Aqueous Solution of [EMIM][OAc]: Property formulations for use in air conditioning equipment design

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Abstract

Liquid desiccant air conditioning (LDAC) is a promising alternative to vapor compression refrigeration based space cooling and dehumidification for the reduction of energy consumption and the improvement of indoor air quality. However, its use in the air conditioning market is still very limited due to its high installation cost, intensive carryover, and high cost of operation and maintenance associated to the corrosion of the current desiccant liquids. Substitutes for the traditional desiccant liquids with better properties and no corrosion are highly needed. Ionic liquids, which are salts comprised of organic cations and inorganic anions or organic anions, have high thermal stability, negligible or no vapor pressure, varied solubility in water, low or no corrosion to metals, and low driving temperatures to achieve dew point temperatures. All of those characteristics make them as perfect substitutes for traditional desiccant liquids. Up to date, a very few research groups investigated ILs as potential alternatives to traditional desiccant liquids for LDAC. The study in the paper aimed to identify the ionic liquids as ideal desiccant liquids to achieve better cost-effectiveness and higher system performance of LDAC. There were 13 different ionic liquids (IL) identified and screened for the most promising candidate. 1-Ethyl-3-methylimidazolium acetate, [EMIM][OAc], was selected as an ideal candidate for the capable of the most adsorption and desorption. The paper was mainly focused on the development of calculation models for the thermo-physical properties of the aqueous solution of [EMIM][OAc] to represent the property data needed for use as the desiccant liquid in sorption-based air conditioning equipment. It aims to provide convenient methods for use in the design and model of the sorption-based air conditioning. The calculation models for the following thermo-physical properties of the aqueous solution of [EMIM][OAc] were proposed and presented in the paper: the vapor pressures, specific heat capacity, density, and dynamic viscosity at various temperatures and concentrations.

Keywords

Liquid desiccant, Sorption, Thermo-physical properties, Ionic liquid, 1-Ethyl-3-methylimidazolium acetate, [EMIM][OAc]

1 Introduction

Air conditioning is a process of controlling both air temperature and humidity for indoor thermal comfort, preventing mold growth, and enhancing building durability. Currently, more than 90% of air conditioning systems use a vapor compression refrigeration (VCR) cycle to remove the moisture in the humid air by use of the condensation. Such air conditioning system requires inefficient overcooling and reheating, which in turn significantly reduces the system efficiency and increases energy consumption and associated cost.

Liquid desiccant air conditioning has been investigated as a promising alternative to VCR-based space cooling and dehumidification for the reduction of energy consumption and the improvement of indoor air quality [1-6]. LDAC separates the sensible cooling and latent cooling to meet the indoor thermal comfort requirements independently. Compared to conventional VCR-based air conditioning, LDAC has a lower electricity consumption, a higher system coefficient of performance (COP), as well as reduced air flow rate and VCR size for sensible cooling only [5][7]. LDAC uses the liquid desiccant, which have a high affinity for water, in contact with the humid air absorbing the moisture. Since the absorption gives off heat to air, a cooling process, which is provided by either a vapor compression cooling or a sensible energy wheel, is necessary to achieving the desired temperature of supply air. In order to reuse the desiccant, a thermal driven regeneration process is needed to remove the moisture absorbed in the desiccant.

The selection of desiccants plays a profound role in the design and system performance of LDAC. The liquid desiccants commonly used in LDAC are glycols and solution of halide salts including propylene glycol, triethylene glycol, and solutions of lithium chloride (LiCl), lithium bromide (LiBr), calcium chloride ($CaCl_2$), and mixture of salts. Triethylene glycol with low toxicity and compatibility with most of metals was commonly used in LDAC at the earliest time, but the high viscosity and volatility made it unacceptable in air conditioning application [30]. Late, halide salts are mostly used in LDAC to dry air to 15% and 6% relative humidity because of their low viscosities and high absorption capabilities, however they are expensive and strongly corrosive to most ferrous / nonferrous metals resulting in a high initial cost and an operational & maintenance cost. Other alternatives of desiccants are salts of weak organic acids such as potassium and sodium format and acetate. They are less corrosive and less volatile compared to halide salts, but their capabilities of dehumidification are limited, which can only dry air up to 25-30% relative humidity. LDAC has been available since 1930, but its use in the air conditioning market is still very limited due to its high installation cost, intensive carryover, and the high cost of maintenance associated to the corrosion of liquid desiccants [7,8]. With the increase of building demands for ventilation and better humidity control, researchers are continuously seek the promising desiccant liquids, to reduce the cost, carryover, and corrosion, while improving the overall system performance [9-15].

The ionic liquids are salts comprised of organic cations with either inorganic anions or organic anions and they are in the liquid phase when exposed to room temperature and atmospheric pressure. The ionic liquids have high thermal stability, negligible or no vapor pressure, high solubility in water, low or no corrosion to metals, and low driving temperatures to achieve dew point temperatures, all of which make them as potential substitutes for traditional desiccant liquids for the reduction of the cost and improvement of system performance. Up to date, a very few research groups investigated ILs as potential alternatives to traditional desiccant liquids for LDAC [16-18]. Luo, et al. (2012) investigated ILs with non-halide anions and halide anions and compared the thermal stability, surface vapor pressure, and dehumidification capability of the two candidates of [Dmim][OAc] and [Emim][BF4] with LiCl and LiBr [16]. The other research groups did not provide the information of the particular ionic liquids they used.

The objective of the research in the paper was to identify the ionic liquids as ideal substitutes for traditional desiccant liquids to achieve better cost-effectiveness and higher system performance of LDAC. There were 13 ionic liquids identified for the screen tests in the research. 1-Ethyl-3-methylimidazolium

acetate, [EMIM][OAc], was selected as the best option from the screened IL candidates as capable of providing the most adsorption and desorption in the research. The work presented in the paper focuses on summarizing the thermos-physical properties of the aqueous solution of [EMIM][OAc] and proposing calculation formulations for use in the field of the sorption-based air conditioning.

2 Ionic Liquids Studied

In the study of the paper, the screening tests were conducted across the 13 candidates for identifying the most promising candidate(s) that can provide the highest vapor adsorption and desorption. As shown in Fig. 1, the 13 kinds of ILs are based on imidazolium and pyrrolidinium cations and different anions. They were dried on a freeze drier for three days and the final moisture contents were recorded. The water adsorption screening tests were carried out inside a humidity chamber, Humilab, in which the temperature and humidity are able to be controlled as desired. The screen tests consisted of four consequent groups. At first, the temperature was set at 25°C and the humidity was maintained at 30%, 50%, and 80%, respectively. Secondly, the humidity was set at 80% and the temperature was increased from 25 to 50 and 70 °C, respectively. Thirdly, the temperature was maintained at 70 °C and the humidity was decreased from 80% to 50% and 30 %, respectively. Finally, the humidity was maintained at 30% and the temperature was decreased from 70 to 50 and 25 °C, respectively. To allow enough time for reaching equilibrium, each step was maintained for 24 hours before the measurement. All the tests were repeated for three times. The average maximum adsorption and minimum adsorption were calculated by using the weight percentage of pure ionic liquid in the aqueous solution and summarized in Table 1. As shown, among the 13 screened ILs, 1-Ethyl-3-methylimidazolium acetate exhibited the highest capability of absorbing vapor and desorbing water and was identified as the most promising candidate. Its molecular formula is $C_8H_{14}N_2O_2$ and its molar-mass is 170.21 g/mol. It can be abbreviated as [EMIM][OAc] / [emim][OAc] or [C_2MIm][OAc][19].

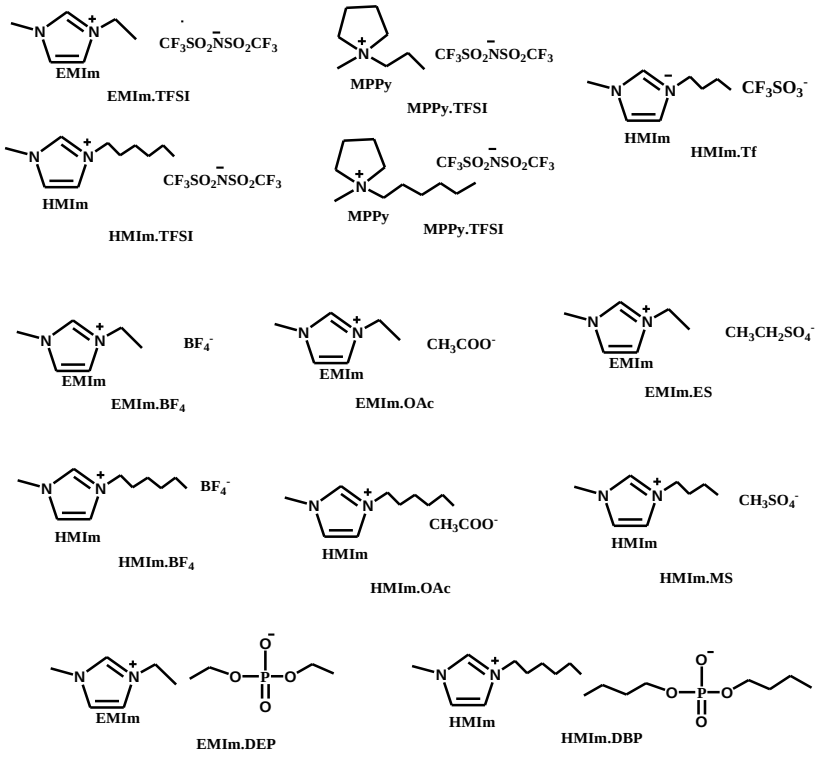

Fig. 1 Structures of the 13 ionic liquids tested

Table1. Summary of moisture adsorption of ionic liquids

Ionic Liquids	EMIm TFSI	HMIm TFSI	MPPy TFSI	HMpy TFSI	BMIm Tf	EMIm BF4	HMIm BF4	EMIm OAc	HMIm OAc	EMIm ES	BMIm Ms	EMIm DEP	BMIm DBP
Initial water content (ppm)	43	46	54	46	116	318	252	1265	249	266	435	515	443
Maximum Adsorption (wt.%)	99.24	99.48	99.52	99.77	94.89	91.15	93.69	67.66	84.86	78.64	76.21	75.28	86.25
Minimum adsorption (wt.%)	99.92	99.91	99.97	99.98	99.94	98.78	99.20	91.09	96.67	95.53	93.93	92.32	97.35
Working Range (wt.%)	0.68	0.43	0.45	0.21	5.05	7.63	5.51	23.43	11.81	16.89	17.72	17.04	11.1

Moisture adsorption = IL/(IL + H_2O)*100

Although a large number of studies were found in the literature on the properties of pure [EMIM][OAc] or the solution with little water [20-26], only a very few reported the properties for the aqueous solution of 1-Ethyl-3-methylimidazolium acetate [26]. Based on the literatures, we summarized the data of the thermos-physical properties for the aqueous solution of [EMIM][OAc] and generated the calculation formulations for predicting the thermos-physical properties of the aqueous solution of [EMIM][OAc] by using both thermodynamic principles and statistical methods. The calculation formulations of the following thermos-physical properties of the aqueous solution of [EMIM][OAc] are described:

- vapor pressures
- specific heat capacity
- density
- dynamic viscosity

The results of this study will contribute to the development of liquid desiccant air conditioning and other sorption-based air conditioning technologies for industrial and research applications.

3 Vapor pressure of the aqueous solution of [EMIM][OAc]

The dehumidification capability of the liquid desiccant can be indicated by its equilibrium vapor pressure, The equilibrium vapor pressure of the liquid desiccant equals thermodynamically the partial vapor pressure of air above the desiccant surface, which is the production of the relative humidity of air and the saturated vapor pressure of water at the temperature of air. The equilibrium vapor pressure of the liquid desiccant increases roughly exponentially with the temperature of the desiccant. Moreover, it reduces as the concentration of the liquid desiccant increases. By using the equilibrium vapor pressure as the partial vapor pressure of the air, the lowest relative humidity, to which of air the liquid desiccant can dehumidify, can be found; thus, the dehumidification capacity of the liquid desiccant at a given concentration and temperature can be indicated in a typical psychrometric chart. For instance, Fig. 2 shows the dehumidification capacity of LiCl solution at different concentrations and temperatures on a psychrometric chart. As shown, the LiCl solution at a concentration of 45% has an equilibrium vapor pressure same as the partial vapor pressure of air with 11.6% of relative humidity at the same temperature. For instance, the equilibrium vapor pressure of the 45% concentrated LiCl solution at 20 ^oC is 0.2718 kPa and it is same as the partial vapor pressure of the humid air at 20 ^oC and 11.6% of relative humidity. This indicates that the LiCl solution at 45% is able to dehumidify air to 11.6% of the relative humidity.

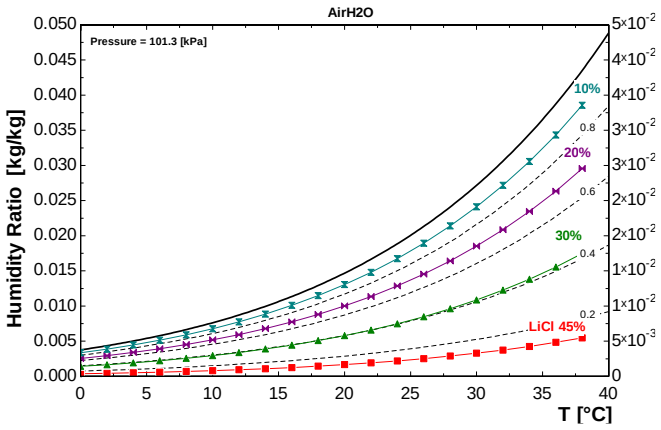

Fig. 2 Dehumidification capability of LiCl solution at different concentrations

In order to identify the dehumidification capacity, the equilibrium vapor pressure must be known. According to **Raoult's Law** [27]**,** the partial pressure of water vapor, P_1 , of the aqueous solution of [EMIM][OAc] can be determined by using the activity coefficient of water vapor in a binary mixture of water and [EMIM][OAc], as shown in Eq. 1.

$$\boldsymbol{P_1 = y_1 P = P'_1 * x_1 * \gamma_1} \qquad \textit{Eq. 1}$$

P is the sum of the partial pressure of the binary mixture/ the aqueous solution; P'_1 is the saturated vapor pressure at the same temperature as the aqueous solution; x_1 is the mole fraction of water; and γ_1 is the activity coefficient of water vapor for the departure of the liquid phase from the ideal solution behavior. The activity coefficient of water vapor in a binary system was given by the NonRandom, Two-Liquid (NRTL) equation as shown in Eq. 2 [28].

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad \textit{Eq. 2}$$

x_2 is the mole fraction of [EMIM][OAc] in the aqueous solution. Parameter G and τ can be obtained using Eq. 3-6.

$$G_{12} = e^{(-\alpha_{12}\tau_{12})} \qquad \textit{Eq. 3}$$

$$G_{21} = e^{(-\alpha_{12}\tau_{21})} \qquad \textit{Eq. 4}$$

$$\tau_{12} = \frac{\Delta g_{12}}{RT} \qquad \textit{Eq. 5}$$

$$\tau_{21} = \frac{\Delta g_{21}}{RT} \qquad \textit{Eq. 6}$$

Where, α and $\Delta g$are the parameters specific to the aqueous solution, independent of composition and temperature. According to Römich, et al. (2012), the values of parameters Δg_{12}, Δg_{21}, and α_{12} that are used to determine γ1 are shown in Eqs. 7-9 [25].

$$\Delta g_{12} = 28938\, J/mol\,; \qquad \textit{Eq. 7}$$

$$\Delta g_{21} = -25691 \frac{J}{mol}; \qquad \textit{Eq. 8}$$

$$\alpha_{12} = 0.10243 \qquad \textit{Eq. 9}$$

Based on the equations of NRTL and Raoult's Law, a model was developed to estimate the equilibrium vapor pressure of the aqueous solution of [EMIM][OAc] at various concentrations and temperatures. To validate the model, the equilibrium vapor pressure predicted by the model was compared with the data

published by Römich, et al. (2012) [25]. Römich's data, indicated in the points on the curves in Fig.3, were obtained through the graph digitization of the published paper by using Engauge Digitizer [29].

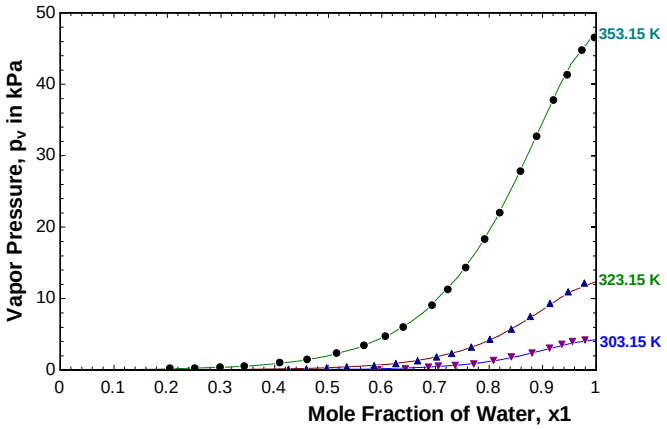

Fig. 3 Validation of the model developed- vapor pressure vs. mole fraction of water of aqueous solution of [Emim].[OAc] (Curves: the calculation results; Points: the data from Römich, et al[25])

Fig.3 shows the relation between the equilibrium vapor pressure and the mole fraction of the water in the aqueous solution of [EMIM][OAc], and it can be seen that the results from the developed model matched well to the curves in Römich, et al. (2012). Sorption industrial engineers and researchers commonly use the mass fraction of the liquid desiccant. Therefore, Fig. 4 was produced to show the vapor pressure with the mass fraction/concentration of [EMIM][OAc] in the aqueous solution for use in both industry and research. It shows that for a given concentration of [EMIM][OAc] in the aqueous solution, the higher the temperature was, the higher the equilibrium vapor pressure was; and for a given temperature, the higher the concentration was, the lower equilibrium vapor pressure was. In this paper, the concentration of [EMIM][OAc] in the aqueous solution stands for the mass fraction of [EMIM][OAc] in the aqueous solution.

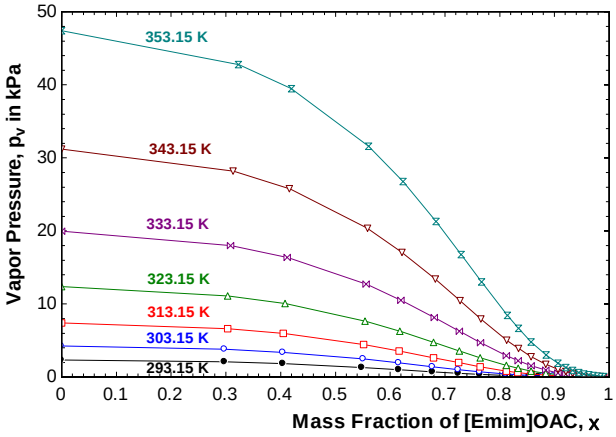

Fig. 4 Vapor pressure vs. mass fraction of [Emim].OAc in the aqueous solution

To present the dehumidification capacity of the aqueous solution of [EMIM][OAc], the equilibrium vapor pressures of the aqueous solution of [EMIM][OAc] at various temperatures are indicated on the psychrometric chart in Fig. 5. It shows the dehumidification capabilities of the aqueous [EMIM][OAc] solution at the concentrations of 30%, 55%, 65%, and 75%. Overall, it was determined that as the concentration was increased, the equilibrium vapor pressure became smaller resulting in the increased dehumidification capability. For example, a 75% aqueous solution of [EMIM][OAc] was able to dehumidify the air to 20% or higher relative humidity, while a 55% solution could only dehumidify the air to 60% or higher relative humidity.

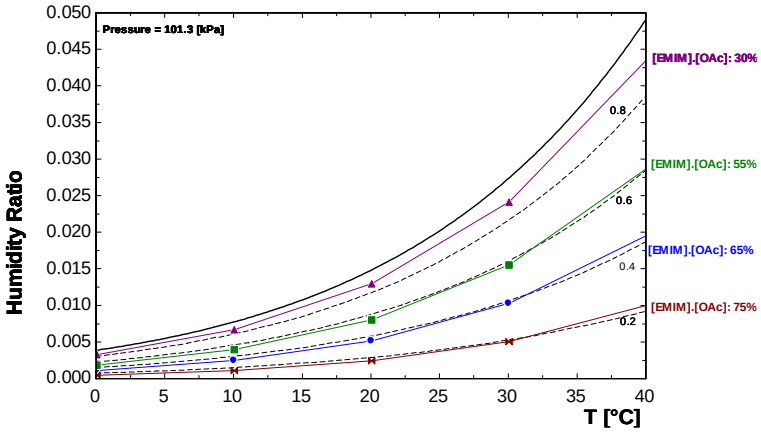

Fig. 5 Dehumidification capability of the aqueous solution of [EMIM].[OAc] at different concentrations

The dehumidification capacity of a desiccant liquid is the most crucial thermos-physical property for determining the candidates for LDAC application. Therefore, Fig. 6 shows our comparison between [EMIM][OAc], the most commonly used liquid desiccants like the solutions of LiCl, LiBr, and [Dmim][OAc] and [Bmim][OAc], which are the ILs recently reported [16]. It can be seen that the aqueous solution of [EMIM][OAc] is able to provide dehumidification results similar to the solutions of LiCl or LiBr. [Dmim][OAc] and [Bmim][OAc] did not demonstrate such capacity according to the data provided by Luo et al. 2012 [16].

Based on the review conducted by Sanjeev Jain et. al (2007) on the current experimental performance of liquid desiccant dehumidifiers in labs and in practices, the typical concentrations for LiCl and LiBr solution for LDAC were at the range of 37%- 41%, and 50-54%, respectively as shown in Table 2 [10].

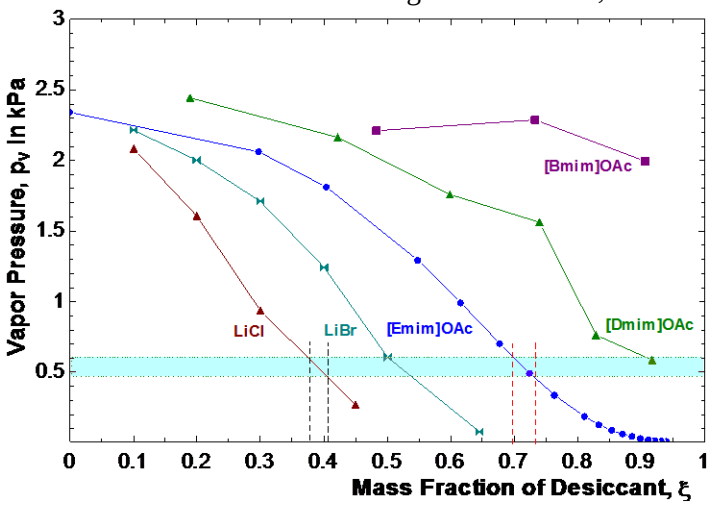

Figure 6 Comparison of equilibrium vapor pressure vs. concentration of various liquid desiccants at 20°C

This result indicates that the common target of the partial vapor pressure of humid air for typical LDAC systems was 0.35-0.46 kPa, as the blue band indicated in Fig.5, which is the partial vapor pressure range of humid air at 20 °C with 15-20% relative humid. By using the same target, 68-75% of the mass fraction of [Emin][OAc] in its aqueous solution at 20°C is recommended for LDAC systems to have same equilibrium vapor pressure to the partial vapor pressure of the air at 20 °C with 15-20% relative humidity. More experiments are needed to substantiate recommending its application to actual LDAC equipment.

Table 2 Experimental performance data of liquid desiccant dehumidifiers [10]

Source of data	Desiccant				Air					*L/G*	ε_y	Remarks
	Type	Temp. (°C)	Conc. (%)	Flow rate/flux (l/min)	Flow rate/flux (m^3/min)	Temp. (°C)	Humidity (g/kg)	ΔT (°C)	ΔW (g/kg)			
Ani et al. [44]	LiCl	25–27	35–40	3.76–5.01	4.9–6.4							SP, CF, COP_{hyb}: 2.6–4.9
Ducool [16]	LiCl		40		40–96	30	18.9	−4.0	−7.2			SP, CF, COP_{hyb}: 2.7–3.0
Elsarrag et al. [20]	TEG	29–35	92	1.7–2.2[a]	0.94–2[a]		17–26		−5.5 to −11	1.9–2.3	0.45–0.85	SP, CF, ΔP: 35–140 Pa/m
Fumo and	LiCl	30.1	34.6	6.124[a]	0.89[a]	30.1	18	1.2	−7.6	6.88	0.75–0.84	RP, CF, 210 m^2/m^3,
Goswami [31]		30	34.3	6.113[a]	1.513[a]	30.2	18.1	2	−7.3	4.04		Des. Δconc = 0.1%,
		30.5	34.4	6.287[a]	1.183[a]	40.1	18	−7	−6.5	5.31		Des. ΔT = 1.4–2.7
		30.1	33.9	6.273[a]	1.214[a]	30.3	14.2	0.8	−3.9	5.17		
Jilier/Genius [19,40]	Mixture				77.9–113.3	35	22.3	−18.3	−13.7			Hybrid COP: 2.4,
					77.9–113.3	35	14.1	−17.2	−7.2			ΔP: 100Pa
Jain et al. [37]	LiBr							−2 to −11	−2 to −8			Cooled FF, ST, PF
Jain et al. [42]	TEG	22.9	96.8	0.057[b]	0.07[b]	20.6	12.48	2.5	−8.1	0.81	0.96	Cooled FF, ST, CF,
		23	92.4	0.063[b]	0.07[b]	31	16.88	−8.3	−11.23	0.90	1.06	ΔP: 1736 Pa, drift:
		20.5	95.2	0.058[b]	0.07[b]	19.4	8.71	2.1	−4.54	0.83	1.01	5.6–9 g/min
		20.2	95.5	0.057[b]	0.07[b]	28.6	16.93	−4	−12.46	0.81	0.94	
		21.8	92.2	0.052[b]	0.051[b]	21	8.95	1.2	−4.21	1.02	0.88	
Kathabar [17]	LiCl								Up to −20			
Lazzarin et al. [46]	LiBr	16.1–34.1	53–57	0.018–0.13[b]	3.67	23.6–35.4	1.4–18.7		−3 to −11	0.35–1.9	0.25–0.85	RP, CF
Liu et al. [64,65]	LiBr	20.1–29.5	42.6–54.8	0.3–0.64[b]	0.31–0.47[b]	24.7–33.9	10–21				0.4–0.7	SP, cross flow
Longo and	LiCl	23.4–24	39.2–40.6	0.10–1.17[a]	0.43–0.47[a]	24.3–37.6	7.3–23.3		−2 to −17	0.23–2.6	0.3–0.9	RP, CF,
Gasparella [2]	LiBr	23.7	51.9–53.9	0.16–1.39[a]	0.44–0.47[a]	23.6–36.7	8.2–22.8		−3 to −18	0.35–3.0	0.3–0.9	ΔP = 25–45 Pa/m,
	KCOOH	21.9–24.8	72.8–74.0	0.09–1.23[a]	0.48–0.52[a]	22.6–35.8	8.8–20.7		−2 to −13.5	0.2–2.5	0.3–0.9	Negligible sensitivity of ε_y and ΔP to desiccant
Mago-Goswani [47]	LiCl	27–30	35	0.35–0.51[b]	0.6–0.7[b]	26–29	11.6–13.9		−2 to −4			RP, CF
Oberg and	TEG	24–36	94–96	4.5–6.5[a]	0.5–15[a]	24–36	11–23		−8.5 to −10	4.5–11	0.8–0.9	RP, CF, ΔP: 30–210 Pa/m
Goswami [29]												
Niagara Blower [3]	PG					4.4	3.12	−2.77	−1.4			Cooled spray type
Pietruschka et al. [34]	LiCl and	27	43	1.67	3.3	26	11.6	5	−4.2			SP, cross flow
	$CaCl_2$	27	43	1.67	3.3	26	11.6	−1	−5.7			Cross flow PHE, cooled
Saman and	$CaCl_2$		40	0.06[b]	0.16–0.47[b]	23	7.4			0.13–0.38	0.2–0.9	PHE, cross flow, cooled
Alizadeh [48]						33	17		−3		0.3–0.9	m_w: 0.08 kg/s
Abdul-Wahab	TEG	28–45	93–98	0.13–10[a]	1.5–2.613[a]	25.4–44			−0.1 to 0.24[c]	0.06–2.07	0.1–0.7	SP of wood, CF
et al. [43]		31	95.6	0.23	2.07	31			−0.15 to 0.2[c]	0.11	0.16–0.4	77–200 m^2/m^3
Zurigat et al. [49]	TEG	28.2–45.5	93–98	0.13–0.82[a]	1.5–2.07[a]	25.4–44	16.2–20.7			0.1–0.4	0.19–0.45	SP of wood/Al, CF
		31.5	95.6	0.13[a]	2.07[a]	29.9	20.6		−4.6	0.06	0.31	Wood SP
		31.4	95.6	0.82[a]	2.07[a]	29.9	16.9		−4.8	0.40	0.43	Wood SP
		31	95.6	0.23[a]	1.73[a]	30.6	21.8		−3	0.13	0.19	Al SP

Al, Aluminium; RP, random packings; SP, structured packing; COP_{hyb}, hybrid COP; PHE, plate heat exchanger; CF, counter flow; FF, falling film/wetted wall; ST, shell and tube; PF, parallel flow; PG, propylene glycol; m_w, water flow rate.

[a] Measured in kg/m^2 s.
[b] Measured in kg/s.
[c] Measured in g/s.

4 Specific heat capacity of the aqueous solution of [EMIM][OAc]

The specific heat capacity of the pure [EMIM][OAc] or the aqueous solution with little water were studied and reported by a few researchers [20,21,22]. Ma et. al reported that the specific heat capacity of the pure [EMIM][OAc] solution was 2.4 kJ/kg.K from 15 to 35°C according to their experimental results[20]. Ahmadi validated the data from Freire et al. (2011) and concluded that the molar heat capacity of the solution of [EMIM][OAc] was 314.4 J/mol K, which is 1.84 kJ/kg. K. at 25 °C, less than the value reported by Ma et al. The specific heat capacity of water is 4.814 kJ/kg.K at 25 °C [21,22]. Therefore, the specific heat capacity of the aqueous solution of [EMIM][OAc] should be between the specific heat capacities of water and [EMIM][OAc] depending upon the concentration, which was proven by Römich, et al. 2012 [25]. The measured data of the specific heat capacity of the aqueous solution of [EMIM][OAc] at different temperatures and concentrations were determined and reported by Römich, et al. (2012). We used that data to correlate the specific heat capacity of the aqueous solution of [EMIM][OAc] at the temperature and the concentration. The measured data were 96 data points. The root mean square (RMS) of our regression was 2.3428E-02 and R^2 was 99.89%. Eq.10 is the formulation we obtained for calculating the specific heat capacity of the aqueous solution of [EMIM][OAc].

$$C_{p\_[EMIM][OAc]_{H2O}} = 2.761077 + 0.008120T - 1.106151 * 10^{-5}T^2 - 2.649514\xi - 0.918307\xi^2 + 0.003580T\xi \qquad Eq.\ 10$$

Where, T is the temperature of the aqueous solution of [EMIM][OAc] in K, and ξ is the mass fraction of [EMIM][OAc] in the aqueous solution. Fig. 7 shows the comparison between the calculation results predicted by the formulation and the experimental data from Römich, et al. (2012), from which great

agreement with each other is apparent. By using the proposed formulation, more specific heat capacities of the aqueous solution of [EMIM][OAc] at various temperatures and concentrations, ξ_{il}, were calculated and presented in Fig. 8. The higher the concentration of [EMIM][OAc] was, the lower the specific heat capacity was, since water has a higher specific heat capacity than [EMIM][OAc]. For the aqueous solution of [Emin][OAc] at 68-75% concentration, the specific heat capacity was in the range of 2.5 – 3 kJ/kg K.

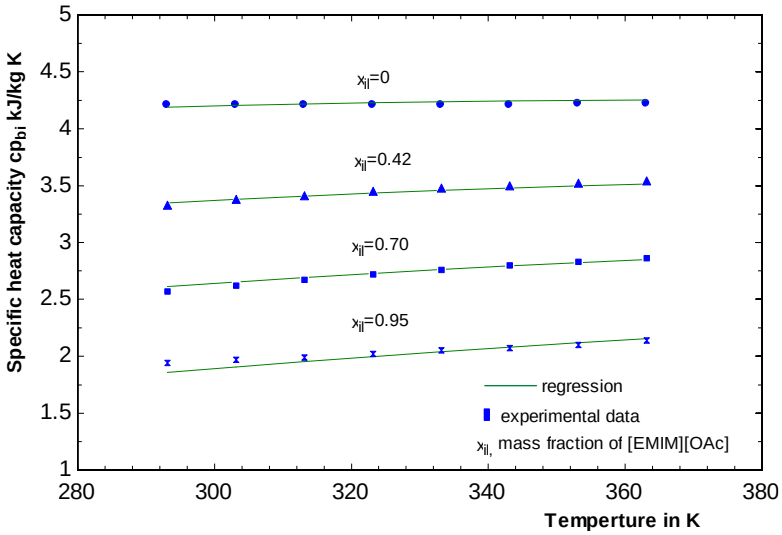

Fig.7 Comparison of the calculated specific heat capacity from the regression model and the experimental data from Römich, et al

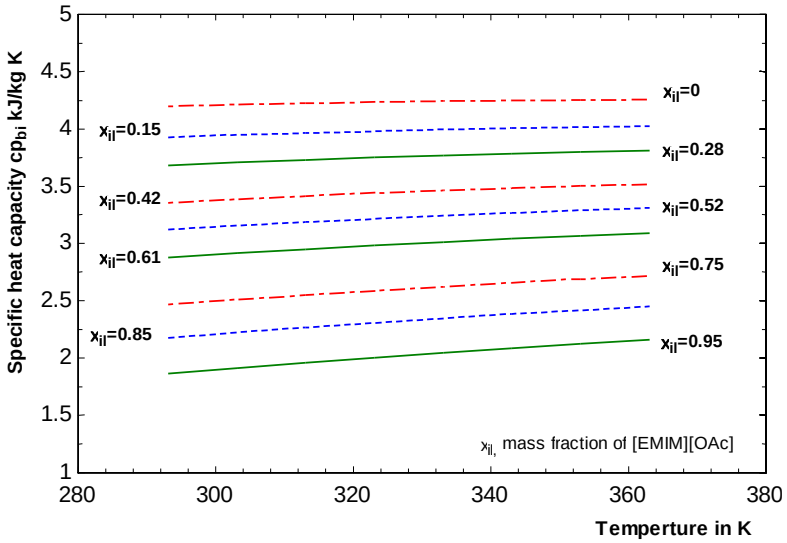

Fig. 8 Specific heat capacity of aqueous solution of [EMIM][OAc] vs. various temperatures and mass fractions of [EMIM][OAc]

5 Density of the aqueous solution of [EMIM][OAc]

The densities of the pure [EMIM][OAc] or the aqueous solution with little water also were studied by many researchers [20,22,26]. Ma et al. (2012) reported that the densities of the tested [EMIM][OAc] from 298.15 to 338.15°K were from 1,101.9 kg/m^3 to 1,075 kg/m^3, respectively [20]. Freire et al. (2012) found that the densities of the [EMIM][OAc] tested at 0.1 Mpa from 278.15 to 363.15°K were from 1,112.4kg/m^3 to 1,060.6 kg/m^3 [22]. The data from both research groups agreed well with each other. The data from Almeida et al. (2012), however, were lower than the data from the two research groups

mentioned earlier[26]. The densities of the pure [EMIM][OAc] tested were in the range of 1,047.2 kg/m^3 to 978.5 kg/m^3 for temperatures of 283.15 to 363.15 °K, respectively.

The pure [EMIM][OAc] is generally heavier than water at the same volume. Therefore, the higher the concentration of the aqueous solution of [EMIM][OAc] was, the higher the density of the aqueous solution was. This conclusion was proven by the data of Römich, et al. (2012) using various densities of the aqueous solution of [EMIM][OAc] at different temperatures and concentrations [25]. We used the experimental data provided by Römich, et al. (2012) to correlate the densities of an aqueous solution of [EMIM][OAc] to various temperatures and concentrations by means of regression. There were 20 data points and the RMS of the regression was 0.6129 and R^2 was 99.8%. The formulation for calculating the densities of the aqueous solution of [EMIM][OAc] are presented in Eq.11.

$$\rho_{[EMIM].[OAc]_{H_2O}} = 1.012482 * 10^3 - 0.918103T + 6.25 * 10^{-5}T^2 + 758.0905\xi - 497.846\xi^2 + 0.302582T\xi \qquad Eq.\ 11$$

Where, T is the temperature of the aqueous solution of [EMIM][OAc] in K and ξ is the mass fraction of [EMIM][OAc] in the aqueous solution. Fig. 9 shows the comparison between the calculation results predicted by the proposed formulation and the experimental data from Römich, et al. (2012). They matched very well [25]. Using the proposed formulation, more densities of the aqueous solution of [EMIM][OAc] at various temperatures and concentrations were calculated and shown in Fig. 10. As predicted, the higher concentration of [EMIM][OAc] was, the higher the density of the aqueous solution of [EMIM][OAc] was. Compared to LiCl and $CaCl_2$ solution with similar equilibrium vapor pressure at 20°C with a concentration of 40%, the density of the aqueous solution of [EMIM][OAc] is 10% less than the densities of the solutions of LiCl and $CaCl_2$.

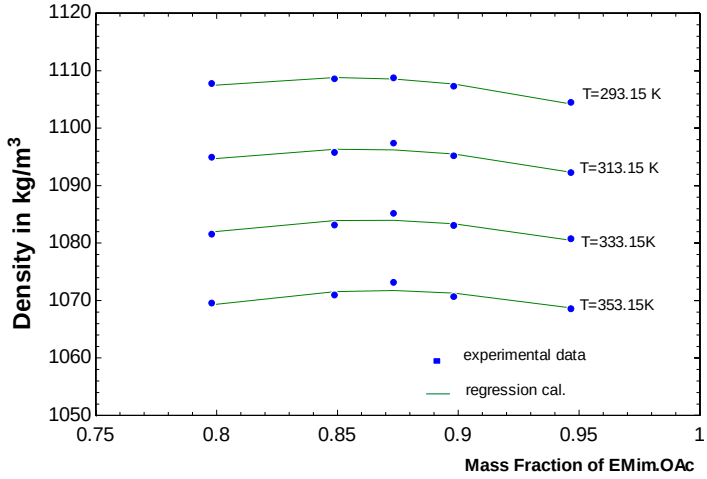

Fig.9 Comparison of the calculated densities from the regression model and the experimental data from Römich, et al

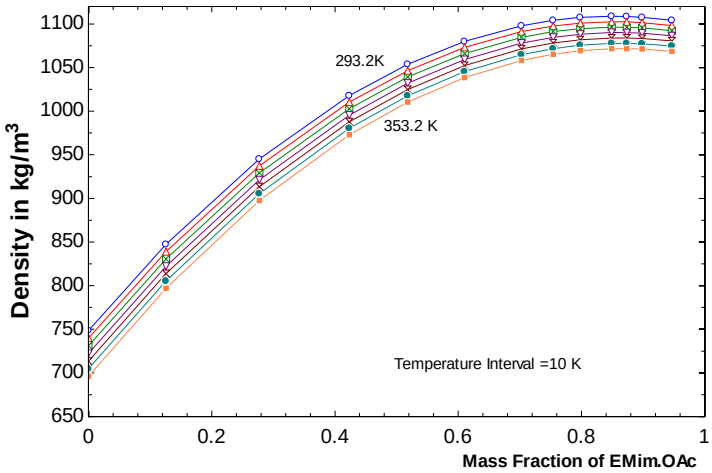

Fig. 10 Densities of aqueous solution of [EMIM][OAc] vs. various temperatures and mass fractions of [EMIM][OAc]

6 Dynamic Viscosity of the aqueous solution of [EMIM][OAc]

The dynamic viscosities of the pure [EMIM][OAc] or the aqueous solution with little water were studied by two research groups [22,26]. Freire et al. (2011) reported that the dynamic viscosities of the pure [EMIM][OAc] were from 723.62 mPa·s to 10.95 mPa·s at 278.15 to 363.15°K, respectively [21]. The data of the dynamic viscosities from Almeida et al. (2012) were higher than the comparable data from Freire et al. (2012) [26]. They reported that the dynamic viscosities of the solution of [EMIM][OAc] at 283.15 to 363.15 °K were 1,037 mPa·s, which reduced to 15.1 mPa·s at 0.1 MPa.

The dynamic viscosities of water at 283.15 to 363.15 °K are 1.3 mPa.s to 0.315 mPa.s, which are much smaller than the dynamic viscosities of the [EMIM][OAc] reported above. Therefore, the higher the concentration of the aqueous solution of [EMIM][OAc] was, the higher the dynamic viscosities of the aqueous solution of [EMIM][OAc] were. It was proven by the data of Römich, et al. (2012)[25]. We used the experimental data of the dynamic viscosities of the aqueous solution of [EMIM][OAc] obtained by Römich, et al. (2012) to correlate the dynamic viscosities to the various temperatures and concentration. There were 20 data points and the RMS of the regression was 0.02 and R^2 was 99.94%. Eq. 12 is the formulation obtained for the calculation of the dynamic viscosities of the aqueous solution of [EMIM][OAc]. The natural logarithm of the dynamic viscosity of the aqueous solution of [EMIM][OAc] exhibited better correlation with changes in the temperature and concentration.

$$Ln(\eta_{[EMIM][OAc]\_H_2O}) = 3.025114 - 0.150834T + 2.20875 * 10^{-4}T^2 - 0.40864\xi - 9.363176\xi^2 + 0.030720T\xi \quad \textit{Eq. 12}$$

Where, T is the temperature of the aqueous solution of [EMIM][OAc] in K and ξ is the mass fraction of [EMIM][OAc] in the aqueous solution. Fig. 11 shows the comparison between the calculated results and the experimental data from Römich, et al. (2012). The dynamic viscosities given by the formulation matched well with the experimental data. By using the proposed formulation, more dynamic viscosities of the aqueous solution of [EMIM][OAc] were calculated and shown in Fig. 12. As expected, the higher the concentration of the aqueous solution of [EMIM][OAc] was, the higher the dynamic viscosity of the aqueous solution of [EMIM][OAc] was. The dynamic viscosity of the aqueous solution of [EMIM][OAc] at 20 °C with 75% concentration is 25-30 m.Pa.s, 2-3 times of the ones of LiCl / CaCl2 aqueous solution at a concertation of 40% with the similar humidity removal capacity.

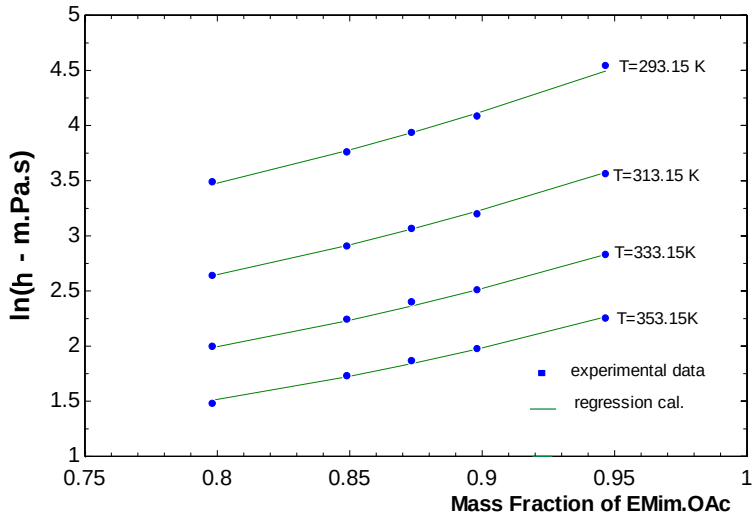

Fig. 11 Comparison of the calculated dynamic viscosities from the regression model and the experimental data from Römich, et al

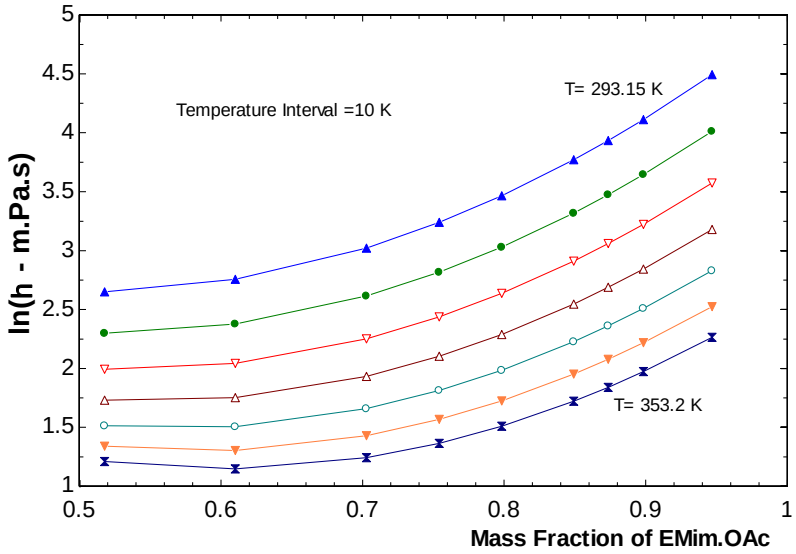

Fig. 1 Dynamic viscosities of aqueous solution of [EMIM][OAc] vs. various temperatures and mass fractions of [EMIM][OAc]

7 Discussion

This paper introduced the calculation formulations of the most important thermo-physical properties of aqueous solutions of [EMIM][OAc]. They are necessary in the design and modeling of IL-based sorption systems to predict the dehumidification capacity and system performance. The data used for generating the formulations were obtained from the experiments in recently published studies. Due to the limited data sources related to aqueous solutions of [EMIM][OAc], the properties calculated by the proposed formulations may be different from the data obtained under future experimental conditions. We therefore do not have total confidence in the specific values predicted by the proposed formulations since our conclusions are based only on the limited data available now. However, we consider the proposed formulations well within the acceptable boundaries for engineering calculation and design and will significantly contribute to the design and performance prediction of sorption systems which use an aqueous solution of [EMIM][OAc] and thereby assist sorption engineers and researchers in their work.

Acknowledgements

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References

[1] T.M. Abdulrahman, B.M. Sohif, M. Sulaiman, K. Sopian, and A.A. Abduljalil, Review: Survey of the control strategy of liquid desiccant systems, *Renewable and Sustainable Energy Reviews* 58 (2016) 250-258.

[2] A. Lowenstein, Review of liquid desiccant technology for HVAC applications, *HVACR Res.* 14 (2008) 819–839.

[3] D.G. Waugaman, A. Kini, C.F. Kettleborough, A review of desiccant cooling systems, *Journal of Energy Resources Technology* 115, no. 1 (1993) 1–8.

[4] W. Kessling, E. Laevemann, M. Peltzer, Energy storage in open cycle liquid desiccant cooling systems, *International Journal of Refrigeration*, 21, no. 2 (1998) 150–156.

[5] Y.J Dai, R.Z Wang, H.F Zhang, and J.D Yu, Use of liquid desiccant cooling to improve the performance of vapor compression air conditioning, *Applied Thermal Engineering* 21 (2001) 1185-1202.

[6] M. M. Rafique, p. Gandhidasan, and M.S. B Haitham . "Liquid desiccant materials and dehumidifiers – A review." *Renewable and Sustainable Energy Reviews*, no. 56 (2016): 179-195.

[7] A. Lowenstein, S. Slayzak, and E. Kozubal, A Zero Carryover Liquid-Desiccant Air Conditioner for Solar Applications, *ASME International Solar Energy Conference.* Denver, Colorado, ASME, 2006.

[8] P. R. Burns, J.W. Mitchell, and W. A. Beckman, Hybrid desiccant cooling system in supermarket applications, *ASHRAE Trans* 91, no. 1 (1985) 457–468.

[9] X. H. Liu and Y. Jiang, Coupled heat and mass transfer characteristic in packedbed dehumidifier/regenerator using liquid desiccant, *Energy Convers. Manag.* 49, no. 6 (2008) 1357–1366.

[10] J. Sanjeev and P.K. Bansal, Performance analysis of liquid desiccant dehumidification systems, International Journal of Refrigeration, 30 no. 5 (2007) 861-872.

[11] D. Seenivasan, V. Selladurai, and P. Senthil, Optimization of liquid desiccant dehumidifier performance using Taguchi method, *Adv. Mech. Eng.* 6 (2014) 1-6.

[12] S. M. Huang, L. Z. Zhang, K. Tang, and L.X. Pei, Fluid flow and heat mass transfer in membrane parallel-plates channels used for liquid desiccant air dehumidification, International Journal of Heat and Mass Transfer, 55 no.9-10 (2012) 2571-2580.

[13] W. Z. Gao, Y.R. Shi, Y.P. Cheng, and W.Z. Sun, Experimental study on partially internally cooled dehumidification in liquid desiccant air conditioning system, *Energy and Buildings* 61 (2013) 202-209.

[14] M. H. Kim, J. Y. Park, M. K. Sung, A. S. Choi, and J. W. Jeong, Annual operating energy savings of liquid desiccant and evaporative-cooling-assisted 100% outdoor air system, *Energy and Buildings* 76 (2014) 538-550.

[15] X. H. She, Y. G. Yin, and X. S. Zhang, Thermodynamic analysis of a novel energy-efficient refrigeration system subcooled by liquid desiccant dehumidification and evaporation, *Energy Conversion and Management* 78 (2014) 286-296.

[16] Y. M. Luo, S. Q. Shao, F. Qin, and C. Q. Tian, Investigation on feasibility of ionic liquids used in solar liquid desiccant air conditioning system, *Solar Energy*, 86 no. 9 (2012) 2718-2724.
[17] M. T. Zegenhagen, C. Ricart, T. Meyer, R. Kühn, and F. Ziegler, Experimental Investigation of A Liquid Desiccant System for Air Dehumidification Working With Ionic Liquids, *Energy Procedia* 70 (2015) 544-551.
[18] A. Kudasheva, T. Kamiya, Y. Hirota, and A. Ito, Dehumidification of air using liquid membranes with ionic liquids, *Journal of Membrane Science* 499 (2016) 379-385.
[19] S. J. Zhang, X. M. Lu, Q. Zhou, X. H. Li, X. P. Zhang, and S. Li, *Ionic Liquids Physicochemical Properties*, Elsevier, 2009.
[20] X. X. Ma, L. Li, J. Wei, W. B. Duan, W. Guan, and J. Z. Yang, Study on Enthalpy and Molar Heat Capacity of Solution for the Ionic Liquid [C2mim][OAc] (1-Ethyl-3-methylimidazolium acetate), *Journal of Chemical & Engineering Data*, 57 no. 11 (2012) 3171-3175.
[21] A. Ahmadi, R. Haghbakhsh, S. Raeissi, and V. Hemmati, A simple group contribution correlation for the prediction of ionic liquid heat capacities at different temperatures, *Fluid Phase Equilibria*, 403 no. 15 (2015) 95-103.
[22] M.G. Freire, Thermophysical Characterization of Ionic Liquids Able To Dissolve Biomass, *Journal of Chemical & Engineering Data* 56, no. 12 (2011) 4813-4822.
[23] Niazi, A. A. , B. D. Rabideau, and A. E. Ismail, Effects of Water Concentration on the Structural and Diffusion Properties of Imidazolium-Based Ionic Liquid–Water Mixtures, *The Journal of Physical Chemistry B* 117, no. 5 (2013) 1378-1388.
[24] A. Radhi, K. A. Le, M. E. Ries, and T. Budtova, Macroscopic and Microscopic Study of 1-Ethyl-3-methyl-imidazolium Acetate−DMSO Mixtures, *The Journal of Physical Chemistry B* 119, no. 4 (2015) 1633-1640.
[25] C. Römich, N. Merkel, A. Valbonesi, K. Schaber, and S. Sauer, Thermodynamic Properties of Binary Mixtures of Water and Room-Temperature Ionic Liquids: Vapor Pressures, Heat Capacities, Densities, and Viscosities of Water + 1-Ethyl-3-methylimidazolium Acetate and Water + Diethylmethylammonium Methane Sulfonate, *J. Chem. Eng. Data*, 57, no. 8 (2012) 2258-2264.
[26] H. F. D. Almeida, H. Passos, J. A. Lopes-da-Silva, A. M. Fernandes, M. G. Freire, and J. A. P. Coutinho, Thermophysical Properties of Five Acetate-Based Ionic Liquids, *Journal of Chemical & Engineering Data* 57, no. 11 (2012) 3005-3013 .
[27] L. Theodore and F. Ricci, *Mass transfer operations for the praticing Engineer*, John Wiley & Sons, Inc., 2010.
[28] H. Renon and J. M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, *AIChe Journal* 14, no. 1 (1968) 135-144.
[29] Engauge Digitizer, http://markummitchell.github.io/engauge-digitizer/, 2016 (accessed 16.10.18).
[30] E. Elsarrag, Dehumidification of Air by Chemical Liquid Desiccant in a Packed Column and Its Heat and Mass Transfer Effectiveness, HVAC&R research (2011) 3-16.