lengths in the DBU structure so that we can have surface active AILs capable of self association in solvents in different extent depending on the composition and provide them wide variation in physicochemical properties to profoundly influence the kinetics of Michael reaction.

The aim of the work therefore, has been the preparation of new AIL, 8-hexyl-1,8-diazabicyclo[5.4.0]-undec-7-ene-8-iumhydroxide ([C_6DBU]OH) and its binary systems with water and study their physicochemical properties in relation with aggregation behavior and molecular level interactions. Kinetic studies have been systematically and intensively conducted on Michael addition reaction between acetylacetone and 2-cyclohexene-1-one using thin-layer chromatographic (TLC) technique in presence of [C_6DBU]OH and its binary systems and results have been compared with those for NaOH, DBU, and [HDBU]OH and its binary systems to understand the mechanism of Michael addition reaction and explain the role of [C_6DBU]OH systems as catalysts and media.

II. Experimental

A. Materials

1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (Sigma Aldrich), 1-chlorohexane (Sigma-Aldrich), NaOH (Merck), Acetylacetone (Scharlau, Spain), and 2-cyclohexen-1-one (Sigma-Aldrich) were of analytical grades and used as received without further purification. Ionized water (conductivity: 0.055 μScm^{-1} at 25.0°C) from HPLC grade water purification system (BOECO, Germany) was used.

B. Synthesis of [C_6DBU]OH and [HDBU]OH

The [C_6DBU]OH and [HDBU]OH were synthesized following the procedure reported earlier [15]. In brief, [C_6DBU]OH was synthesized by alkylation of DBU using 1-chlorohexane at room temperature. The salt synthesized ([C_6DBU]Cl) was subjected to anion metathesis using solid NaOH pellets to get [C_6DBU]OH. The crude [C_6DBU]OH was washed with water and dried under vacuum at 65°C. [HDBU]OH was prepared by neutralization of the base DBU by water as a weak acid in an ice bath.

C. Methods

Thermogravimetric and differential thermal analysis (TG-DTA) were conducted under N_2 atmosphere (100 $mLmin^{-1}$) with a Seiko Instruments Analyzer (TG DTA 6200). The accuracy of measurements of temperature and mass, were ± 1°C and 10^{-3} mg respectively. Samples were heated from 30°C to 400°C in an Al-pan under a nitrogen atmosphere. The heating rate was 10°C min^{-1}. The onset degradation temperatures, T_d, was evaluated from the point of intersection of the tangents of the TGA curve.

Fourier Transform (FT) mid infrared (MIR) and near infrared (NIR) spectra were recorded by a FT spectrophotometer *Frontier*™ by PerkinElmer with 20 scans for each sample at 4.0 cm^{-1} resolution. KBr pellet was used and one drop of the liquid sample was added on the pellet using micropipette (5-10 µL) for recording FTMIR spectra. Rectangular quartz cell of path length 1.0 mm was used for measurement of FTNIR spectra where uncertainty was 1% for the measurements.

Viscosity of pure ILs and their binary systems with water was measured with an Anton-Paar falling ball automated viscometer (Lovis-2000M/ME) with an accuracy of $\pm 10^{-6}$ mPa.s. The diameter of the ball and capillary for sampling and angle of measurement have been selected depending on the approximate viscosity of the mixture. Temperature was controlled by means of a built-in Peltier thermostat within ±0.01 K.

Hydrodynamic diameter (D_h) of the aggregates of ILs in the binary systems was measured using a particle size analyzer, Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, UK) by Dynamic Light Scattering (DLS) measurements at different

temperatures. A He-Ne laser beam of 632.8 nm wavelength was used as the light source and the measurements were made at a fixed scattering angle of 90°. A measuring glass cell of 10 mm diameter was used. The particle size detection limit was about 0.3 nm - 5 μm. The accuracy of the D_h determined by DLS measurements was ± 2%.

D. Reaction of Acetylacetone and 2-Cyclohexene-1-one Catalyzed by the Pure and Binary Mixtures of [C_6DBU]OH with H_2O at Room Temperature

A mixture of acetylacetone (5 mmol) and 2-cyclohexene-1-one (5 mmol) was taken in a test tube. Binary mixtures of [HDBU]OH with water were prepared at various molar ratio to have compositions varying from water-rich conditions to [C_6DBU]OH-rich conditions. Michael addition reaction was carried out using these mixtures as catalyst. The reaction was carried out at room temperature (≈20°C) under stirring condition using a magnetic stirrer. Crystalline product, 3-(3-cyclohexanonyl) pentyl-2,4-dione, was obtained after solvent extraction where diethyl ether was used as the solvent. The product was characterized by chemical and FTIR, ^{1}H NMR, and ^{13}C NMR spectral analyses.

E. Kinetic Measurement

The kinetics of the reaction was monitored by TLC technique where commercially available aluminum plates coated with silica gel 60 F_{254} were used as the stationary phase. Samples were applied on the plate by capillary tube. The spotted plate was developed in ascending process and mixture of chloroform and *n*-hexane (1:1 by volume) was used as the eluent. The spots developed on plate were located using UV lamp. The reaction mixture showed the presence of spots for both the reactants and the product on the plate after few min from the commencement of the reaction. When the reaction mixture showed no spots for reactant it indicated the completion of the reaction and the time was recorded as the reaction completion time (*t*). The initial concentration of the substrate, acetylacetone was 3.791 molL^{-1}, and the average rate was evaluated as the initial concentration of acetylacetone.

III. Results and Discussion

A. Physicochemical Properties of the Prepared Binary Mixtures of [C_6DBU]OH with Water

Fig. 1 shows the FTMIR spectra of [C_6DBU]OH and its binary systems with water. Generally, solubilized water molecules exist in three distinct states: trapped, bound, and free water [18]. The bands of O-H stretching (3200-3600 cm^{-1}) and C-H stretching (3090-3160 cm^{-1}) change significantly with added water. The wavenumber of the O-H stretching band remains almost unchanged until $X_{[C_6DBU]OH}$ = 0.4. When the content of [C_6DBU]OH exceeds $X_{[C_6DBU]OH}$ = 0.4, the O-H stretching band appears at 3680 cm^{-1} along with the free and bound water (arrow in Fig. 1). This may be due to the fact that when water is added to [C_6DBU]OH, the water molecules are either trapped in the core of the aggregates of the [C_6DBU]OH with water or thermodynamically bound to the polar region of the free cations or/and anions of [C_6DBU]OH through intermolecular hydrogen bonding interaction.

The trapped water is regarded as the water species dispersed among the long hydrocarbon chains of [C_6DBU]OH [19]. This trapped water exists as monomers (or dimers) and has no hydrogen bonding interactions with the surroundings. Furthermore, a small amount of water dissolved in a nonpolar/hydrophobic solvent is also considered to be trapped water. Amongst the trapped water molecules, some are intermolecularly hydrogen bonded with them and some are free [20]. As the trapped water molecules are matrix-isolated dimers or monomeric in nature, they absorb in the high-frequency region [19].

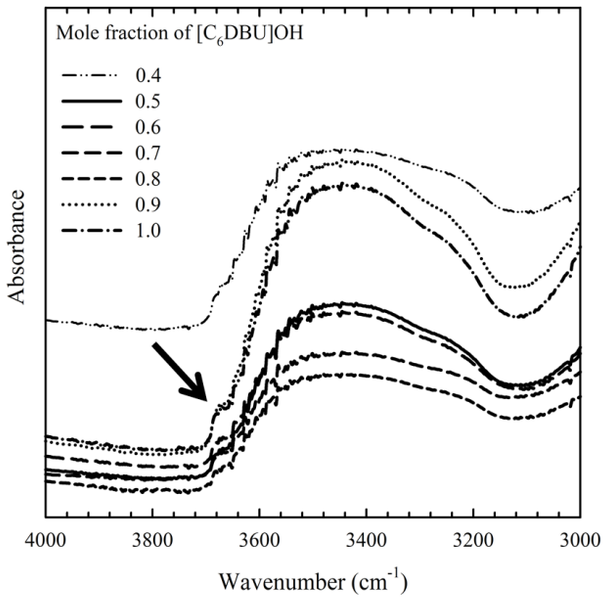

Fig. 1: FTMIR Spectra of [C_6DBU]OH and its Binary Systems with Water in the Frequency Range from 3000 to 4000 cm^{-1}

FTNIR spectra of [C_6DBU]OH and its binary systems with water showed the combination bands arising from the symmetric stretching, anti-symmetric stretching, and bending vibration of water molecules. The raw spectrum was corrected for baseline and smoothened followed by deconvolution into several Gaussian peaks for the analysis of different water species in the binary systems. Fig. 2 shows the deconvoluted spectrum of [C_6DBU]OH-water binary system with 0.9 mole fraction of [C_6DBU]OH in the range of 6500-7500 cm^{-1}, where the broad band has been fitted to eight Gaussian peaks (R^2 = 0.9991). The 7080-7400 cm^{-1} region was assumed to arise from the CH vibrations of the cation [21]. The band at 7020 cm^{-1} is the combination band of -OH in water molecule bonded to [C_6DBU]OH as the absorbance rises significantly in this region

with increasing amount of water. Water mainly remains in the monomeric form in [C_6DBU]OH-rich region and interacts with the anions [22].

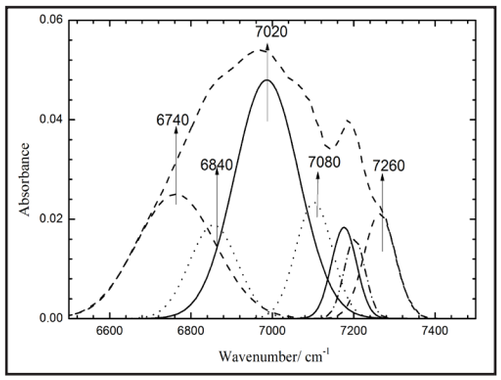

Fig. 2: Deconvoluted Spectrum of [C_6DBU] OH-Water Binary Mixture with $X_{[C_6DBU]OH}$ = 0.9

The smaller bands at 6740, 6840 cm^{-1} originate from the hydrogen bonded water clusters. The bands for associated water appear at lower wavenumber region compared to that for water bound to [C_6DBU]OH. This is due to the fact that the hydrogen bonds between water molecules are much stronger than that between water and anions [23].

The anion, hydroxyl group, in water has its own specific absorption band with first overtone band at 7020 cm^{-1}. As the concentration of hydroxyl group is increased, the intensity of the water bands decreases. The band at 5275 cm^{-1} for the [C_6DBU]OH-water binary systems (Fig. 3) indicates that its position depends on the dominant species in which water is trapped [24]. The trapped water appeared at $X_{[C_6DBU]OH}$ > 0.4, i.e., [C_6DBU]OH-rich compositions of [C_6DBU]OH-water binary systems (arrow in Fig. 3).

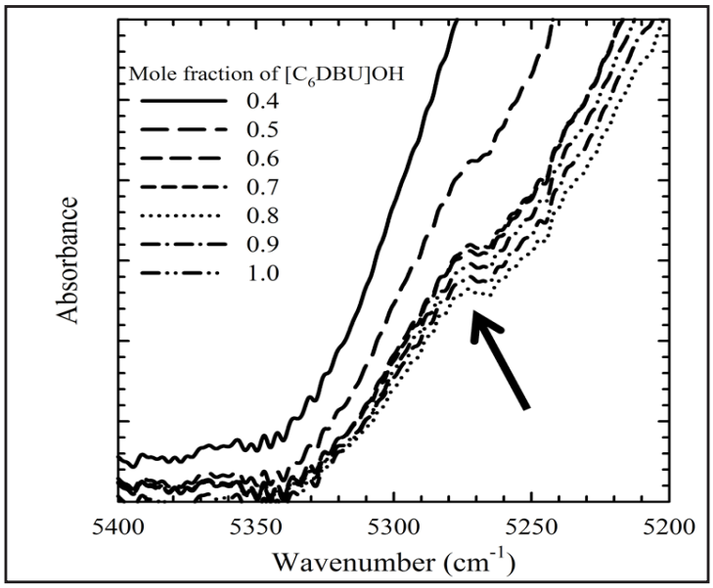

Fig. 3: FTNIR Spectra of [C_6DBU]OH and its Binary Systems with Water in the Frequency Range from 5200 to 5400 cm^{-1}

B. Particle Size Analysis by DLS Measurements

DLS measurements have been carried out to analyze the size of the aggregates formed in the [C_6DBU]OH-water binary systems (Fig. 4). It is apparent that with increasing concentration of [C_6DBU]OH($X_{[C_6DBU]OH}$ = 0.1-0.4), the size of the aggregates increases. At $X_{[C_6DBU]OH}$ = 0.5, the aggregates show a narrow distribution. With further increase in concentration of [C_6DBU] OH in the range of $X_{[C_6DBU]OH}$ = 0.6-1.0, the size of the aggregates increases further. As the [C_6DBU]OH is hydrophobic and contains a long alkyl hydrocarbon chain (hexyl) in the cation, formation of micelle and reverse micelle like aggregates may be feasible [25]. In water-rich region with $X_{[C_6DBU]OH}$ = 0.1-0.4, formation of micelle, while in [C_6DBU]OH-rich region with $X_{[C_6DBU]OH}$ = 0.6-1.0, formation of reverse micelle may be envisaged. Peak broadening is observed for [C_6DBU]OH-rich condition to indicate the presence of aggregates of various sizes.

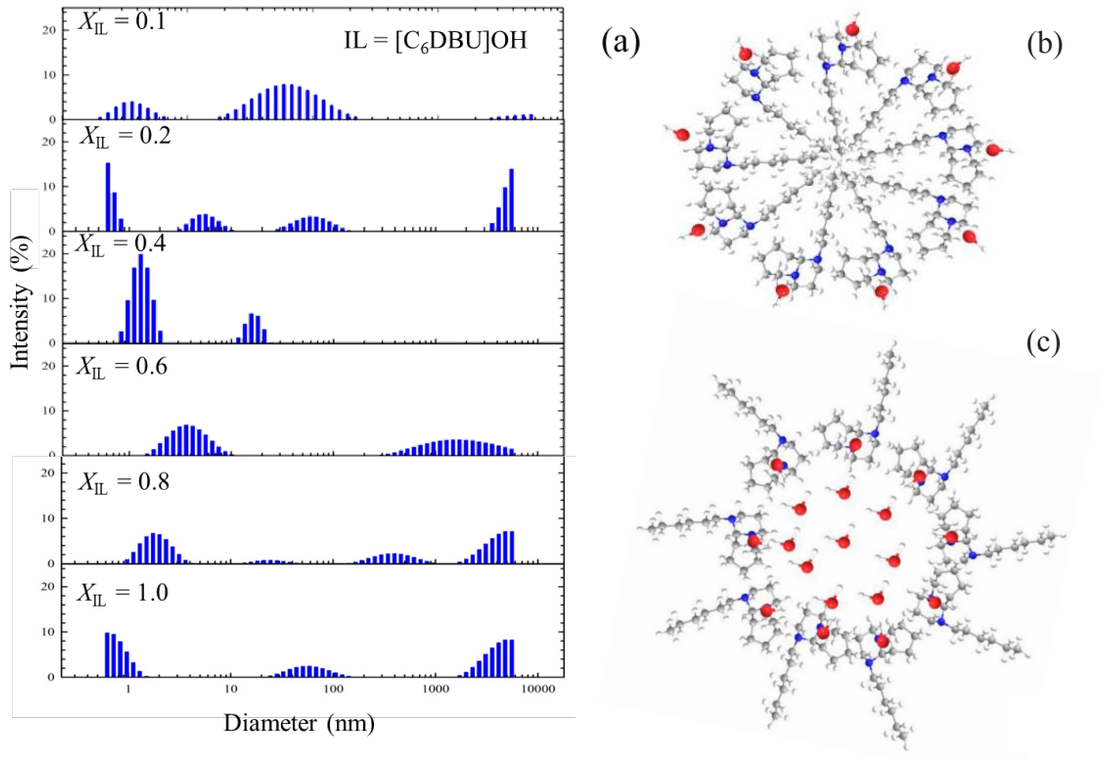

Fig. 4: (a) Particle Size Distribution in [C_6DBU]OH and its Binary Systems with Water at $X_{[C_6DBU]OH}$ = 0.1 to 1.0, (b) Micelle-like Aggregation of [C_6DBU]OH with Water, and (c) Reverse Micelle-Like Aggregation of [C_6DBU]OH with Water

C. TG-DT Analysis of [C_6DBU]OH and its Binary Systems with Water

Thermal properties of [C_6DBU]OH and its binary systems with water were studied using TG-DTA and the T_d for different compositions of [C_6DBU]OH and water was evaluated. The curve at $X_{[C_6DBU]OH} < 0.5$ (Fig. 5) shows decrease in the T_d with addition of [C_6DBU]OH. This is due to the fact that with decrease in water content, the interaction between water and the cation decreases. Moreover with decreasing water content in the binary mixtures, the T_d decreases possibly due to decrease in the extent of aggregation (micelle) of [C_6DBU]OH and water.

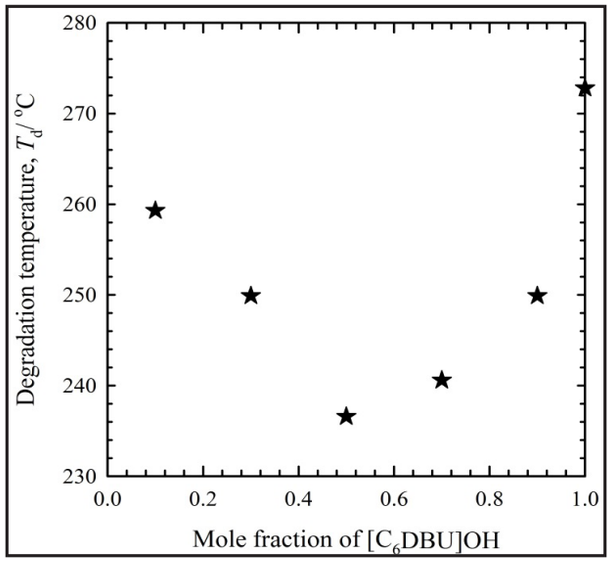

Fig. 5: The Variation of Degradation Temperature with Mole Fraction of [C_6DBU]OH for the Binary Systems of [C_6DBU]OH and Water

At $X_{[C_6DBU]OH} > 0.5$, the degradation temperature increased with increasing concentration of [C_6DBU]OH. This may due to the formation of reverse micelle-like aggregation in this surfactant-like hydrophobic IL, [C_6DBU]OH. But the curve at $X_{[C_6DBU]OH} = 0.5$ showed the lowest T_d. This is due to the disruption of micellar aggregates.

The miscibility of an IL with water is mostly determined by the associated anion [22, 26, 27] and the anion might be involved in an attractive hydrogen-bonding interaction [28]. It is worth noting that even the hydrophobic ILs can absorb some water from air and the cations have been found to be responsible for this [22]. In fact, the interaction between the cation and the water is secondary. Though [C_6DBU]OH is hydrophobic in nature, the water molecule could form hydrogen bonds with the protons of the cation [29]. In the cation, there are two N-atoms and the positive charge is in the alkylated DBU ring. This makes the carbon between the two N-atoms electron deficient to create a favorable situation to form hydrogen bonds with water molecules [30].

D. Viscosity

Viscosity is an important macroscopic property of ILs and their binary mixtures with water and reflects the microscopic characteristics determined by numerous interrelated parameters like molar mass, shape, and size of the ions, and intermolecular and inter-ionic forces such as Coulombic interactions, hydrogen bonding or van der Waals interactions. To investigate the nature of the molecular interactions between water and [C_6DBU]OH viscosity deviation, $\Delta\eta$, was evaluated from experimental viscosity using equation (1).

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad (1)$$

Where x_1 and x_2 are the mole fractions calculated from mass fractions, η_1 and η_2 are the viscosities of pure components 1 and 2 respectively, η_m is the viscosity of the mixture. Fig. 6 shows viscosity deviation of [C_6DBU]OH-water systems at different temperatures.

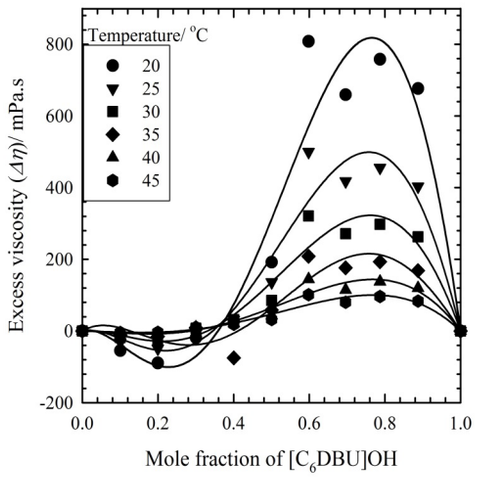

Fig. 6: Excess Viscosity as a Function of Mole Fraction of [C_6DBU]OH in its Binary Systems with Water

A close examination of Fig. 6 indicates that, the excess viscosity is negative at $X_{[C_6DBU]OH} < 0.5$ and positive at $X_{[C_6DBU]OH} > 0.5$. The negative deviation of viscosity suggests that viscosities of aggregates formed between unlike molecules are relatively less than those of pure components. The $\Delta\eta$ decreases as the number and strength of H-bonds are decreased. This indicates that H-bonding in [C_6DBU]OH is more dominant in determining the viscosities than in typical polar protic molecular solvents [31]. The negative $\Delta\eta$ obtained for this system suggests that there may be a reduction in the number and strength of H-bonds upon mixing. It should be noted that the negative viscosity deviation may also occur where dispersion forces are dominant for the systems having different molecular sizes [32]. This also indicates the possibility of formation of micellar aggregates in water-rich compositions of [C_6DBU]OH-water binary systems. The positive $\Delta\eta$ values are discussed in terms of ion-dipole interaction between [C_6DBU]OH and water. The $\Delta\eta$ increases as the number and strength of H-bonds increase, which supports the formation of reverse micelles in water-deficient composition of the binary systems of [C_6DBU]OH and water.

E. Kinetic Study

a. Michael Addition Reaction using Bases and AIL Systems as Catalyst

Michael addition reaction of acetylacetone and 2-cyclohexene-1-one was carried out using bases (NaOH, DBU), and ([C_6DBU]OH) and its binary systems with water at room temperature (≈ 20 °C) and the catalytic activity was compared. The reaction completion time was measured by using TLC technique and the average rate was calculated. In case of NaOH, it required large amount of ethanol to make a solution and average rate of the reaction was 2.53×10^{-4} molL^{-1}s^{-1}. When DBU was used as the base, the rate was 2.63×10^{-4} molL^{-1}s^{-1} and it was completely miscible with both reactants. But for [C_6DBU]OH, the average rate was 3.72×10^{-4} molL^{-1}s^{-1}and it required no solvent. It is very interesting that for the binary system of [C_6DBU]OH and water at all compositions the rate was higher than that for the the pristine IL. For instance, at $X_{[C_6DBU]OH} = 0.5$, the rate was 12.64×10^{-4} molL^{-1}s^{-1}. For [C_6DBU]OH, the rate of the reaction was approximately 1.4 times faster than that of the bases, DBU and NaOH and for binary system of the [C_6DBU]OH with $X_{[C_6DBU]OH} = 0.5$, the rate of the reaction was 4.8 times faster than that of the organic bases. Thus, [C_6DBU]OH serves both as reaction medium and catalyst and the binary systems of [C_6DBU]OH showed better catalytic performance.

b. Rate of the Michael Addition Reaction in Presence of NaOH with Different Concentrations of [C_6DBU]OH

The reaction between acetylacetone and 2-cyclohexene-1-one was carried out in presence of fixed amount of NaOH using different concentrations of [C_6DBU]OH as the catalyst. With addition of very small amount of [C_6DBU]OH (0.005 mmol), the average rate of the reaction increased (arrow in Fig. 7).

Therefore, [C_6DBU]OH acted as a catalyst for the reaction.

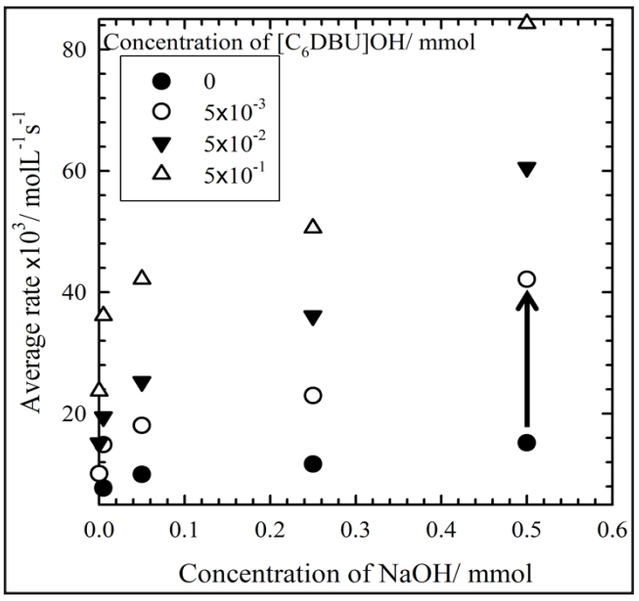

Fig. 7: Average Rate for Michael Addition Reaction in Presence of NaOH with Different Concentrations of [C_6DBU]OH

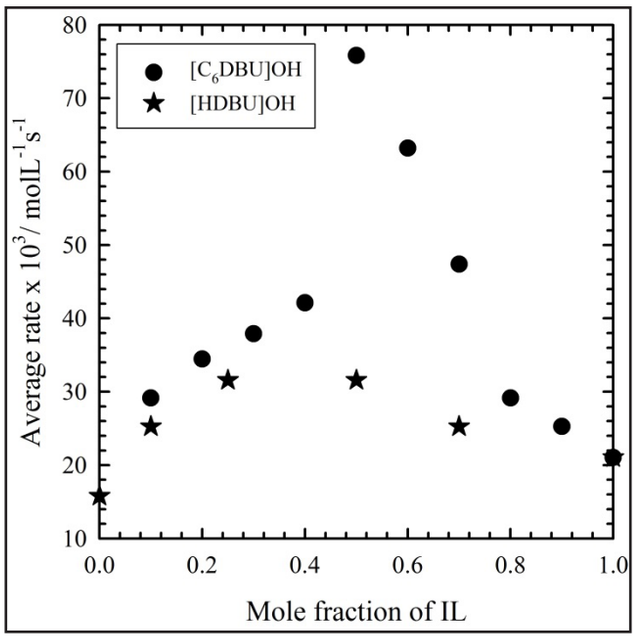

Fig. 8: Average Rate with Mole Fraction of IL ([HDBU]OH and [C_6DBU]OH) for the Michael Addition Reaction Catalyzed by the ILs and Their Binary Systems with Water

c. Michael Addition Reaction Catalyzed by the Binary Mixtures of [C_6DBU]OH and Water at Room Temperature

The average rate plotted against mole fraction of [C_6DBU]OH in the binary systems of [C_6DBU]OH with water is shown in Fig. 8. With increasing mole fraction of [C_6DBU]OH ($X_{[C_6DBU]OH}$ = 0-0.5), the rate of the reaction increases. With increasing mole fraction of [C_6DBU]OH, the number of ions increases to enhance the rate of the reaction. This is consistent with the inference from the physicochemical properties of [C_6DBU]OH and its binary systems with water that micelle-like structure may be formed in water-rich region and reverse micelle-like structure in [C_6DBU]OH-rich region (*vide supra*). In case of micelle-like structure, the nonpolar part of the cation is pointed to the center of the micelle and the polar part is directed to the outside of the micelle and the anion is in the bulk aqueous phase along with the polar part. Such arrangement makes the anion available for catalysis and enhances the rate. In case of reverse micelle-like structure, the polar part is pointed to the center of the reverse micelle and the nonpolar part is directed towards outside of the reverse micelle and the anion is in the core along with the polar part. Therefore, anions are not so available for catalysis and with the addition of [C_6DBU]OH ($X_{[C_6DBU]OH}$ = 0.5 - 1.0), the rate has been found to decrease.

d. Comparison of the Kinetics of Michael Addition Reaction: [C_6DBU]OH and its Binary Systems with Water vs. [HDBU]OH and its Binary Systems with Water

The average reaction rate of [C_6DBU]OH and its binary systems with water at different mole fractions has been compared with those for [HDBU]OH in Fig. 8. [C_6DBU]OH and its binary systems showed faster rate of the reaction compared to [HDBU]OH and its binary systems. It should be noted here that [C_6DBU]OH is aprotic and hydrophobic in nature whereas [HDBU]OH is protic and hydrophilic. Here, the anion (OH^-) is the same in both the ILs, however, for [C_6DBU]OH the cation is alkylated DBU, (C_6DBU^+) and for [HDBU]OH the cation is protonated DBU ($HDBU^+$). The interactive forces of ILs change with change in alkyl chain length and the cumulative effect of the electrostatic interaction between the ionic species and the induction interactions between the ions, aggregates, and clusters determine the properties of the ILs [2]. In the present case, the carbon number in the substituent group of the cation of [HDBU]OH is 0 and [C_6DBU]OH is 6. The packing of cations and anions in [C_6DBU]OH is probably loose due to large size of the cation having hexyl group. Moreover the hexyl group is nonpolar and hydrophobic in nature which also disturbs the tight packing of ions. Therefore, the anion is more mobile in [C_6DBU]OH and available for catalysis of the reaction. The

rate of the reaction therefore becomes faster for [C_6DBU]OH and its binary systems compared to [HDBU]OH and its binary systems.

F. Yield of the Product of the Michael Addition Reaction

A crystalline solid was produced as a result of Michael reaction of acetylacetone and 2-cyclohexen-1-one. The product was isolated, purified, and characterized as 3-(3-cyclohexanonyl) pentyl-2,4-dione. The yields of the Michael addition reaction catalyzed by DBU, [HDBU]OH, [C_6DBU]OH, and the binary systems were in the range of 74-80 % where all experiments were carried out under the same reaction conditions. But the average rate was different for each experiment. When the same reaction was carried out in ethanol solution with NaOH, the yield was poor (40%) and the reaction completion time was longer. However, catalysis by IL-based systems enhanced the rates as well as yields of the reactions. The process is simple, environmentally friendly and did not generate any side reaction or by-product. On the other hand, when the reaction was carried in presence of ethanol and organic bases, the reaction resulted in sticky products, which were difficult to handle.

IV. Conclusions

Physicochemical properties of binary systems of [C_6DBU]OH and water change with composition. A number of attractive interactions like van der Waals force, dispersion, Coulombic, hydrogen bonding, etc exists in ILs. Upon addition of water to [C_6DBU]OH hydrogen bonding and ion-dipole interactions induce strong association or self-assembly. The aggregation behavior of [C_6DBU]OH depends on the specific interactions in the binary systems with water leading to changes in physicochemical properties. Michael addition reaction of acetylacetone and 2-cyclohexen-1-one is catalyzed by [C_6DBU]OH and its binary systems with water. The catalytic activity of the binary systems of the [C_6DBU]OH has been found to be better than that of the AIL itself and the bases, DBU and NaOH. [C_6DBU]OH served as a better catalyst compared to a PIL, [HDBU]OH for the synthesis. The binary systems of [C_6DBU]OH do not require any external solvents and the process as a whole has been very efficient. Therefore, the binary systems of AIL are better catalysts and they provide an environmentally benign and cost-effective route for the Michael addition reaction.

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