



REVIEW

Vapour-Liquid Equilibrium for Systems Containing Ionic Liquids

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Ionic liquids are a class of liquid state chemicals at room temperature, which have been proven to be promising solvent or entrainer in separation processes like extraction and extractive distillation, *etc.* Recent measurements reported on vapour-liquid equilibrium data are reviewed in this work. A brief summary about the screening is also displayed. Comparing the existing vapour-liquid equilibrium data and results, some suggestions are put forward to offer a reference for further development of ionic liquids.

Key Words: Ionic liquid, Vapour-liquid equilibrium, Azeotrope, Extractive distillation.

INTRODUCTION

The first low melting salt, ethylammonium nitrate (melting point 385.15 K), was synthesized by Walden¹ in 1914. However, the unique characteristics and potential use of this substance didn't receive the desired notice. Afterwards, in 1951, Hurley and Wier² developed the low melting salts with chloroaluminate ions for low-temperature electroplating of aluminum. Then, these liquids were researched mainly for electrochemical applications during the 1970s and 1980s. In the mid 1980s, Fry and Pienta³ and Boon *et al.*⁴ proposed that, the low melting point ionic liquids could be used as solvents in organic synthesis. In 1992, Wilkes and Zaworotko⁵ synthesized the air- and moisture-stable tetrafluoroborate ([BF₄]). And the understanding that the salts with melting point below 373.15 K created a new media for chemical reactions became widespread and the term "room temperature ionic liquids" (RTILs or ILs) was eventually assigned to them. In 1999, the commercial ionic liquids became available⁶ and the research activities on this topic have been increasing dramatically ever since.

Room-temperature ionic liquids, sometimes referred to as molten salts or ionic liquids, are a class of chemicals consisting primarily of relatively large organic cations and inorganic or organic anions with very low melting points (mainly below 373.15 K).

Typically, the organic asymmetric substituted cations of the ionic liquids are imidazolium, pyridinium, pyrrolidinium, quaternary ammonium and tetraalkylphosphonium, *etc.* And

the anions are halide (X), metallic halide complex ([M_mX_n]), nitrate ([NO₃]), acetate ([OAc]), trifluoromethanesulfonate ([CF₃SO₃]), tetrafluoroborate ([BF₄]), hexafluorophosphate ([PF₆]), alkylsulfate ([RSO₄]) and dialkylphosphate ([R₂PO₄]), *etc.* Among these anions, the halides are highly corrosive to steel^{7,8}, [M_mX_n] is sensitive to moisture⁹ and [PF₆] as well as [BF₄] are subject to hydrolysis or decompose¹⁰. In contrast, ionic liquids with [RSO₄] and [R₂PO₄] anions are probable for practical applications. These cations and anions can be virtually varied at will to change their chemical and physical properties, such as modifying the length of the alkyl groups or the substitutes of the organic cations¹¹. Theoretically 10¹⁸ combinations are possible in total, so ionic liquids are regarded as designable^{12,13}.

Comparing with the conventional salts and organic solvents, ionic liquids have some special properties. Firstly, their melting points are lower than 373 K, which makes them in liquid state at room temperature; besides, they are thermally stable up to 473 K and have a liquid range of about 300 K. Secondly, they exhibit a negligible vapour pressure, which means that their emission in technical applications will be considerably lower than volatile organic solvents. Therefore, they're labeled "green". Thirdly, they have shown excellent solubility for a wide range of organic, inorganic and polymeric materials⁹, though it may be influenced by the structure and conformation of the groups¹⁴. The typical ionic liquids are less corrosive and have relatively low viscosity in contrast to high melting salts¹⁵.

Because of their traits, ionic liquids have already shown potentials for solvents and catalysts in chemical synthesis. And their use as solvents or entrainers in separation technology, such as extraction and distillation, is also promising.

The most significant advantages of ionic liquids using in extractive distillation are displayed in three aspects. Firstly, when an ionic liquid is used as an entrainer, it is withdrawn as the column bottom's effluent with the heavier components, which prevents its presence in distillate. Secondly, a higher concentration of electrolyte could exist along the column because of its greater solubility. Finally, the ionic liquid can be completely separated by flash distillation owing to its negligibly low vapour pressure. And a pure ionic liquid stream can be easily added to the reflux stream avoiding the problems associated with the handling of fused or solid salts¹⁶.

Arlt and co-workers¹⁷ suggested using ionic liquids for extractive distillation of azeotropes and they reported the effect of various ionic liquids on several azeotropic binary systems¹⁸⁻²³. Moreover, the researches on ionic liquids using in extractive distillation are emphasized and expanding in the recent decade and they are mainly focusing on the fundamental data of the various ionic liquids and the interrelations among the ionic liquid-containing systems, including the excess Gibbs free energy, infinite dilution activity coefficient, vapour-liquid and liquid-liquid equilibrium data and so on. However, the progress hasn't been concluded yet. So the main purpose of this article is to present a rough review about the work having accomplished on ionic liquids in recent years, on which basis some comparisons and conclusions are displayed to offer a general reference for further development.

All the cations and anions of ionic liquids mentioned in the article are displayed, including the name, acronym and structure (Table-1).

EXPERIMENTAL

Vapour-liquid equilibrium

Ethanol-water: As the most widely-used solvent, ethanol is miscible with water at any ratio and forms an azeotrope in which ethanol is about 95 % (mass fraction). There have been numerous experimental studies carried out on this system using ionic liquids.

Jork *et al.*²⁰ measured the isothermal vapour-liquid equilibrium for four ternary ethanol-water-ionic liquid systems. The ionic liquids were [EMIM][BF₄], [BMIM][BF₄], [OMIM][BF₄] and [BMIM][Cl], which were derived from [BMIM][BF₄] by systematic variation of the cation or the anion. And the binary vapour-liquid equilibrium for water-[EMIM][BF₄] was also obtained at 373.15 and 403.15 K, respectively. It was concluded that the ionic liquids investigated could increase the relative volatility of ethanol remarkably and eliminate the azeotropic system behaviour. Ionic liquid composing of small anions and cations exhibited the best entrainer properties and replacing the [BF₄] with [Cl] increased the capability of the ionic liquid dramatically.

Calvar *et al.*²⁴⁻²⁸ also investigated the impact of a series of ionic liquids, namely: [BMIM][Cl], [HMIM][Cl], [EMIM][C₂H₅SO₄], [BMIM][CH₃SO₄] and [EMPY][C₂H₅SO₄]. During these researches, isobaric vapour-liquid equilibrium data of

binary ethanol-ionic liquid and water-ionic liquid systems as well as ternary ethanol-water-ionic liquid system were acquired at atmospheric pressure (101.3 kPa) using a circulation still. It was observed that all the ionic liquids investigated, except [HMIM][Cl], could break this azeotrope and show the possibility as entrainers of the ethanol-water mixture. Furthermore, comparison between [EMIM][C₂H₅SO₄] and [EMPY][C₂H₅SO₄] indicated that the pyridinium-based ionic liquid had more influence than the imidazolium-based ionic liquid. Nevertheless, there were no more comparisons among other ionic liquids and the minimum amount of ionic liquids needed to break the azeotrope was not clarified, either.

Isobaric vapour-liquid equilibrium for this system containing ionic liquids at atmospheric pressure was also examined by Zhao *et al.*²⁹. The ionic liquids utilized were [MMIM][DMP], [EMIM][DEP], [BMIM][Br], [BMIM][Cl] and [BMIM][PF₆]. All of them showed a salting-out effect, which led to an enhancement of relative volatility even to an elimination of the azeotropic point. And the salting-out effect turned out to follow the order of [BMIM][Cl] > [BMIM][Br] > [BMIM][PF₆], which could be seen as the influences of different anions. While for the phosphate-type ionic liquids [MMIM][DMP] and [EMIM][DEP], neither anion nor cation was the same, which could have different impacts on the system, although the salting-out effect of [MMIM][DMP] was observed to be higher than [EMIM][DEP].

Relatively comprehensive and detailed research and comparison were conducted by Ge *et al.*³⁰. The experiments for obtaining the isobaric vapour-liquid equilibrium data were carried out in the way of continuous synthesis, in which analysis of liquid phase composition was avoided, considering the deficiency of ionic liquids' basic parameters. Eight ionic liquids were investigated in total: [BMIM][BF₄], [EMIM][BF₄], [BMIM][N(CN)₂], [EMIM][N(CN)₂], [BMIM][Cl], [EMIM][Cl], [BMIM][OAc] and [EMIM][OAc]. The concentration of ionic liquid was varied from a low level (0.1, mass fraction) to up to 0.8 and even 0.9, while the mole fraction of ethanol was kept almost stable at 0.95 (on ionic liquid-free basis). The effects of ionic liquids on the relative volatility of ethanol were depicted separately by their effect on the activity coefficients. Among the eight ionic liquids, [EMIM][Cl] had the largest effect, while [EMIM][OAc] also showed significant influence, with a minimum mass fraction of 0.048 to break the azeotrope.

The isobaric vapour-liquid equilibrium of ternary ethanol-water-ionic liquid ([HMIM][Cl] and [BMIM][Cl]) systems were measured by Zhang *et al.*^{31,32}, including boiling temperatures of water-[HMIM][Cl] with different ionic liquid mass fractions. The NRTL equation was used for correlation, in which parameters from several sources were tested. And the quality of correlation appeared to be sensitive to the parameters utilized for this binary system.

[EMIM][triflate] was also suggested by Orchilles *et al.*³³ using as the entrainer in the extractive distillation of ethanol-water azeotrope. The isobaric vapour-liquid equilibrium data indicated a minimum mole fraction of 0.054 was required for [EMIM][triflate] to eliminate the azeotrope.

Methanol, ethanol, water-ionic liquid: Separation of water and methanol from ethanol is of vital importance in food

TABLE-1
 LIST OF CATIONS AND ANIONS

No.	Name	Acronym	Structure	No.	Name	Acronym	Structure
Cations							
1	1-Methyl-3-methylimidazolium	[MMIM]		5	1-Octyl-3-methylimidazolium	[OMIM]	
2	1-Ethyl-3-methylimidazolium	[EMIM]		6	1-Ethyl-3-ethylimidazolium	[EEIM]	
3	1-Butyl-3-methylimidazolium	[BMIM]		7	1-Ethyl-3-methylpyridinium	[EMPY]	
4	1-Hexyl-3-methylimidazolium	[HMIM]		8	1-Butyl-1-methylpyrrolidinium	[BMPYR]	
Anions							
1	Nitrate	[NO ₃]		8	Diethyl phosphate	[C ₄ H ₁₀ O ₄ P], [DEP]	
2	Acetate	[OAc]		9	Dibutyl phosphate	[C ₈ H ₁₈ O ₄ P], [DBP]	
3	Tetrafluoroborate	[BF ₄]		10	Bromine	[Br]	Br ⁻
4	Methylsulphate	[CH ₃ SO ₄]		11	Chlorine	[Cl]	Cl ⁻
5	Hexafluorophosphate	[PF ₆]		12	Bis(trifluoromethylsulfonyl)imide	[BTI], [(CF ₃ SO ₂) ₂ N]	
6	Ethyl sulphate	[C ₂ H ₅ SO ₄]		13	Dicyanamide	[N(CN) ₂]	N≡C—N ⁻ —C≡N
7	Dimethylphosphate	[(CH ₃) ₂ PO ₄], [DMP]		14	Trifluoromethanesulfonate	[CF ₃ SO ₃], [triflate]	

industry, as methanol is an inevitable companion of ethanol produced *via* fermentation processes. Also for the edible ethanol used in the alcoholic beverage sector, the methanol residue is restricted to an increasingly low limit of 2-150 mg/L (GB 10343-2002). Though researches on the ionic liquid-containing ethanol-water system have been developed rapidly, attentions on the methanol-ethanol-water mixture is quite scarce.

Zhao *et al.*³⁴ measured the vapour pressure data for ternary systems: ethanol-methanol-ionic liquid ([MMIM][DMP],

[EMIM][DEP], [BMIM][DBP]) and ethanol-water-[MMIM][DMP] at ionic liquid mass fraction of 0.5. The data were correlated to predict the isothermal vapour-liquid equilibrium of corresponding systems. All ionic liquids were found to have salting-out effect for ethanol and follow the order of [EMIM][DEP] > [MMIM][DMP] > [BMIM][DBP] for the ethanol-methanol system. Moreover, the azeotropic phenomenon in ethanol-water could be completely removed.

Jiang *et al.*³⁵ examined the influence of [EEIM][DEP] on ethanol-methanol, ethanol-water and methanol-water. The

corresponding vapour pressures were predicted using the binary NRTL parameters. Wang *et al.*^{36,37} obtained the vapour pressure data for water, methanol and ethanol as well as their mixtures with ionic liquid ([EMIM][DMP] and [EMIM][C₂H₅SO₄]) at different temperatures and ionic liquid concentrations. And the isobaric vapour-liquid equilibrium were predicted with the binary NRTL parameters.

All the ionic liquids mentioned above ([MMIM][DMP], [EMIM][DEP], [BMIM][DBP], [EEIM][DEP], [EMIM][DMP] and [EMIM][C₂H₅SO₄]) could enhance the relative volatility of ethanol in both methanol-ethanol and ethanol-water systems, showing the interaction energy between different solvents and ionic liquids follows the order of water > methanol >> ethanol. Considering the effect of ionic liquids on the three binary systems in detail, the azeotropic phenomenon in the ethanol-water system could be completely removed. The ethanol component in the ethanol-methanol system was converted from a heavy component to a light one. And a complex salt effect was observed for the methanol-water system, which displayed a salting-out effect in the methanol-rich region and a salting-in effect in the water-rich region.

As a result of these effects, the separation of methanol and water from ethanol within only one step is facilitated by the addition of a proper ionic liquid.

Esters-alcohols: The binary ester-alcohol systems, such as ethyl acetate-ethanol and methyl acetate-methanol, are significant mixtures and materials in industry. At atmospheric pressure, the ethyl acetate-ethanol system shows a minimum boiling point azeotrope at 0.553 (mole fraction of ethyl acetate), while methyl acetate and methanol also forms an azeotrope with the minimum boiling point, in which methyl acetate is 66.8 % (mole fraction). In order to break it, various entrainers and salts have been estimated. As a promising green solvent, ionic liquid was also examined and proposed as an entrainer in extractive distillation for the ester-alcohol systems.

Orchilles *et al.*^{38,39} measured the isobaric ternary vapour-liquid equilibrium for the ethyl acetate-ethanol and methyl acetate-methanol systems containing ionic liquid [EMIM][triflate], as well as the corresponding binary mixtures at 100 kPa. The electrolyte NRTL model was used to correlate the binary experimental data and predict the ternary vapour-liquid equilibrium, which agreed well with the experimental values. [EMIM][triflate] was indicated to produce a significant salting-out effect and break the azeotropes when its mole fraction is greater than 0.20 and 0.129 for ethyl acetate-ethanol and methyl acetate-methanol systems, respectively.

Another ionic liquid, [EMIM][OAc], was considered to have better effect than [EMIM][triflate]³⁹. Cai *et al.*⁴⁰ measured both vapour-liquid equilibrium and liquid-liquid equilibrium for the ternary system containing [EMIM][OAc], which also showed a notable salting-out effect. Moreover, the minimum quantity required to break the azeotrope was 0.087 in mole fraction. Unlike [EMIM][triflate], there is an immiscible zone for this ternary system, because [EMIM][OAc] is partially miscible in methyl acetate. This indicates that the interaction between [EMIM][OAc] and methyl acetate is weaker than that between [EMIM][triflate] and methyl acetate, while their interactions between methanol are strong. It may be one reason for the higher selectivity of [EMIM][OAc] on this system.

For the ethyl acetate-ethanol system, Li *et al.*^{41,42} did a series of researches as well. The isobaric vapour-liquid equilibrium data was firstly obtained for ethyl acetate-ethanol-[EMIM][BF₄] at 101.3 kPa. And ionic liquid [EMIM][BF₄] was found to perform better than [EMIM][triflate]³⁸. Besides, the salting-out effect became more and more obvious with the increase of ionic liquid's concentration. During the further research, the impacts of [BMIM][BF₄] and [OMIM][BF₄] were evaluated and compared with the former work. A complicated result was concluded: the separation ability of ionic liquids followed the order of [EMIM][BF₄] > [BMIM][BF₄] > [OMIM][BF₄] at low ionic liquid concentration (below 0.1); while at higher ionic liquid concentration (0.1-0.3), their abilities were in the order of [OMIM][BF₄] > [EMIM][BF₄] > [BMIM][BF₄]. Furthermore, the selectivity of [EMIM][triflate] was proved to be higher than [BMIM][BF₄] but lower than [EMIM][BF₄].

Zhang *et al.*⁴³ measured the isobaric T-x-y data for the quaternary system water-ethanol-ethyl acetate-[BMIM][OAc] at low water mole fractions. [BMIM][OAc] was found to be able to decrease the activity coefficients of water and ethanol, while increase that of ethyl acetate. Hence, the relative volatility was elevated significantly.

Another binary ester-alcohol system, dimethyl carbonate (DMC)-methanol, was investigated by Kim *et al.*⁴⁴. dimethyl carbonate, used as a benign solvent, is prepared from the catalytic oxidative carbonylation of methanol and forms an azeotrope with it. Two ionic liquids, [EMIM][C₂H₅SO₄] and [BMIM][BF₄], were adopted to change the vapour-liquid equilibrium of dimethyl carbonate-methanol. And both of them were proved to have similar effects and could eliminate the azeotropic phenomenon when the concentrations of ionic liquids were higher than 0.1.

2-Propanol-water: Doker *et al.*⁴⁵ measured the isothermal vapour-liquid equilibrium for 2-propanol-water containing ionic liquid for the first time. The ionic liquids used were [EMIM][(CF₃SO₂)₂N] and [BMIM][(CF₃SO₂)₂N]. Additionally, the vapour-liquid equilibrium for the corresponding binary systems were also obtained at the same temperature (353.15 K). In the work, the Wilson, NRTL and UNIQUAC models were utilized to correlate the binary data and exhibited a satisfactory precision.

The group of Zhang⁴⁶⁻⁴⁸ did a series of researches on 2-propanol-water. They investigated several ionic liquids including [BMIM][BF₄], [EMIM][BF₄], [BMIM][N(CN)₂], [EMIM][N(CN)₂], [BMIM][OAc], [EMIM][OAc] and [BMIM][Cl]. The isobaric T-x-y data were measured at different ionic liquid mass fractions, while the mole fraction of 2-propanol calculated on ionic liquid-free basis was kept almost unchanged at 0.95. They got the conclusion that, the activity coefficients were mainly decided by the anions, with their interactions with water and 2-propanol in the same order, namely [Cl] ≈ [OAc] > [N(CN)₂] > [BF₄]. And the cation had relatively small effect on the activity coefficients. Among the ionic liquids studied, those with [OAc] or [Cl] as the anion and [EMIM] as the cation, had the most significant ability to enhance the relative volatility. Another binary system 1-propanol-water was also examined and obtained the similar results as 2-propanol-water.

Li *et al.*^{49,50} also measured the isobaric vapour-liquid equilibrium for 2-propanol-water-ionic liquid ([BMIM][BF₄] and [EMIM][BF₄]) using methods different from Zhang⁴⁸. The data they obtained provide reasonable complementarities. And [EMIM][BF₄] was proved to have higher selectivity than [EMIM][triflate].

Westerholt *et al.*⁵¹ examined the impacts of [HMIM][BTI] and [BMPYR][BTI] on three standard systems including 2-propanol-water. Nevertheless, the selected ionic liquids didn't show effective separation capacities for this azeotrope. The ionic liquids [EMIM][C₂H₅SO₄] and [BMIM][BF₄] used for dimethyl carbonate-methanol were also adopted for the 2-propanol-water system⁴⁴. However, the azeotrope did not disappear within the given concentrations of ionic liquid, but shifted significantly from the original azeotropic concentration on ionic liquid-free basis.

Others: Except the widely-researched azeotropes mentioned above, there are still some systems studied by the researchers. The 1-hexene-*n*-hexane systems including 39 ionic liquids were investigated by Lei *et al.*^{22,23}. They found that the suitable ionic liquids were of small molecular volume, unbranched group and sterical shielding effect around anion charge center. The best ionic liquid was [C₈Chin][BTA] among all the ionic liquids investigated. Nevertheless, ionic liquids [HMIM][BTI] and [BMPYR][BTI] were shown to have no obvious effect on 1-hexene-*n*-hexane⁵¹. Additionally, the vapour-liquid equilibrium for THF-water²⁰, acetone-2-propanol⁴⁵, acetone-methanol⁵², chloroform-methanol⁵³ and water-TBA⁵⁴ were also measured and various ionic liquids' impacts were discussed.

Screening and simulation: As a promising design solvent, the ionic liquid may have 10¹⁸ combinations in total theoretically. Therefore, it is not realistic to obtain all the parameters and vapour-liquid equilibrium data for ionic liquids and hence the screening methods should be paid more attention.

Lei *et al.*²² examined 39 ionic liquids for the 1-hexene-*n*-hexane system by computer-aided molecular design (CAMD). On the basis of conformation analysis, the conductor-like screening model for real solvents (COSMO-RS) was utilized to make a priori prediction for suitable ionic liquids. Verma *et al.*⁵⁵ also used this method to predict the ternary vapour-liquid equilibrium for ethanol-water, 2-propanol-water and THF-water including ionic liquids with combinations of 10 cations and 24 anions.

The COSMO-RS model is a novel and efficient method for the priori prediction of thermo-physical data. It is based on quantum chemistry and uses only atom-specific parameters, which can be used to predict the thermodynamic properties of solvent-ionic liquid systems. Nevertheless, the COSMO-RS model cannot be incorporated into some famous simulation programs such as ASPEN PLUS and PRO/II.

The original and modified UNIFAC models are widely used as predictive thermodynamic models and have been applied to predict the phase equilibrium of systems with ionic liquids^{56,57}. Lei *et al.*⁵⁸ obtained the UNIFAC group parameters for 12 main groups and 24 subgroups, which could be used not only for predicting the vapour-liquid equilibrium of the systems with ionic liquids, but also for screening the suitable ionic liquids in separation processes.

Conclusion

Ionic liquid has been widely investigated in recent years and proven to be a promising green solvent or entrainer in the extractive distillation process. To facilitate the future use of ionic liquids, lots of elementary work has been accomplished, including the vapour-liquid equilibrium data for binary and ternary systems. And various kinds of ionic liquids were shown to have satisfactory effects and selectivity for different azeotropes.

Besides high selectivity, in practice, an entrainer should have a low viscosity, a high flash point and a boiling point at least 40 K higher than the boiling points of the components to be separated. And they should be stable, nonflammable and non-corrosive as well. Therefore, for example, the ionic liquids with [PF₆] and [BF₄] anions are not suitable as entrainers, because of their tendency to decompose. In these cases, the availability and price should also be taken into consideration.

Among the recent researches, simulation of the separation process about the ionic liquid-containing systems using commercial software is quite scarce, not to mention the practical progress. And that will be one significant task in the future.

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