Measurement and Correlation of Phase Equilibria in Aqueous Two-Phase Systems Containing Functionalized Magnetic Ionic Liquids and $\text{K}_2\text{HPO}_4/\text{K}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ at 298.15 K

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ABSTRACT: Functionalized magnetic ionic liquids (MILs)([C₂TMG][TEMPO-OSO₃], [C₃TMG][TEMPO-OSO₃], [C₄TMG][TEMPO-OSO₃]) and three inorganic salts (K₂HPO₄/K₂CO₃/Na₂CO₃) were used to form aqueous two-phase system at 298.15 K. Three classical experienced equations were applied for the correlations of the binodal curves. All of them demonstrated satisfactory performance in data association. The binodal curves were investigated in detail. Both K₂HPO₄ and K₂CO₃ was excellent phase forming salts for all the three MILs. Both of them can meet the need of practical applications. There is a narrow biphasic region for the MIL+ Na₂CO₃+water system because of a relatively low solubility of salt in water. Additionally, tie-line data were experimentally obtained for the three MILs with K₂HPO₄ or K₂CO₃ at 298.15K. Three empirical formulas including Othmer-Tobias equation, Bancroft equation together with another equation derived from binodal theory were used to fit the tie-line data. Consequently, Othmer-Tobias has shown ideal correlation performance and the reliability of our experimental tie-line data can be ensured. Hopefully, these aqueous two-phase equilibrium data should be useful in the areas of chemical separation, purification and analysis.

Keywords: magnetic ionic liquid, aqueous two-phase, binodal curve, tie-line, phase equilibrium

1. Introduction

Ionic liquids (ILs) are considered as green alternative to traditional volatile organic solvents for their negligible flammability, volatility, high ionic conductivity, ideal thermal and chemical stabilities as well as a strong solubilization capability for a variety of organic and inorganic compounds.[1-3] Generally, they are composed of unsymmetrical organic cations and symmetrical/unsymmetrical inorganic/organic anions. Several possible variations of cation and anion allow fine-tuning of their properties.[4-5] The possibility of designing many related properties has made ILs very useful in a broad range of potential applications. Because of these outstanding physicochemical properties, ILs have become preferable candidates in fields of separation, electrochemistry, extraction and chemical synthesis.[4-7]

Aqueous two-phase system (ATPs) was firstly obtained by Beijerinck[8] in 1896 by mixing gelatin and agar. In the late 1950s, Albertsson employed polymer-polymer ATPs for separation and purification process of biological materials.[9] For a long time, the development of low-cost, recyclable as well as biocompatible aqueous two phase systems which are capable of offering few stages in the separation and purification of added-value products is in high demand in the biotechnological industry.[10] The proposed ATPs has large proportion of water in both phases which can provide a biocompatible environment for biological materials. It also reveals lower environmental impact compared to other separation/extraction processes which employ organic solvents. Therefore, a large number of studies have been performed to develop ATPs as a benign bioseparation technique in recent years.[11-12] Guan et al. studied the application of ATPs in the recovery of penicillin[13] and acetylspiramycin.[14] The partitioning behavior of antibiotics in the ATPs based ILs as a novel biphasic system was also reported. Dallora et al.[15] measured partitioning behavior of trypsin, lysozyme and bovine serum albumin in an ATPs containing PEG 1500, 4000, 6000 and ammonium carbonate. Shahriari et al.[16] reported the partition coefficient of cephalixin and its relevant biphasic system phase behavior. Besides, the application of ATPs has been extended to separation and purification of cells, viruses, proteins, enzymes, nucleic acids, membranes, other high value-added biomolecules[17] as well as dyes[18] and metal ions.[19] Gutowski[20] et al. combined ILs and ATPs for the first time in 2003, which can be formed by mixing certain IL and inorganic salts such as K_3PO_4 , and K_2HPO_4 . This kind of new ATPs has a number of advantages shared by both IL and ATPs, such as low viscosity, high thermal stability,

high extraction efficiency and no use of volatile organic solvents.[21] Current ILATPs studies mainly focused on imidazolium-based IL,[20] pyridinium-based IL and so on, which have been successfully used in the separation of pharmaceuticals, antibiotics, proteins, and amino acids. However, ILATPs still had shortcomings such as low isolation efficiency of two aqueous phases because of small density difference.[26]

Magnetic ionic liquid (MIL) is functionalized IL which demonstrates a response to an external magnetic field.[27] The magnetic susceptibility of MILs is obtained from high-spin transition metals or radical moieties within either the IL cation or anion.[28] Imidazolium-based MIL [BMIM][FeCl₄] was firstly synthesized and reported by Hayashi et al.[27] in 2004. Since then, MILs have become a hotspot of research in field of extraction, separation and so on. Jiang et al.[29] found the benzene solubility would increase in the paramagnetic MIL [Bmim][FeCl₄] when a rotational magnetic field was used. Deng et al. investigated the performance of MIL [3C₆PC₁₄][FeCl₄] as an extraction solvent for the separation of phenolic compounds from aqueous solution in the presence of a neodymium magnet. After that, two studies reported the application of hydrophilic imidazolium-based MILs for the analysis of trazine herbicides in oilseeds and vegetable oils.[31] However, both of them required hexane as a diluent for the sample. Wang et al.[32] studied the application of [bPy][FeCl₄] as an effective extractant to extract asphaltene fractions from coal direct liquefaction residues. Some MILs have been employed as extraction solvent for the preconcentration of DNA from a cell lysate.[33] They also demonstrated good compatibility with the polymerase chain reaction which allowed high throughput DNA amplification in the MIL microdroplet.[34] The above successful applications were all realized with metal-containing MILs. Moreover, there exists another kind of MIL which is non-metal organic MIL based on a radical ion. The first MIL with organic anion was discovered and proposed by Yoshida[35] in 2007. There were few reported literatures referring to the organic MIL as well as their applications.

Magnetic ionic liquid aqueous two-phase system (MILATPs) is a novel extraction system proposed by us recently.[26] The composition of MILATPs is MIL, inorganic salt and water. For the MILATPs, the advantages of magnetic separation, organic solvent free and rapid extraction can be simultaneously realized. Conventional ILATPs suffer from the difficulty of phase isolation due to small density difference of two phases, while MILATPs can enhance its phase separation

efficiency with an external magnetic field. The MIL phase can be attracted by a strong magnet and quickly gather at a required position. This technique is showing great potential in the extraction and separation field and is successfully applied in the microextraction analysis of some environmental pollutant in our recent study.[36] The synthesis, characterization and some basic physical property of the functionalized MILs were introduced previously.[26] However, it is far from enough for the further exploration of these MILATPs.

Generally, liquid-liquid phase equilibrium data are the basic information for the design of ATPs application. Knowledge of specific and accurate aqueous two-phase data of MILs with different salts is extremely important reference for the ATPs application in the fields of separation, purification and chemical analysis. In this work, the liquid-liquid equilibrium composition of the MILATPs was studied, which contained tetramethyl guanidinium-based organic MIL and different salts ($K_2HPO_4/K_2CO_3/Na_2CO_3$) at 298.15 K. The binodal curves for different systems were fitted by three thermodynamic equations. The phase-forming abilities of different MILATPs systems were compared in detail. Additionally, the tie-line data were determined for a series of MILATPs and correlated with three thermodynamic equations. The obtained experimental data can provide reference for the future application of the MILATPs.

2. Experimental

2.1. Materials.

All reagents used were of analytical grade or above. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl free radical (4-OH-tempo) and 1,1,3,3-tetramethylguanidine were purchased from Best Reagent Co., Ltd. (Chengdu, China). Anhydrous potassium phosphate was supplied by Guangfu Superfine Chemical Industry Institute (Tianjin, China). Moreover, chlorosulfonic acid was obtained from Aike Chemical Reagent Co., Ltd. (Chengdu, China). The other used chemicals and reagents were supplied by Kelong Chemical Co., Ltd (Chengdu, China). All these purchased chemicals were used directly without any purification. Ultrapure water was obtained from ultra-pure water purification system (0.4mm filter) manufactured by Millipore (Bedford, MA). The measured MILs in this MILATPs were $[C_nTMG][TEMPO-OSO_3]$ ($n=2$ to 4) and there chemical structures are shown in Fig. 1. These tetramethyl guanidinium-based MILs with mass fraction greater than 0.99 were synthesized and purified according to our developed method.[26]

Insert Figure 1

2.2. Apparatus and procedures.

Phase diagrams were constructed using binodal curves, which were determined by the cloud point method[37] with three different salts ($K_2HPO_4/K_2CO_3/Na_2CO_3$) at temperature of 298.15 K, respectively. The equilibrium process was conducted in a vessel containing a magnetic stirrer at constant temperature and atmospheric pressure. The vessel was immersed in a jacketed glass vessel using a CY20A water thermostat (Boxun Industry & Commerce Co.,Ltd., Shanghai, China) with an uncertainty of ± 0.05 K to keep constant temperature of the vessel by extrinsic cycle pattern. Mass value was determined by a FA/JA type electronic analytical balance (uncertainty of ± 0.0001 g). An IL solution of known mass fraction was taken into the vessel with vigorous stirring for 15 min. Then a salt solution of known mass fraction was added dropwisely to the vessel with an interval of 5 min between every two drops. When the mixture turned cloudy, the stirring was stopped and the two phases occurred steadily. The composition of the mixture for each point on the binodal curve was weighed, noted and calculated by mass. Afterwards, a certain amount of water was added and then a clear one-phase system was obtained. The system was then kept stirring at constant temperature for another 15 min. Repetitive operation was kept on to form the phase equilibrium line.

For the determination of each tie-line, known weight of MIL, water and salt were added into a vessel successively to make a ternary mixture. The composition of the ternary mixture should be at the biphasic region of the binodal curve. The mixture was stirred at constant temperature, and left to equilibrate for 30 min to obtain a complete separation of two phases. The top phase was collected to another vessel with a syringe and these two phases were separately weighed. Then each tie line was calculated according to Eq (1-4) proposed by Merchuk[38].

$$w_1^t = a \exp(b(w_2^t)^{0.5} - c(w_2^t)^3) \quad (1)$$

$$w_1^b = a \exp(b(w_2^b)^{0.5} - c(w_2^b)^3) \quad (2)$$

$$w_1^t = w_1^m / \alpha - w_1^b(1 - \alpha) / \alpha \quad (3)$$

$$w_2^t = w_2^m / \alpha - w_2^b(1 - \alpha) / \alpha \quad (4)$$

Where w_1^t , w_2^t , w_1^b , w_2^b , w_1^m and w_2^m represent the equilibrium mass fractions of MIL (1) and

potassium phosphate (2) for top phase (t), bottom phase (b) and the mixture (m), respectively. α is the mass ratio of the top phase to the total mixture.

From the binodal curve experiment, parameters a , b , c were obtained. In the tie-line experiment, the mass fraction of MIL and salt in the mixture as well as the mass ratio of the top phase to the mixture were known. Four unknown numbers w_1^t , w_2^t , w_1^b and w_2^b were determined through the four equations. Thus, the composition of the top phase and the bottom phase was determined and the tie-line was finally obtained. The latter refers to the distance between the points of the bottom phase composition and the top phase composition in the binodal curve. The TLL for different composition of MILATPs at 298.15 K were calculated according to Eq (5).

$$TLL = [(w_1^t - w_1^b) + (w_2^t - w_2^b)]^{1/2} \quad (5)$$

Where w_1^t , w_2^t , w_1^b and w_2^b represent the equilibrium mass fractions of MIL (1) and potassium phosphate (2) for top phase (t) and bottom phase (b), respectively.

The TLLs are expressed in mass fractions, the slopes of tie-lines (STL) were calculated as the ratio between the variation of the MIL and salt concentration in each phase of the MILATPs according to Eq (6).

$$STL = (w_1^t - w_1^b) / (w_2^t - w_2^b) \quad (6)$$

Where w_1^t , w_2^t , w_1^b and w_2^b represent the equilibrium mass fractions of MIL (1) and potassium phosphate (2) for top phase (t) and bottom phase (b), respectively.

3. Results and discussion

3.1. Binodal data and correlation

The binodal data of MILATPs containing three MILs ([C₂TMG][TEMPO-OSO₃], [C₃TMG][TEMPO-OSO₃] and [C₄TMG][TEMPO-OSO₃]) and three inorganic salt K₂HPO₄, K₂CO₃, Na₂CO₃ at temperature of 298.15 K were determined and have been shown in Tables 1-3. The binodal curves of the studied systems as well as their fitting lines are given in Fig. 2-4. Recently, there are many empirical equations for the correlation of the binodal data of ATPs. The experimental data of the binodal curves for MILATPs were fitted by the frequently used empirical equation proposed by Merchuk[38] as following:

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3) \quad (7)$$

Where a , b and c are adjustment parameters and w_1 and w_2 are the mass fractions of the MIL and salt, respectively. This equation has been widely used to fit the binodal curves of polymer + salt ATPs[39], IL + salt ATPs[40] and ATPs based on hydrophilic organic solvents. In this work, Eq (7) is satisfactorily used to fit the binodal data of our investigated systems. The adjusted parameters (a , b , and c) and the correlation coefficient (R^2) with different inorganic salts are presented in Table 4. All the R^2 are higher than 0.999 and Merchuk equation is found suitable for our MILATPs. In order to further investigate the data theoretically, other two nonlinear empirical expressions with multiple fitting parameters (Eq 8 and 9) were applied to model the binodal data:

$$w_1 = a_1 \exp(-w_2 / b_1) + a_2 \exp(-w_2 / b_2) + c \quad (8)$$

$$w_1 = \exp(a + bw_2^{0.5} + cw_2 + dw_2^2) \quad (9)$$

where the coefficients a_1 , a_2 , b_1 , b_2 , a , b , c , and d are fitting parameters. The fitting parameters at different temperatures as well as the correlation coefficient (R^2) are shown in Tables 5 and 6. The parameters listed in Table 5 and 6 can also accurately correlate the data of the binodal curve for the investigated system. From the results of all these correlation performance, both Eq (7) and Eq (9) have similar and satisfactory correlation coefficients, better than the fitting performance of Eq (8). It can be concluded that Merchuk equation and Eq (9) can predict the characteristic of the binodal curve more precisely than Eq (8).

Insert Table 1

Insert Table 2

Insert Table 3

Insert Figure 2

Insert Figure 3

Insert Figure 4

Insert Table 4

Insert Table 5

Insert Table 6

3.2. Tie-line data and correlation

From the experimental binodal curves, all three MILs revealed satisfactory phase behavior

with K_2HPO_4 and K_2CO_3 . MILATPs with Na_2CO_3 had obviously weaker phase forming ability. The liquid-liquid equilibrium tie-line data of the MILs + K_2HPO_4 + water and MILs + K_2CO_3 + water systems were determined at 298.15 K and the results are presented in Table 7 and Fig. 5. In this work, several commonly used models including empirical equations were applied to fit the tie-line data. And the data for this kind of systems are often correlated to the Othmer-Tobias (Eq 10) and Bancroft (Eq 11) equations:

$$(1 - w_1^t) / w_1^t = k_1 \left[(1 - w_1^b) / w_2^b \right]^n \quad (10)$$

$$w_3^b / w_2^b = k_2 (w_3^t / w_1^b)^r \quad (11)$$

Where w_1^t , w_1^b and w_2^b are the mass fraction of the MILs (1) in the top and bottom phases and that of the salt (2) in the bottom phase, w_3^t and w_3^b are the mass fractions of water in the top phase and bottom phase, respectively. The correlated parameters k_1 , n , k_2 and r as well as their R^2 are demonstrated in Table 8. Currently, these two equations have been widely used to describe the tie-line compositions of aqueous two-phase systems, especially those systems composed of ionic liquid[42]. The reliability of our experimental tie-line data can be ensured by Othmer-Tobias correlation[43] with all the regression coefficients (R^2) higher than 0.99. This equation is a well-known empirical method that assures the consistency of the experimental data. The fitting results by Bancroft equation were also acceptable, which are a little worse than those of Othmer-Tobias equation. In order to provide more thermodynamic equation to fit and explain the tie-lines, another equation (Eq 12) based on binodal theory was applied to describe the experimental data. It was suggested by Guan [44] on the basis of excluded volume theory. This equation is expressed as follow:

$$\ln(w_2^t / w_2^b) = \beta + k(w_1^b - w_1^t) \quad (12)$$

where k is the salting-out coefficient and β represents a constant related to the activity coefficient. The fitting parameters of this equation as well as R^2 are also shown in Table 8. The equation was commonly used to correlate polymer-salt ATPs.[45] According to excluded volume theory, the system composition on the binodal curve was a saturated solution of polymer in the presence of salt. When the polymer filled the effective available volume, it could be excluded to form another aqueous phase. Our MILATPs also demonstrated acceptable correlation performance with Eq (12). For our systems, MIL and inorganic salt can simultaneously exist in a uniform solution when both

of their concentrations are relatively low. When their concentrations rise, MIL will be salted out from the solution to form another aqueous phase. TLL and STL can provide us basic parameters for reference. When the TLL is longer, the composition difference between top phase and bottom phase is more obvious. In practical applications, an MILATPs with quite different chemical environment of top phase and bottom phase is probably expected because this kind of system can be beneficial for selective extraction or separation of specific biochemical substances. For example, point 1 of $[C_3TMG][TEMPO-OSO_3] + K_2CO_3 + H_2O$ in Table 7 can correspond to a system with MIL completely concentrated in the top phase and inorganic salt nearly completely gathered in the bottom phase, which should be regarded as a candidate with ideal phase behavior in potential extraction application. On the other hand, STL is also very useful. Experimental tie-lines are nearly parallel to each other in the same system and this is in agreement with reported literatures.[46-48] By measuring the STL of a system, the phase composition of any given mixture can be accurately estimated.

Insert Table 7

3.3. Phase behavior comparison from binodal curves

The phase behavior of MILs with different inorganic salts was investigated in detail. A series of pre-experiments were performed in advance and it was found that $(NH_4)_2SO_4$, Na_2SO_4 , KOH , $NaOH$, $NaCl$ as well as KCl could not drive any MIL aqueous solution to separate into two phases. However, all the MILs could form ATPs in the presence of K_2HPO_4 , K_2CO_3 or Na_2CO_3 . Further experiments of binodal curve measurement were conducted and the binodal curves are shown in Fig. 2-4. It can be found that both K_2HPO_4 and K_2CO_3 have excellent phase forming ability for all the three MILs. Although in a certain range of salt concentration, Na_2CO_3 exhibited a relatively better phase separation ability for $[C_2TMG][TEMPO-OSO_3]$ and $[C_4TMG][TEMPO-OSO_3]$ MILs than K_2HPO_4 and K_2CO_3 , the narrow range of biphasic region for Na_2CO_3 containing systems can greatly limit the practical application of the systems. Actually, the solubility of Na_2CO_3 in water at room temperature is rather low. When Na_2CO_3 is nearly saturated in the aqueous solution, there still exists considerable amount of MIL dissolved in the solution with mass fractions of 4.7% for $[C_2TMG][TEMPO-OSO_3]$, 4.8% for $[C_3TMG][TEMPO-OSO_3]$ and 1.5% for $[C_4TMG][TEMPO-OSO_3]$, respectively. No more MIL can be salted out to form another phase. As

for the other two inorganic salts, MIL mass concentration can easily decrease to lower than 0.1% in the inorganic salt-rich phase by dissolving adequate amount of inorganic salt. $[C_{2-4}TMG][TEMPO-OSO_3] + K_2HPO_4/K_2CO_3 + H_2O$ systems have a wide range of biphasic region of MILATPs which is valuable in extraction and separation field. Particularly in microextraction application, only inorganic salts with pretty strong phase-forming ability can drive a very small amount of MIL to be separated from the system. In general, from the experimental data, it can be inferred that K_2HPO_4 and K_2CO_3 are much better phase-forming salts than Na_2CO_3 in possible practical application. In addition, both K_2HPO_4 and K_2CO_3 have wide range of biphasic regions and can meet the need of separation technology. When considering potential applications of these MILATPs, specific two phase splitting data can provide us valuable references.

Insert Table 8

Insert Figure 5

4. Conclusions

Three lately proposed functional MILs can form novel MILATPs with three inorganic salts. The liquid-liquid equilibrium data of MILATPs were obtained for the systems of $[C_{2-4}TMG][TEMPO-OSO_3] + K_2HPO_4/K_2CO_3 + H_2O$ at $T=298.15K$. The binodal curves of these systems were correlated by Merchuk equation and other two empirical nonlinear equations with satisfactory fitting performances. Investigation of binodal curves indicates that K_2HPO_4 and K_2CO_3 have ideal phase forming ability with all tested MILs and K_2HPO_4 shows a little better phase separation performance than K_2CO_3 . Both of them can meet the need of practical application. Furthermore, the tie-line data were measured for the systems containing K_2HPO_4 or K_2CO_3 , and then they were fitted by Othmer-Tobias, Bancroft equation and another equation. The reliability of our experimental tie-line data can be ensured by Othmer-Tobias correlation with all the regression coefficients higher than 0.99. These aqueous two-phase equilibrium data can provide useful reference for future application of related ATPs.

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Table captions

Table 1 Binodal curve data as the mass fraction (w) for the $[\text{C}_2\text{TMG}][\text{TEMPO-OSO}_3]$ MILATPs with different salts at 298.15 K under 0.1MPa. w_1 and w_2 are the mass fractions of the MIL and salt, respectively.

Table 2 Binodal curve data as the mass fraction (w) for the $[\text{C}_3\text{TMG}][\text{TEMPO-OSO}_3]$ MILATPs with different salts at 298.15 K under 0.1MPa. w_1 and w_2 are the mass fractions of the MIL and salt, respectively.

Table 3 Binodal curve data as the mass fraction (w) for the $[\text{C}_4\text{TMG}][\text{TEMPO-OSO}_3]$ MILATPs with different salts at 298.15 K under 0.1MPa. w_1 and w_2 are the mass fractions of the MIL and salt, respectively.

Table 4 Values of the parameters of equation 7 for the MILs + Salt + H_2O MILATPs at 298.15K under 0.1MPa.

Table 5 Values of the parameters of equation 8 for the MILs + Salt + H_2O MILATPs at 298.15K under 0.1MPa.

Table 6 Values of the parameters of equation 9 for the MILs +Salt + H_2O MILATPs at 298.15K under 0.1MPa.

Table 7 Experimental tie line data as mass fraction for the MILs + Salt + H_2O ATPs at 298.15K under 0.1MPa.

Table 8 Adjusted parameters of equations 10-12 for the MIL + Salt + H_2O MILATPs at 298.15K under 0.1MPa.

Figure captions

Figure 1. The chemical structures-of the MILs

Figure 2. Binodal curves of $[C_2TMG][TEMPO-OSO_3]$ with different inorganic salts at temperature of 298.15K at 0.1MPa. w_1 , w_2 are the mass fraction of MIL and inorganic salt, respectively.

Figure 3. Binodal curves of $[C_3TMG][TEMPO-OSO_3]$ with different inorganic salts at temperature of 298.15K at 0.1MPa. w_1 , w_2 are the mass fraction of MIL and inorganic salt, respectively.

Figure 4. Binodal curves of $[C_4TMG][TEMPO-OSO_3]$ with different inorganic salts at temperature of 298.15K at 0.1MPa. w_1 , w_2 are the mass fraction of MIL and inorganic salt, respectively.

Figure 5. Tie lines of the $[C_nTMG][TEMPO-OSO_3]$ ($n= 2, 3, 4$) + K_2HPO_4 (or K_2CO_3) + H_2O MILATPs at 298.15K. The curve is the fitted binodal curve and the straight line is tie-lines.

Table 1 Binodal curve data as the mass fraction (w) for the $[\text{C}_2\text{TMG}][\text{TEMPO-OSO}_3]$ MILATPs with different salts at 298.15 K under 0.1MPa. w_1 and w_2 are the mass fractions of the MIL and salt, respectively.

K_2HPO_4		K_2CO_3		Na_2CO_3	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
1.813	69.43	2.391	76.01	2.416	47.12
2.954	58.51	5.172	54.06	3.673	40.37
3.713	52.74	7.753	42.13	4.174	38.11
5.319	44.00	10.10	33.69	4.610	36.75
7.242	35.49	12.29	26.73	5.724	32.91
8.309	31.89	13.57	23.36	6.753	29.36
9.527	27.33	14.74	20.66	7.413	27.28
10.90	24.14	15.72	18.80	7.952	25.71
11.81	22.20	17.01	16.10	9.547	21.72
13.14	19.57	17.92	14.18	10.29	19.92
14.21	17.83	18.29	13.67	10.71	18.92
15.36	16.09	19.01	12.32	11.06	18.01
15.90	14.89	19.23	12.28	11.60	16.47
16.85	13.56	19.53	11.62	12.05	15.90
17.34	12.66	19.66	11.27	12.57	14.75
18.23	11.61	20.28	10.37	12.97	13.93
18.93	10.75	20.58	9.815	13.00	13.93
19.02	10.31	20.58	9.685	13.04	13.87
19.66	9.616	20.90	9.271	13.13	13.68
19.87	9.169	21.18	8.875	13.37	13.22
20.32	8.569	22.05	7.781	13.53	12.85
20.81	8.031	22.19	7.540	13.99	11.93
21.08	7.626	22.63	7.095	14.42	11.23
21.38	7.265	22.99	6.544	14.98	10.22
21.72	6.833	23.42	6.142	15.72	9.007
22.17	6.417	23.72	5.713	16.17	8.294
22.52	5.921	23.87	5.513	16.64	7.581
22.73	5.687	24.26	5.201	16.91	7.151
23.03	5.438	24.56	4.871	17.40	6.467
23.34	5.106	24.97	4.496	17.77	6.048
23.61	4.823	25.97	3.813	18.11	5.572
23.86	4.693	26.51	3.337	18.37	5.135
24.00	4.569	27.09	2.984	18.93	4.738
24.15	4.446	27.36	2.687		
24.31	4.341	28.71	2.071		
24.53	4.172	30.10	1.365		
24.70	4.020	32.12	0.8413		
24.85	3.905	34.12	0.4374		
25.08	3.797	36.55	0.2147		
26.01	3.347	38.41	0.1047		

27.12	2.682
28.51	2.001
30.41	1.331

Table 2 Binodal curve data as the mass fraction (w) for the $[\text{C}_3\text{TMG}][\text{TEMPO-OSO}_3]$ MILATPs with different salts at 298.15 K under 0.1MPa. w_1 and w_2 are the mass fractions of the MIL and salt, respectively.

K_2HPO_4		K_2CO_3		Na_2CO_3	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
0.9365	53.99	1.550	67.24	2.913	80.94
4.988	36.78	3.842	52.76	3.613	67.81
6.348	33.34	5.304	48.66	4.372	57.51
8.883	27.93	7.472	40.23	5.017	50.49
9.894	25.66	9.055	35.85	5.913	42.64
10.56	24.04	10.69	30.27	6.429	39.13
11.13	22.75	11.65	27.64	7.457	31.97
12.68	20.64	12.89	25.38	8.537	26.09
12.81	19.69	13.34	22.94	9.455	23.09
13.90	18.18	13.79	21.77	9.732	21.93
14.33	17.21	14.41	20.95	9.825	21.59
14.62	16.44	14.99	19.30	11.01	17.84
15.41	15.36	15.51	18.22	11.13	17.30
15.74	14.63	16.28	16.97	11.26	16.80
15.93	14.03	16.06	16.00	11.39	16.51
16.70	13.23	16.34	15.42	11.47	16.28
16.86	12.74	16.73	14.83	11.63	16.09
17.08	12.24	17.15	14.24	11.91	15.04
17.52	11.61	17.25	13.54	12.52	13.69
17.61	11.23	17.93	12.64	12.74	12.90
17.98	10.72	18.41	11.46	13.01	12.31
18.06	10.44	18.62	10.58	13.42	11.64
18.45	10.00	18.98	9.857	13.81	10.96
18.59	9.731	19.44	9.058	13.86	10.74
18.91	9.321	19.69	8.452	14.29	9.999
19.00	9.084	20.29	7.813	14.74	9.284
19.82	8.543	20.60	7.329	15.19	8.454
20.93	7.262	21.17	6.828	15.40	7.857
21.56	6.055	21.55	6.230	15.81	7.239
22.59	5.041	22.09	5.393	15.74	7.224
22.88	4.515	22.69	4.662	16.09	6.722
23.88	3.709	23.26	3.765	16.41	6.219
24.60	3.219	24.18	2.982	16.87	5.800
26.71	1.884	25.19	2.712	17.21	5.326
29.71	0.7804	26.12	2.305	17.65	4.781
31.76	0.3850	26.64	1.987		
34.84	0.1207	27.24	1.666		
36.71	0.04718	27.81	1.439		
		27.98	1.236		
		28.59	0.9599		

30.13	0.4381
31.85	0.2102
33.41	0.1030
35.61	0.03215

Table 3 Binodal curve data as the mass fraction (w) for the $[\text{C}_4\text{TMG}][\text{TEMPO-OSO}_3]$ MILATPs with different salts at 298.15 K under 0.1MPa. w_1 and w_2 are the mass fractions of the MIL and salt, respectively.

K_2HPO_4		K_2CO_3		Na_2CO_3	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
0.5132	71.37	2.424	78.39	3.171	43.54
1.732	57.71	3.147	70.15	3.964	39.40
2.923	50.35	5.123	53.27	4.581	35.90
4.148	44.63	6.813	42.94	4.971	34.27
5.636	38.66	8.796	34.81	5.454	31.79
6.534	35.58	9.911	29.12	5.791	30.54
7.479	32.60	11.25	25.37	5.912	29.81
8.851	28.83	11.99	22.25	6.133	29.27
10.05	25.93	12.35	21.78	6.512	27.31
10.17	25.21	12.96	20.50	6.959	25.97
10.88	23.56	13.52	18.51	7.413	24.07
11.66	21.96	13.81	18.04	7.898	22.13
12.14	20.76	14.32	16.71	8.739	19.93
12.42	19.94	14.81	15.30	9.236	17.99
12.80	18.90	15.16	14.61	9.803	16.12
13.18	18.02	15.52	13.82	10.18	14.61
13.39	17.43	16.01	12.92	10.70	13.13
13.68	16.86	16.43	11.84	10.98	12.21
14.07	16.04	16.85	10.98	11.47	11.35
14.28	15.52	17.27	10.18	11.52	10.86
14.49	15.15	17.68	9.423	11.85	9.973
14.64	14.74	18.01	8.781	12.26	8.877
14.94	14.28	18.33	8.309	13.17	7.334
15.20	13.80	18.74	7.642	13.55	6.625
15.64	13.19	18.91	7.394	14.34	5.022
15.74	12.89	19.30	6.785	14.62	4.420
15.83	12.55	19.74	6.163	15.13	3.638
16.29	12.11	19.97	5.864	15.95	2.827
16.47	11.59	20.12	5.764	16.40	2.392
16.52	11.31	20.28	5.449	16.94	1.881
16.85	10.72	20.68	4.756	17.25	1.650
17.08	10.19	21.03	4.763	17.51	1.468
17.35	9.724	22.75	2.912		
17.48	9.220	23.58	2.563		
17.69	8.820	25.78	1.402		
17.90	8.464	26.94	0.7617		
18.18	7.993	27.96	0.6932		
18.64	7.376	28.68	0.3869		
19.40	6.248	29.72	0.2375		
19.90	5.799	31.85	0.09300		

20.79	4.712	34.46	0.03371
21.96	3.542		
23.01	2.595		
24.23	1.847		
25.75	1.126		
27.28	0.5938		
30.41	0.1941		
33.07	0.05831		
35.13	0.01413		

Table 4 Values of the parameters of equation 7 for the MILs + Salt + H₂O MILATPs at 298.15K under 0.1MPa.

Salt	a	b	c	R ²
[C ₂ TMG][TEMPO-OSO ₃] +Salt + H ₂ O				
K ₂ HPO ₄	1.3611	-4.2801	30.374	0.9996
K ₂ CO ₃	1.5309	-4.5209	80.2122	0.9999
Na ₂ CO ₃	0.89951	-4.1129	173.38	0.9998
[C ₃ TMG][TEMPO-OSO ₃] +Salt + H ₂ O				
K ₂ HPO ₄	0.71657	-2.9242	111.32	0.9996
K ₂ CO ₃	0.97981	-3.0353	136.69	0.9994
Na ₂ CO ₃	3.3420	-8.3492	130.45	0.9997
[C ₄ TMG][TEMPO-OSO ₃] +Salt + H ₂ O				
K ₂ HPO ₄	0.92312	-3.54729	149.42	0.9996
K ₂ CO ₃	1.7832	-5.2650	131.80	0.9996
Na ₂ CO ₃	0.99472	-4.5594	429.21	0.9997

Table 5 Values of the parameters of equation 8 for the MILs + Salt + H₂O MILATPs at 298.15K under 0.1MPa.

Salt	a ₁	b ₁	a ₂	b ₂	c	R ²
[C ₂ TMG][TEMPO-OSO ₃] +Salt + H ₂ O						
K ₂ HPO ₄	0.70377	0.13316	0.32878	0.022631	-0.067496	0.9995
K ₂ CO ₃	1.5308 × 10 ⁵	1.5722 × 10 ³	0.95474	0.10797	-0.043040	0.9986
Na ₂ CO ₃	0.69248	0.13548	2.2857	4.9985 × 10 ³	-0.12641	0.9998
[C ₃ TMG][TEMPO-OSO ₃] +Salt + H ₂ O						
K ₂ HPO ₄	2.9030 × 10 ⁻⁴	-0.067704	0.71072	0.17247	-0.14606	0.9974
K ₂ CO ₃	2.8093	-1.0064	3.4628	0.44213	-5.5411	0.9978
Na ₂ CO ₃	1.0986	0.017363	0.95246	0.073536	-0.038348	0.9998
[C ₄ TMG][TEMPO-OSO ₃] +Salt + H ₂ O						
K ₂ HPO ₄	0.35368	0.0030851	0.73998	0.11488	-0.060962	0.9965
K ₂ CO ₃	3.1610 × 10 ⁻⁵	-0.050309	1.0786	0.086840	-0.047300	0.9989
Na ₂ CO ₃	0.85624	0.12157	8.8125	-0.028706	-0.22636	0.9996

Table 6 Values of the parameters of equation 9 for the MILs +Salt + H₂O MILATPs at 298.15K under 0.1MPa.

Salt	a	b	c	d	R ²
[C ₂ TMG][TEMPO-OSO ₃] +Salt + H ₂ O					
K ₂ HPO ₄	0.45467	-7.0519	8.1990	-34.566	0.9993
K ₂ CO ₃	0.74357	-8.4120	12.971	-45.596	0.9998
Na ₂ CO ₃	0.15388	-7.7761	14.248	-69.865	0.9998
[C ₃ TMG][TEMPO-OSO ₃] +Salt + H ₂ O					
K ₂ HPO ₄	-0.13809	-6.0860	12.438	-54.066	0.9995
K ₂ CO ₃	0.27527	-7.2083	15.627	-66.311	0.9994
Na ₂ CO ₃	1.6875	-13.788	17.432	-63.199	0.9998
[C ₄ TMG][TEMPO-OSO ₃] +Salt + H ₂ O					
K ₂ HPO ₄	0.015129	-5.4986	9.4393	-56.550	0.9994
K ₂ CO ₃	0.95770	-9.9691	16.257	-64.360	0.9997
Na ₂ CO ₃	0.92956	-16.084	40.624	-178.25	0.9997

Table 7 Experimental tie line data as mass fraction for the MILs + Salt + H₂O ATPs at 298.15K under 0.1MPa.

		Overall			Top phase			Bottom phase			
	TLL	STL	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
[C ₂ TMG][TEMPO-OSO ₃] + K ₂ HPO ₄ + H ₂ O											
1	81.99	-1.984	11.37	32.74	55.89	73.34	1.492	25.16	0.1364	38.40	61.46
2	56.64	-2.024	9.737	24.72	65.54	52.81	3.447	43.74	2.033	28.53	69.44
3	45.51	-2.026	10.76	21.79	67.45	44.73	5.019	50.25	3.922	25.17	70.91
4	30.10	-2.030	19.75	14.96	65.29	34.87	7.513	57.62	7.863	20.81	71.32
[C ₂ TMG][TEMPO-OSO ₃] + K ₂ CO ₃ + H ₂ O											
1	87.24	-1.981	11.55	35.79	52.66	77.90	2.290	19.81	0.02451	41.61	58.36
2	62.80	-2.008	12.92	26.50	60.59	56.94	4.576	38.48	0.7262	32.57	66.71
3	39.55	-1.998	15.77	20.05	64.19	39.00	8.422	52.58	3.636	26.12	70.24
4	61.94	-2.001	40.33	12.72	46.95	56.13	4.821	39.05	0.7264	32.51	66.76
[C ₃ TMG][TEMPO-OSO ₃] + K ₂ HPO ₄ + H ₂ O											
1	77.24	-1.719	11.41	32.41	56.18	66.80	0.142	33.06	0.01601	38.96	61.03
2	53.14	-1.687	32.50	10.46	57.05	46.64	2.072	51.29	0.9316	29.17	69.90
3	43.67	-1.683	21.47	14.86	63.68	39.61	4.072	56.31	2.070	26.38	71.55
4	33.33	-1.700	11.37	19.32	69.30	32.64	6.817	60.55	3.907	23.72	72.38
[C ₃ TMG][TEMPO-OSO ₃] + K ₂ CO ₃ + H ₂ O											
1	91.89	-2.175	13.56	32.38	54.07	83.50	0.2251	16.27	5.705 ×10 ⁻⁵	38.61	61.39
2	64.58	-2.189	10.98	24.42	64.59	59.38	2.315	38.30	0.6451	29.15	70.21
3	45.69	-2.205	18.54	17.92	63.54	43.96	6.397	49.64	2.350	25.27	72.38
4	59.99	-2.205	37.72	11.37	50.91	55.60	3.262	41.14	0.9643	28.04	70.99
[C ₄ TMG][TEMPO-OSO ₃] + K ₂ HPO ₄ + H ₂ O											
1	86.96	-2.312	9.276	30.60	60.13	79.84	0.08535	20.07	0.02204	34.61	65.37
2	70.72	-2.322	10.93	24.18	64.89	65.35	0.7417	33.91	0.4009	28.72	70.88
3	63.95	-2.287	12.72	21.79	65.49	59.36	1.397	39.24	0.7681	27.01	72.22
4	38.80	-2.334	20.17	13.90	65.94	41.14	4.914	53.95	5.475	20.20	74.33
[C ₄ TMG][TEMPO-OSO ₃] + K ₂ CO ₃ + H ₂ O											
1	83.73	-2.283	12.02	30.91	57.07	76.71	2.574	20.718	0.01471	36.17	63.82
2	68.38	-2.282	12.81	25.82	61.37	62.79	3.917	33.29	0.1601	31.36	68.47
3	56.97	-2.313	14.76	21.72	63.52	52.94	5.213	41.85	0.6505	27.82	71.53
4	38.52	-2.314	20.72	15.42	63.85	38.08	7.924	53.99	2.720	23.20	74.08

Table 8 Adjusted parameters of equations 10-12 for the MIL + Salt + H₂O MILATPs at 298.15K under 0.1MPa.

MIL	Eq. 10			Eq. 11			Eq. 12		
	k ₁	n	R ²	k ₂	r	R ²	k	β	R ²
MIL + K ₂ HPO ₄ + H ₂ O									
C ₂	0.02793	2.799	0.9955	5.382	-0.2435	0.9777	4.857	0.3305	0.9985
C ₃	0.02257	3.222	0.9988	4.313	-0.1368	0.9834	11.77	2.414	0.9796
C ₄	0.008727	3.308	0.9961	5.150	-0.1572	0.9751	10.08	2.517	0.9396
MIL + K ₂ CO ₃ + H ₂ O									
C ₂	0.01070	3.821	0.9990	4.097	-0.1668	0.9819	4.163	0.3645	0.9985
C ₃	0.001710	4.887	0.9990	4.010	-0.1186	0.9872	9.253	2.716	0.9819
C ₄	0.006896	3.813	0.9986	4.813	-0.1438	0.9855	3.796	0.2862	0.9990

Note: C₂ represents MIL [C₂TMG][TEMPO-OSO₃], C₃ represents MIL [C₃TMG][TEMPO-OSO₃], C₄ represents MIL [C₄TMG][TEMPO-OSO₃], respectively.