

Liquid-Liquid Equilibrium Study of 1-Dodecyl-3-Methyl-Imidazolium Dicyanamide + KH₂PO₄ + Water

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ABSTRACT: *The phase behavior of a new ternary Aqueous Two-Phase System (ATPS) based on [1-Dodecyl-3-Methyl-Imidazolium][Dicyanamide] ionic liquid and an inorganic salt of KH₂PO₄ was investigated at two different salt concentrations and different temperatures of 288.15, 298.15, and 308.15 K, all under atmospheric pressure (0.1 MPa). This surface-active ionic liquid was chosen due to its similar properties to cationic surfactants and its widespread use in separation processes. The chemical structure of the synthesized ionic liquid was investigated using Fourier Transform InfraRed (FT-IR), Nuclear Magnetic Resonance (NMR), Diffuse Reflection Spectroscopy (DRS), residual chlorine test, and melting point test. The achieved experimental data correlated with the symmetrical local composition model of UNIQUAC-NRF with symmetric Pitzer–Debye–Hückel (PDH) theory. The results showed a minor influence of temperature on the separation process, and the salt ability in phase separation was increased at higher concentrations. A good agreement between correlated data and the experimental results was also found.*

KEYWORDS: *ATPS, Ionic Liquid, Pitzer–Debye–Hückel, UNIQUAC-NRF, KH₂PO₄.*

INTRODUCTION

Ionic Liquids (ILs) that are obtained by the combination of organic cations and organic/inorganic anions were first introduced as molten salts by *Bockris* and *Reddy* in 1970, also, the capability of this new material to form aqueous two-phase system was studied for the first time by *Gutowski* and *co-workers* [1]. ILs are applied in multidisciplinary areas such as catalysis, extraction, dye-synthesized, solar cells, catalytic cracking, radical

polymerization, oil industry, etc., and are suitable substitutes for conventional organic solvents due to their unique physiochemical characteristics like high conductivity, good thermal and electrochemical stability, non-flammability, negligible vapor pressure, low melting temperature, optimal solubility and being eco-friendly. In fact, the characteristics of ILs not only depend on the type combination ratio [1, 2,3].

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1021-9986/2023/8/2704-2713

10\$/6.00

Recently, a new group of ILs with a long alkyl chain attached to a cationic charged head are synthesized, which are known as Surface-Active Ionic Liquids (SAILs). These types of ionic liquids have micelle formation during dissolving in water, because of their combination of anions and cations with amphiphilic properties (both hydrophilic and hydrophobic). Research on SAILs has received extensive attention mainly due to their properties similar to cationic surfactants which make them suitable alternatives in separation processes [4]. For instance, imidazolium-based SAILs can be used in major pharmaceuticals, cosmetics, paints, detergents, and various biochemical reactions because of superior surface activity compared to traditional ionic surfactants [5]. Interaction between SAILs and different drugs such as anesthetic drugs lidocaine hydrochloride, procaine hydrochloride, sodium diclofenac, tetracaine, chlorpromazine hydrochloride, doxorubicin hydrochloride, and penicillin has been studied with the aim of achieving stable drug-IL complexes [6].

The demulsification process (separation of water from crude oil emulsions) is one of the major challenges in the petroleum industry. One such commercial demulsifier agent commonly used for this purpose is SAILs. According to the literature [7,8,9], ionic liquids cation-containing like imidazolium and ILs with longer alkyl chain lengths provided better demulsification. They cause significantly lower interface tension and displace the natural surfactants, because of their higher dependency on migrating to the interface [7-9].

According to the wide application of SAILs in different industries, in this work, the aqueous two-phase system behavior of newly synthesized SAIL was studied, and accurate Liquid-Liquid Equilibrium (LLE) data were investigated to comprehend the extraction processes such as emulsification and biomolecule extraction processes in future studies.

As the Imidazolium- based ionic liquids have various considerable applications in biomolecule separation and purification including extraction of proteins, polysaccharides, antibodies, drugs, and enzymes (such as α -lactalbumin β -lactalbumin, xylanase, bovine lactoferrin, β -glucosidase and penicillin acylase) [10,11] and also the oil industry [3] because of its significant potential to form an aqueous biphasic system [1], this cation base was selected. Also, a long-chain alkyl was considered because, in the

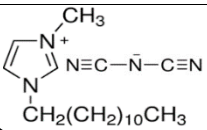
extraction process, hydrophobic ILs have to be used to create the IL/water biphasic systems [12].

The effect of the anion types of [Cl], [PF₆], [Br], [NTF₂], [BF₄], etc. as one of the important parameters that affect the ILs performance, were studied in emulsification and medical industries [3~12], so, in this study dicyanamide (DCN) was selected as new ones based on two reasons. The first reason is that this anion led to considerable improvement in the viscosity and electrochemical properties of imidazolium-based ionic liquids. It lowers the viscosity values, which will enable easy processing the ILs [13]. Another motivation is the presence of three coordination sites on this anion. The number of coordination sites can play a role in extraction efficiency [14]. Another point is that according to the Hofmeister effect, KH₂PO₄ was selected because of its kosmotropic nature which leads to the salting out of big molecules such as proteins [15]. As a result, although there is a long chain of alkyl that causes hydrophobic properties, dicyandiamide as a chaotropic anion [12] and selected inorganic salt will cause the forming of an aqueous two-phase system.

Also, the possible effective parameters on the phase behavior of this new ternary Aqueous Two-Phase System (ATPS) based on [1-Dodecyl-3-Methyl-imidazolium] [Dicyanamide] and inorganic salt of KH₂PO₄, including temperature and salt concentration were investigated separately. Two different concentrations of salt and different temperatures of 288.15, 298.15, and 308.15 K, all at atmospheric pressure (0.1 MPa) were studied.

To design an effective extraction process, we need a precise model to correlate the achieved experimental data. In this study, a symmetrical local composition model of UNIQUAC-NRF along with symmetric Pitzer-Debye-Huckel (PDH) theory was used. The local composition model and PDH theory were applied for the short-range and long-range interactions, respectively, by assuming complete dissociation of salts for the PDH term and ion-pair approach for the salts, water, and ionic liquids in the local composition model [16]. The thermodynamic model including UNIQUAC is used because it seems to have a higher efficiency than other models due to the possibility of calculating the surface and volume. In the selected model, anions and cations are involved but also on a symmetric local composition model is used for the ternary ATPS instead of unsymmetrical ones which

Table 1: Ionic Liquid specifications

IL Structure	Name	Molecular Weight (g/mol) Formula	Appearance	analysis
	[1-Dodecyl-3-Methyl-Imidazolium][Dicyanamide]	317.47 C ₁₈ H ₃₁ N ₅	Pale yellow powder	NMR ^a Residual Chlorine ^b melting point ^c FTIR ^d DRS ^e

a: Nuclear Magnetic Resonance Spectroscopy, H-NMR, and C-NMR, (Varian-INOVA 500MHz model)

b: 0.25 % of Chloride Ion

c: under 313.15 K (40 °C)

d: Fourier Transform Infrared Spectroscopy (JASCO 4700 model)

e: Diffuse Reflection Spectroscopy (PerkinElmer L25 model)

Table 2: Materials used in this study

Name	Source	Mass fraction purity ^a	Purification method	CAS No.
[C ₁₂ mim][N(CN) ₂]	Chemistry & Chemical Engineering Research Center of Iran	> 0.98	None	927681-23-0
KH ₂ PO ₄	Merck	> 0.995	None	7778-77-0
Water	The present Lab		deionized and bidistilled	7732-18-5

a Stated by the supplier

allow us to assume the salt is a pure and fused solid in the solvent [16].

EXPERIMENTAL SECTION

Materials and methods

The ionic liquid [1-Dodecyl-3-Methyl-Imidazolium][Dicyanamide] was synthesized in the Chemistry & Chemical Engineering Research Center of Iran. The specifications of the prepared IL are given in Table 1. As shown, the IL was characterized by different tests such as NMR, FTIR, and DRS. The inorganic salt of KH₂PO₄ was purchased from Merck Company. The supplied material in this work is shown in Table 2.

Apparatus and procedure

The aqueous two-phase systems with different salt and IL concentrations were prepared by using the appropriate amount of the stock solutions in the 15 mL test tubes through weighing (using balance, Kern PLS 510-3 model, within an uncertainty of 0.001 g). The concentration of a stock solution of [C₁₂ mim][Dicyanamide] was 21.1 (w/w%). Also, the concentrations of two used stock solutions for KH₂PO₄ were 27.39 and 31.03 w/w %. Initially, to prepare the aqueous two-phase, the mixtures were mixed strongly by a shaker (VELP Scientifica Z×3 model) through a magnet inside the test tubes. Then tubes were placed in a water bath at a suitable temperature (with

an uncertainty of 0.05 K) for 12 h. When two-liquid phase equilibrium was achieved, the upper and the lower phases were withdrawn by a glass syringe using a long metal needle and weighed carefully and independently. The separated upper and lower phases were diluted in two steps to analyze the salt and IL concentrations appropriately. Each experiment was performed three times to show the repeatability of the data, and the mean values are reported here.

The analysis method

Before carrying out aqueous two-phase experiments, linear calibration curves were constructed for ionic liquid and salt separately by using UV/Visible and atomic absorption spectroscopy, respectively.

The aqueous two-phase systems were prepared by mixing a specified volume of ionic liquid from the stock solution with a determined volume of the aqueous salt stock solution. The measurement of IL and salt concentrations in each phase was done by UV/Vis spectrometer (PG Instrument T80+ model) at λ_{max} = 210 nm and atomic absorption spectroscopy (Shimadzu AA-670 model) respectively.

The diluted species concentrations were calculated by the absorption amount and the standard graphs drawn earlier, then the initial concentration (molarity) of taken ionic liquid and salt cation in both phases were obtained

Table 3: The equilibrium composition of the aqueous two-phase system of {[C₁₂mim][Dicyanamide] (1)+ KH₂PO₄ (2)+ H₂O (3)} in two concentrations at different temperatures and P = 0.1 MPa. ^a

Upper Phase		Lower Phase	
100w ₁	100w ₂	100w' ₁	100w' ₂
1 st Concentration			
T=288.15 K			
43.55 (±1.95)	5.02 (±0.03)	2.56 (±0.18)	36.60 (±0.22)
42.62 (±1.20)	4.12 (±0.11)	2.49 (±0.63)	37.64 (±1.00)
44.35 (±0.27)	4.33 (±0.09)	2.79 (±0.42)	35.86 (±0.10)
45.12 (±0.79)	4.90 (±0.25)	2.90 (±0.99)	35.01 (±0.28)
T=298.15 K			
41.08 (±0.32)	4.73 (±0.18)	2.02 (±0.50)	36.89 (±0.95)
44.71 (±0.25)	4.09 (±0.38)	1.77 (±0.60)	38.81 (±0.01)
41.97 (±0.62)	4.80 (±0.18)	1.84 (±0.91)	34.87 (±0.13)
42.46 (±0.57)	4.44 (±0.04)	1.70 (±0.32)	37.67 (±0.24)
T=308.15 K			
45.12 (±0.96)	4.59 (±0.11)	2.84 (±0.20)	34.46 (±0.27)
47.02 (±0.44)	5.26 (±0.12)	2.48 (±0.62)	35.86 (±1.30)
45.61 (±2.73)	4.69 (±0.15)	2.35 (±0.38)	36.67 (±0.16)
46.12 (±0.28)	3.57 (±0.16)	2.70 (±0.73)	37.17 (±0.13)
2 nd Concentration			
T=288.15 K			
29.28 (±0.14)	1.60 (±0.13)	3.71 (±0.19)	29.87 (±0.04)
30.84 (±0.32)	1.89 (±0.11)	2.56 (±0.12)	29.23 (±0.06)
32.73 (±0.29)	1.35 (±0.08)	2.19 (±0.18)	29.59 (±0.09)
31.58 (±0.16)	1.50 (±0.10)	2.18 (±0.26)	30.17 (±0.19)
T=298.15 K			
32.83 (±0.58)	1.66 (±0.12)	1.82 (±0.64)	30.48 (±0.14)
35.93 (±0.50)	1.04 (±0.20)	2.26 (±0.32)	31.06 (±2.20)
36.69 (±0.11)	2.42 (±0.31)	1.83 (±0.57)	29.31 (±0.16)
34.57 (±0.26)	1.59 (±0.15)	2.06 (±0.58)	30.84 (±0.02)
T = 308.15 K			
35.86 (±1.07)	4.04 (±0.25)	2.34 (±0.52)	30.64 (±0.13)
37.45 (±0.34)	3.49 (±0.38)	3.81 (±0.18)	31.71 (±0.20)
33.09 (±0.23)	3.10 (±0.63)	2.93 (±0.37)	31.66 (±0.42)
36.00 (±0.70)	3.47 (±0.30)	3.01 (±0.61)	29.84 (±0.17)

^a Standard uncertainties u are u(T)= 0.5 K, u(p) = 1 kPa

by using the equation of ($C_i V_i = C_j V_j$). Salt concentrations in both phases were computed by its complete dissociation through ionic stoichiometry. According to the achieved initial concentrations and the molecular mass, the primary mass was calculated. Since the original sample was weighed, the ratio of two weights is reported as the weight percentage.

The experimental data are shown in Table 3, for both the upper and lower phases of the aqueous-two-phase systems of the ternary mixtures of [C₁₂mim][Dicyanamide] + KH₂PO₄ + water. Also, the interference salt effects on the IL analysis and vice versa were detected. The results demonstrated that this interference was less than 5%.

Table 4: UNIQUAC Structural Parameters for the Binary Aqueous Electrolytes [17]

Name	r	q
KH ₂ PO ₄	1.828	1.848

THEORETICAL SECTION

In this work, the correlation of experimental data was investigated using the symmetric local composition model of UNIQUAC-NRF. The activity coefficient (γ) functions of the present model are as below [16]:

$$\ln \gamma_s = \ln \gamma_s^{LC} + \ln \gamma_s^{PDH} ; \quad S = \text{salt} \quad (1)$$

$$\ln \gamma_i = \ln \gamma_i^{LC} ; \quad i = \text{Ionic Liquid, Water} \quad (2)$$

As the first term of Eq. (1), the symmetric short-range interaction contribution is described by the local composition model of UNIQUAC-NRF as developed by *Haghtalab* and *Asadollahi* [17]. The binary interaction parameters in this model, τ_{ij} , were optimized as a function of temperature as [16]

$$\tau_{ij} = \frac{u_{ij} - u_{jj}}{R} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln(T) \quad (3)$$

Where u_{ij} is the interaction parameter between molecules i and j , T and R are absolute temperature and gas constant respectively. The values of the structural parameters including area (q) and volume (r) used for the salt in the UNIQUAC-NRF model was given by *Haghtalab* and *Peyvandi* [17] as shown in Table 4.

Since the structural parameters of the used IL are not mentioned in the literature, we use J_{mol} [19], without further energy optimization, the overlap between the ionic species and just the distance between the anion and cation was adjusted. After calculating the surface area (A_m) and molecular volume (V_m) of the ionic liquid molecule by J_{mol} , the area and volume parameters were determined as follows [16].

$$r = \frac{V_m (1 \times 10^{-8})^3 N_A}{V_{VW}} ; \quad q = \frac{A_m (1 \times 10^{-8})^2 N_A}{A_{VW}} \quad (4)$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1} ; \quad V_{VW} = 15.17 \frac{\text{cm}^3}{\text{mol}} ;$$

$$A_{VW} = 2.5 \times 10^9 \frac{\text{cm}^2}{\text{mol}}$$

The Pitzer-Debye-Hückel (PDH) for molten salt was used to take into account the electrostatic interaction. The detail of the PDH equation is given in the Appendix. The mixing rules should be used in Pitzer-Debye-Hückel

for the ternary systems to calculate density (d), molar mass (M), and dielectric constant (D). The dielectric constant of the aqueous mixture of IL was calculated by the *Singh* and *Kumar* method as [20]:

$$d = \frac{(x_{IL} d_w) d_{IL} + (x_w d_{IL}) d_w}{x_{IL} d_w + x_w d_{IL}} \quad (5)$$

Similarly, the mixture molecular weight and the dielectric (relative permittivity) constant of the mixture were computed using the individual properties of IL and water as:

$$M = \frac{x_{IL} M_{IL} + x_w M_w}{x_{IL} + x_w} \quad (6)$$

$$D = \frac{x_{IL} M_{IL} \epsilon_r^{IL} + x_w M_w \epsilon_r^w}{x_{IL} M_{IL} + x_w M_w} \quad (7)$$

The mole fraction of water and IL were calculated as:

$$x_i = \frac{y_i}{y_{IL} + y_w + v y_s} ; \quad i = \text{water, IL} ; \quad x_s = 1 - x_{IL} - x_w ; \quad v = v_c + v_a \quad (8)$$

RESULTS AND DISCUSSION

All experimental data for the aqueous-two phase system of the ternary mixtures of [C₁₂mim] [Dicyanamide] + KH₂PO₄ + water are express in wt. % as shown in Table 3. Although increasing the length of alkyl chain in imidazolium IL grows its hydrophobicity, it can be easily salted-out by inorganic salt. According to what observed in the laboratory during the experiments and shown in Figs. 1-3, the aqueous two-phase system was formed and no precipitation occurred by using KH₂PO₄. As the concentration of inorganic salt was a significant factor affecting the aqaous two-phase formation, the experiment was performed at two different salt concentrations to investigate its influences on ATPS formation.

In fact, although there is a long chain of alkyl which cause hydrophobic properties, dicyanamide as a chaotropic anion [11] and selected kosmotropic inorganic salt will cause forming of an aqueous two-phase system. The weight fractions of IL (1) against the two concentrations of salt (2) at the three different temperatures are shown in Figs.. 1-3.

Salt Concentration effect on ATPS

In Figs. 1-3, the effect of salt concentrations (two

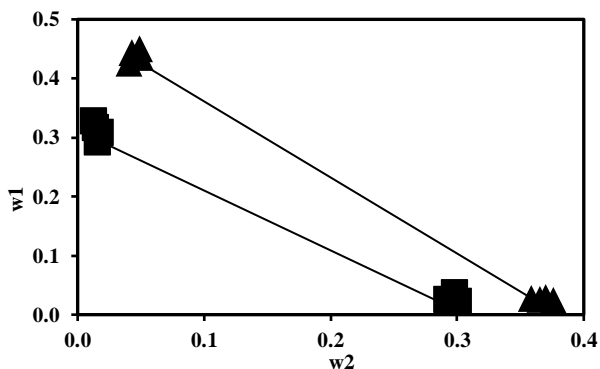


Fig. 1: The weight fraction of the IL against the weight fraction the salt (binodal) in the aqueous two-phase system of $[C_{12}mim][Dicyanamide]$ (1)+ KH_2PO_4 (2)+ H_2O (3) at $T=288.15$ K (■ 27.39 w/w%, ▲ 31.03 w/w%, model UNIQAC-NRF —)

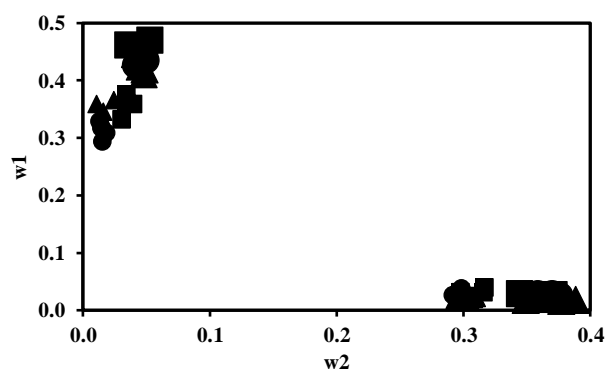


Fig. 4: The weight fraction of the IL against the weight fraction of the salt (binodal) in the aqueous two-phase system of $[C_{12}mim][Dicyanamide]$ (1)+ KH_2PO_4 (2)+ H_2O (3) effect of temperature (● 288.15 K, ▲ 298.15 K, ■ 308.15 K)

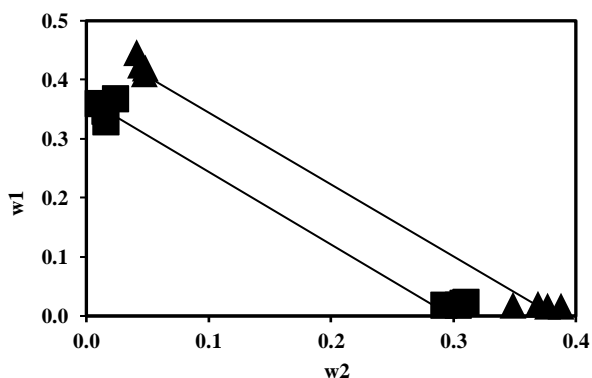


Fig. 2: The weight fraction of the IL against the weight fraction of the salt (binodal) in the aqueous two-phase system of $[C_{12}mim][Dicyanamide]$ (1)+ KH_2PO_4 (2)+ H_2O (3) at $T=298.15$ K (■ 27.39 w/w%, ▲ 31.03 w/w%, model UNIQAC-NRF —)

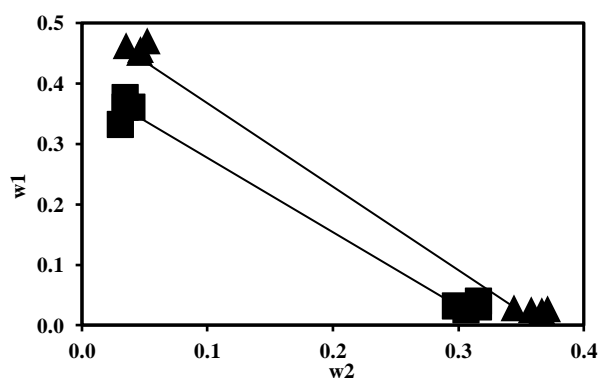


Fig. 3: The weight fraction of the IL against the weight fraction the salt (binodal) in the aqueous two-phase system of $[C_{12}mim][Dicyanamide]$ (1)+ KH_2PO_4 (2)+ H_2O (3) at $T=308.15$ K (■ 27.39 w/w%, ▲ 31.03 w/w%, model UNIQAC-NRF —)

concentrations of 27.39 and 31.03 w/w%) in phase separation of $[C_{12}mim][N(CN)_2]$ -based ATPS is shown, each at one temperature (three temperatures of 288.15, 298.15, and 308.15 K). It is observed that by higher salt concentration, the salt ability to perform phase separation will be increased as the under area is decreasing.

The probable cause is that, as the salt concentration increases, the bottom phase becomes growingly kosmotropic and more structured, thus leading to more degree of transferring for chaotropic ions to the top phase [26]. Also, Gayatri & Swapnali shows the extraction efficiency of lignin increases by increasing the salt concentration that is because of the phase compositions divergence growing, as the free energy of transfer of solute between the phases, increases [27]. In fact the salting out effect of inorganic salt grows by increasing its concentration in aqueous two phase systems [28].

Temperature effect on ATPS

The temperature effect on formation of studied aqueous two phase system was investigated at $T = (288.15, 298.15, \text{ and } 313.15)$ K and shown in Fig. 4 for two concentrations of salts. As it is observed from Fig. 4, although the temperature affected the solubility of solutes, the effect of temperature on the phase forming of ATPS was not remarkable. It only seems that at the higher temperature, the solubility of the solute increase but not considerably.

Overall, temperature influence is not significant in the studied range from 288.15 K to 313.15 K, but variation of temperature could cause in increase or decrease of phase forming ability and change the extraction efficiency consequently [24,25].

Table 5: The interaction parameters for the salt(1) + H₂O(2) binary systems by UNIQUAC-NRF model, experimental data at P = 0.1 MPa

Name	a ₁₂	b ₁₂	c ₁₂	a ₂₁	b ₂₁	c ₂₁	ARD
KH ₂ PO ₄ -H ₂ O	-33.95	155.6	700.41	1208.16	638.01	158.65	0.072

$$* \text{ARD (Average Relative Deviation)} = \frac{1}{N} \left[\sum_i \left(\frac{|y_i^{\text{exp}} - y_i^{\text{cal}}|}{y_i^{\text{exp}}} \right) \right]$$

** a_{ij}, b_{ij} and c_{ij} are the coefficients of interaction parameters due to temperature dependency of interaction energy parameter. a_{ij} and c_{ij} are unitless and b_{ij} has the unit of temperature.

Table 6: The interaction parameters for the ternary system of [C₁₂mim][Dicyanamide] (1)+ KH₂PO₄ (2)+ H₂O (3) by UNIQUAC-NRF model at P= 0.1 MPa

ATPs	τ ₁₂	τ ₁₃	τ ₂₁	τ ₂₃	τ ₃₁	τ ₃₂	RMSD
T= 288.5 K	1432.529	1169.576	-3070.06	500.208	-2226.10	296.58	0.985
T= 298.5 K	2833.11	1211.49	-2409.56	765.99	-1644.28	188.66	1.11
T= 308.15 K	3873.320	806.391	-1107.37	916.47	-1417.76	202.819	1.07

Data correlation

In this work, the system consists of three components of salt, IL, and water, so there are three binaries of salt-water, salt-IL, and IL-water. The adjusted binary interaction parameters of KH₂PO₄-H₂O were correlated using the data obtained from the literature [21] and they are reported in Table 5. These reported values in table 5, are temperature dependant coefficients of interaction parameters based on the present model.

There was no data for the [1-Dodecyl-3-Methyl-Imidazolium][Dicyanamide]-water systems in the literature, so four binary interaction parameters of salt-IL, IL-salt, IL-water, and water-IL were obtained and optimized by correlating the achieved experimental data. The temperature-dependent interaction parameters were calculated and reported in Table 6. The optimization program based on the Simplex method of Nelder and Mead in Matlab is used to optimize the interaction parameter and LLE calculations.

For the initialization of the parameters, minimization of the Eq. (9) as an objective function was used by the given activity coefficient model and experimental data [22, 23].

$$OF_a = \sum_i^N \sum_j^3 (x_{ij}^l \gamma_{ij}^l - x_{ij}^{ii} \gamma_{ij}^{ii})^2 \quad (9)$$

Where *j* and *i* refer to the component in the upper or lower phase; *x* is the mole fraction and *γ* is the activity coefficient.

Finally, to have a good comparison between experimental and calculated data to achieve the best binary interaction

parameters, the Root Means Square Deviation (RMSD) equation used as below [22]:

$$\text{RMSD} = 100 \sqrt{\frac{\sum_{k=1}^N \sum_{j=1}^2 \sum_{i=1}^3 (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{6N}} \quad (10)$$

N is the number of tie lines, *x^{exp}* and *x^{cal}* indicate the experimental and calculated mole fraction respectively. *i*, *j*, and *k* are also demonstrated components, phases, and tie lines respectively.

In the laboratory, the mass fractions of the components were measured, and then they converted to the mole fractions by components molar mass, because the used objective function reported in molar fraction.

The modeling results are shown alongside the obtained experimental data in Figs. 1-3. It is found that the model can predict the thermodynamic behavior of such studied ternary systems.

CONCLUSIONS

In this study a new surface-active ionic liquid, [1-Dodecyl-3-Methyl-midazolium][Dicyanamide], was synthesized and the ternary aqueous two phase system behavior of SAIL+ inorganic salt of KH₂PO₄+ Water was investigated. According to laboratory experiments, the aqueous two-phase system was formed and no precipitation occurred by using KH₂PO₄. In fact, although there is a long chain of alkyl which cause hydrophobic properties, dicyanamide as a chaotropic anion and selected kosmotropic inorganic salt will cause forming of an aqueous two-phase system.

Two possible effective parameters on the phase behavior of this new ternary aqueous two-phase system

(ATPS) including temperature and salt concentration studied. The system was analyzed at two different salt concentrations (= 27.39 and 31.03 w/w %) and different temperatures (= 288.15, 298.15, and 308.15 K), all at atmospheric pressure (0.1 MPa). The results show, although the temperature affected the solubility of solutes, the effect of studied temperature on the phase forming of ATPS was not remarkable and the influence of temperature was minor.

It is also observed that by higher salt concentration (from 27.39 to 31.03 w/w%), the salt ability to perform phase separation will be increased as the bottom phase becomes growingly kosmotropic and more structured, thus leading to more degree of transferring for chaotropic ions to the top phase.

The results show that the effective parameter is salt concentration which means the salt ability in phase separation was increased at higher concentrations.

In order to design a beneficial extraction process, the experimental data were correlated by using a symmetrical activity coefficient model consisting of both the Pitzer-Debye-Huckel and UNIQUAC-NRF terms. The RMSD value for the ternary system containing KH_2PO_4 is 1.11, which proved the ability of the model to correlate the thermodynamic behavior of such IL-containing ATPSs.

Herein we provided information on the phase behavior of a aqueous two phase system of [1-Dodecyl-3-Methylimidazolium][Dicyanamide] and KH_2PO_4 for future studies on its application in the emulsification and biomolecule extraction processes.

Nomenclatures

γ	Activity coefficient
LC	Local composition
τ	Interaction parameter
u_{ij}	Interaction parameter between molecule i and j
T	Absolute temperature
R	Gas constant
q	Area structural parameter
r	Volume structural parameter
A_m	Surface area
V_m	Molecular volume
N_A	Avogadro Number
d	Density
M	Molar mass

D	Dielectric constant
x	Mole fraction
OF	Objective function
RMSD	Root mean square deviation
i, j	Component in the upper or lower phase
N	Number of tie lines
exp	Experimental
Cal	Calculated

Received : Oct. 20, 2022 ; Accepted : Jan. 30, 2023

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