Chemical Engineering Journal 147 (2009) 58–62

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Thermodynamical properties of phase change materials based on ionic liquids

Jiqin Zhu[a,*], Liguang Bai[a], Biaohua Chen[a], Weiyang Fei[b,**]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 100029 Beijing, China
[b] State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, 100084 Beijing, China

ARTICLE INFO

Keywords:
Ionic liquids
Phase change materials
Thermodynamic properties
QSPR

ABSTRACT

Ionic liquids have thermophysical and chemical properties that may be suitable for phase change materials (PCMs). Melting points, heats of fusion and heat capacities for a series of imidazolium-based ionic liquids or ethnolamine tetrafluoroborates have been measured by differential scanning calorimeter. The experimental results indicate that long-chain alkylimidazolium bromides are suited for use as PCMs. A quantitative structure–property relationship (QSPR) model for heat of fusion was constructed using six descriptors based on PM3 semi-empirical method. The calculated results gave reasonable correlation and prediction accuracy for 44 kinds of ionic liquids.

1. Introduction

With the exacerbation of energy shortage all over the world, energy-saving technologies are becoming more and more important for sustainable development. Among them phase change materials (PCMs) can be used to store thermal energy temporarily, and release it when the energy is needed, which offers a useful method for appropriate utilization of energy. PCMs, mainly indicating solid–liquid PCMs, include inorganic PCMs and organic PCMs. Inorganic PCMs possess high fusion heat, high thermal conductivity and small volume change. While they are prone to get supercooling and phase separation, which can decrease severely their thermal storage capacity. At the same time inorganic PCMs are usually corrosive. The common organic PCMs include long chain paraffins, polyatomic alcohols, amides, and so on. Organic PCMs have not the disadvantage of phase separation and are stable. While organic PCMs are highly volatile and flammable, this represents a considerable safety concern for many applications. Also their thermal conductivities are generally low. Therefore new PCMs overcoming the defects of inorganic and organic PCMs are urgently needed.

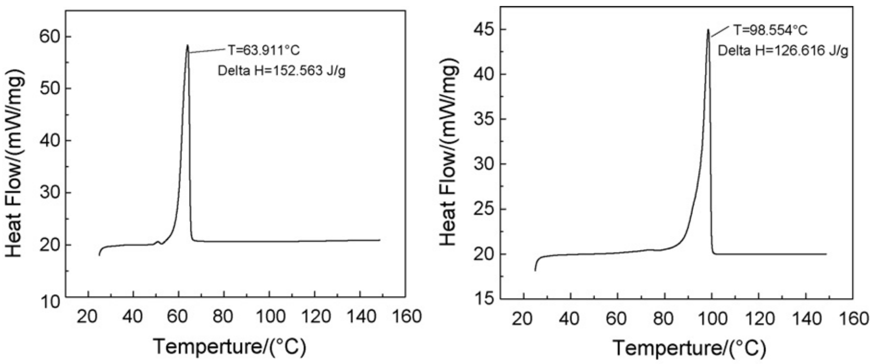
Ionic liquids are salts that have organic cations and inorganic anions. Most of them are liquid at room temperature. As novel materials with many interesting properties, ionic liquids have attracted great attention as catalysts or extraction solvents for the last years [1–4]. Ionic liquids have advantages of high density, wide liquid temperature range, high chemical stability, non-volatility, non-flammability, high heat capacity, and high storage density. Thus ionic liquids could be potential liquid thermal storage media and heat transfer fluids. Especially, the physical and chemical properties of ionic liquids are easy to be tailored using different ions and thus task-specific ionic liquids may be designed and synthesized to meet different requirements. The nature of the cation or anion is considered to be primarily responsible for the properties of ionic liquids. Changes in the cation and anion combinations or the nature of the moieties attached to each ion allow the physical properties of ionic liquids to be tailored.

Wu et al. [5] found that ionic liquids could be excellent liquid thermal storage media and heat transfer fluids in solar thermal power plant. Valkenburg et al. [6] compared the thermal properties of three ionic liquids with those of a present commercial heat-transfer fluid Therminol® VP-1. The results indicate that ionic liquids are suited for use as heat-transfer fluids and in many ways they are superior to present commercial heat-transfer fluids. There are hardly any investigations of novel PCMs based on ionic liquids. IoLiTec develop new PCMs using ionic liquids butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($N_{1114}NTf_2$) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPy NTf_2) [7,8]. While heats of fusion for the two ionic liquids are 16.15 and 27.70 $J\,g^{-1}$, respectively, they are far lower than heats of fusion for paraffins (above 170 $J\,g^{-1}$). For the most important property of PCMs, heat of fusion, the experimental data are also in short supply. To better understand the nature of ionic liquids used as PCMs, the quantitative structure property relationship (QSPR) model is helpful and required. Very few works have studied the quantitative relationships between the structures of ionic liquids and their fundamental properties, such as melting point, viscosity, density and surface tension [9–12]. Quantitative structure property relationship (QSPR) models describing heat of fusion for ionic liquids have not been found in literature up to now.

---

* Corresponding author. Tel.: +86 10 64412054.
** Corresponding author.
E-mail addresses: zhujq@mail.buct.edu.cn (J. Zhu), fwy-dce@tsinghua.edu.cn (W. Fei).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.11.016



(a) $[C_{16}MIM]Br$ (b) $[C_{16}MMIM]Br$

Fig. 1. DSC scan for $[C_{16}MIM]Br$ and $[C_{16}MMIM]Br$.

In this work, we report the results of measurements of melting points, heats of fusion for 10 ionic liquids with different structures, such as 1-akyl-3-methylimidazolium bromide ($[C_nMIM]Br$, $n = 10$, 16), 1-akyl-2,3-dimethylimidazolium bromide ($[C_nMMIM]Br$, $n = 4$, 10,16), 1-butyl-3methylimidazolium chloride ($[C_4MIM]Cl$), 1-butyl-2,3-dimethylimidazolium chloride ($[C_4MMIM]Cl$) and ethnolamine tetrafluoroborates. Heat capacities of $[C_{16}MIM]Br$ and $[C_{16}MMIM]Br$ have also been obtained at atmospheric pressure in steps of 1 K. These properties will allow us to evaluate the feasibility of ionic liquids to be used as PCMs. According to the gainable literature results and our experimental data, a QSPR correlation for heat of fusion was constructed. The calculated results gave reasonable correlation and prediction accuracy for 44 kinds of ionic liquids.

2. Experimental

1-Methylimidazole was purchased from Linhai Kaile chemical factory, with purities ≥99 mass%. 1,2-Dimethylimidazole was purchased from Changzhou Zhongkai Chemical Co. Ltd., with purities ≥98 mass%. 1-Bromohexadecane was purchased from Sinopharm Chemical Reagent Co. Ltd., with purities ≥98 mass%. Chlorobutane, bromobutane, toluene, acetone and ethanol amines were purchased from Beijing Chemical Plant, with purities ≥99 mass%.

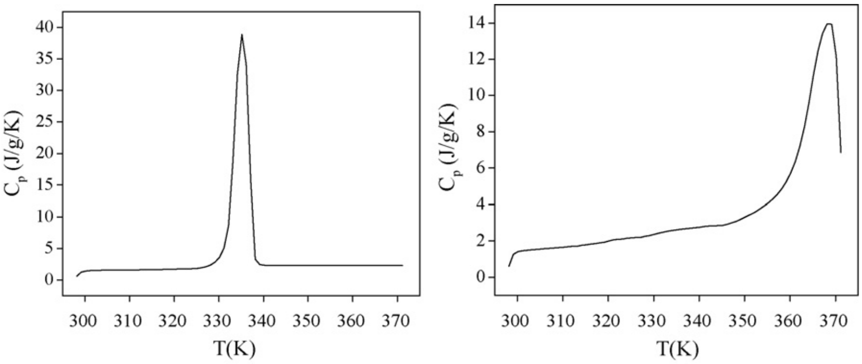
$[C_nMIM]Br$ ($n = 10$, 16), $[C_4MMIM]Cl$ and $[C_nMMIM]Br$ ($n = 4$, 10, 16) were synthesized and purified according to procedues found elsewhere. Monoethnolamine tetrafluoroborate ($[MEA][BF_4]$), diethnolamine tetrafluoroborate ($[DEA][BF_4]$) and triethnolamine tetrafluoroborate ($[TEA][BF_4]$) ionic liquids were kindly provided by Prof. Li ChunXi from our school.

Table 1
Melting points and heats of fusion for ionic liquids.

Ionic liquids	Melting points T_m (K)	Heats of fusion ΔH_m (J/g)
$[C_{10}MIM]Br$	347.58	66.789
$[C_{16}MIM]Br$	337.06	152.563
$[C_4MIM]Cl$	326.57	59.004
$[C_4MMIM]Cl$	365.89	76.384
$[C_4MMIM]Br$	349.66	66.977
$[C_{10}MMIM]Br$	341.35	75.395
$[C_{16}MMIM]Br$	371.7	126.616
$[MEA][BF_4]$	306.76	57.867
$[DEA][BF_4]$	303.84	37.625
$[TEA][BF_4]$	345.26	65.186

Because ionic liquids tend to pick up moisture from the environment and the water contents of ionic liquids have crucial influence on their properties, care should be taken during the preservation and measurements. As mentioned above, the ionic liquids were put into ground glass stoppered flasks, respectively. The ionic liquids were purified by vacuum evaporation for 24 h at 373 K before use. During the procedure, taking the ionic liquids must be as quick as possible to reduce the exposure time. The contact time of ionic liquids with air was so short that the small quantity of absorbed moisture does not affect their properties markedly. The water contents in the ionic liquids were determined by Karl Fischer method. The water contents in all the samples were less than 500 ppm.

Measurements of melting temperatures, heats of fusion and heat capacities were done with a Pyris I differential scanning calorimeter, provided by PerkinElmer. The samples inside the differential scanning calorimeter furnace were exposed to a flowing N_2 atmosphere. Considering that the melting points of ionic liquids studied in this paper were in the range of 313–373 K, measurements for



(a) $[C_{16}MIM]Br$ (b) $[C_{16}MMIM]Br$

Fig. 2. Experimental heat capacities for $[C_{16}MIM]Br$ and $[C_{16}MMIM]Br$.

Table 2
Heat capacities of [C$_{16}$MIM]Br and [C$_{16}$MMIM]Br.

T (K)	[C$_{16}$MIM]Br (J/(g K))	T (K)	[C$_{16}$MMIM]Br (J/(g K))
Crystal			
299.15	1.253	299.15	1.267
303.15	1.550	303.15	1.514
308.15	1.609	308.15	1.617
313.15	1.640	313.15	1.735
318.15	1.700	318.15	1.920
323.15	1.788	323.15	2.315
		328.15	2.456
		333.15	2.751
		338.15	2.625
		343.15	2.764
		348.15	3.085
Liquid			
343.15	2.327		
348.15	2.323		
353.15	2.329		
358.19	2.326		
363.15	2.326		
368.15	2.316		
370.15	2.314		

melting temperatures were determined by heating from 298 to 423 K, both at a rate of 10 K/min. Specific heat capacities of the ionic liquids were measured with the same Pyris I scanning calorimeter from 298.15 to 371.15 K at 1 K/min. The samples of ionic liquids were weighed with an accuracy of 10^{-5} g using an electronic balance. The heat capacities were determined relative to a sapphire sample.

3. Results and discussion

The melting points and heats of fusion for mentioned ionic liquids are shown in Table 1.

[C$_{16}$MIM]Br and [C$_{16}$MMIM]Br have high heat of fusion and moderate melting temperatures. Fig. 1 gives the DSC measurements of two ionic liquids, showing distinct melting points upon heating. The single-peaked shape of the curve of two samples excludes the possibility of a solid–solid transition near melting. They have distinct melting point on heating. Although subcooling of ionic liquids is common, [C$_{16}$MIM]Br and [C$_{16}$MMIM]Br readily crystallize and do not form glasses, which indicates they are favorable candidates for PCMs.

Heat capacity must be known in order to calculate the sensible heat storage density of the ionic liquids. To further investigate the feasibility of [C$_{16}$MIM]Br and [C$_{16}$MMIM]Br as energy storage media

Table 3
Heats of fusion and QSPR descriptors for ionic liquids.

Ionic liquids	ΔH_m		μ (D)	E_{LUMO} (eV)	S (10^{-20} m^2)	V (10^{-30} m^3)	L_H (Å)	E_i (kJ/mol)	References
	(J/g)	(kJ/mol)							
[C$_2$MIM][BF$_4$]	48.19	9.54	15.35	−0.972	367.93	558.97	1.836	−342.8	[16]
[C$_2$MIM][PF$_6$]	70.24	17.99	15.63	−1.33	402.7	619.16	1.652	−342.8	[16]
[C$_4$MIM][PF$_6$]	68.97	19.60	16.03	−1.3830	457.73	724.84	1.645	−330.2	[16]
[C$_4$MIM][NO$_3$]	89.50	17.99	14.65	−1.1206	416.89	652.05	1.672	−366.8	[16]
[C$_4$MIM][(CF$_3$COO)]	76.87	19.14	14.83	−1.0690	460.17	735.80	1.689	−347.8	[16]
[C$_2$MIM] tosylate	69.50	21.57	11.71	−0.7623	592.08	994.95	1.635	−397.1	[16]
[C$_4$MIM] octylsulfate	36.44	12.70	14.06	−0.9203	608.36	1067.70	1.691	−376.2	[16]
[C$_1$MIM] [NTf2]	64.94	24.50	15.59	−1.4574	468.39	783.01	1.727	−309.3	[16]
[C$_2$MIM][NTf2]	55.20	21.60	15.36	−1.4070	490.90	830.11	1.723	−305.1	[16]
[C$_4$MIM][NTf2]	53.49	22.43	15.12	−1.4060	534.12	926.56	1.723	−309.3	[16]
[C$_6$MIM][NTf2]	63.20	28.28	15.72	−1.4150	586.58	1023.78	1.729	−309.3	[16]
[C$_8$MIM][NTf2]	52.96	25.18	15	−1.4080	657.26	1140.79	1.723	−305.1	[16]
[(C$_4$H$_9$OCH$_2$)$_2$IM][BF$_4$]	26.02	8.54	10.98	−0.9342	567.14	975.98	2.425	−357.4	[15]
[(C$_8$H$_{17}$OCH$_2$)$_2$IM][NTf2]	54.03	34.20	12.05	−1.3724	933.00	1661.79	2.125	−314.3	[15]
[(C$_{10}$H$_{21}$OCH$_2$)$_2$IM][NTf2]	115.18	79.36	11.68	−1.3353	1058.18	1869.70	1.735	−314.8	[15]
[C$_3$MMIM][NTf2]	46.95	19.69	14.48	−1.5300	495.81	882.97	1.798	−292.6	[16]
[C$_2$MIM]Br	82.17	15.70	11.33	−0.5196	354.85	515.04	1.676	−425.1	[16]
[C$_3$MIM]Br	69.72	14.30	11.01	−0.5100	375.06	574.14	1.684	−424.7	[14]
[C$_4$MIM]Br	74.39	16.30	10.91	−0.5093	398.79	614.82	1.684	−427.2	[16]
[C$_{10}$MIM]Br	66.79	20.26	11.09	−0.5324	593.94	978.08	1.682	−423.9	This work
[C$_{16}$MIM]Br	152.56	59.11	10.83	−0.5174	764.23	1258.40	1.685	−426.4	This work
[C$_2$MIM]I	69.31	16.50	13.06	−0.8685	352.71	543.51	1.877	−338.6	[14]
[C$_3$MIM]Cl	62.99	10.12	9.1	−0.1545	368.62	563.73	1.473	−475.3	[14]
[C$_4$MIM]Cl	59.00	10.31	9.02	−0.1541	394.73	615.68	1.473	−477.8	This work
[C$_{10}$MIM]Cl	119.38	30.90	8.98	−0.1605	578.28	930.74	1.473	−474.8	[16]
[C$_{12}$MIM]Cl	93.41	26.80	8.97	−0.1610	640.20	1037.58	1.473	−475.4	[16]
[C$_4$MMIM]Cl	76.38	14.41	11.88	−0.8596	415.91	645.97	1.712	−418.0	This work
[C$_4$MMIM]Br	66.98	15.62	10.57	−0.6851	406.32	649.34	1.870	−362.0	This work
[C$_{10}$MMIM]Br	95.40	30.27	12.58	−1.0190	596.03	979.03	1.826	−369.5	This work
[C$_{16}$MMIM]Br	126.62	50.83	9.48	−0.8045	765.63	1273.76	1.894	−381.6	This work
[C$_1$MIM] [CH$_3$SO$_4$]	79.62	16.58	13.19	−0.9330	409.23	619.27	1.645	−390.4	[13]
[C$_2$MIM] *p*-toluenesulfonate	98.56	27.83	11.19	−0.7600	526.83	853.40	1.690	−380.4	[13]
[Pyr][BF$_4$]	134.81	51.26	14.11	−2.3356	688.54	1132.65	1.947	−311.8	[15]
[C$_1$Py][NTf2]	42.60	16.20	17.59	−0.8419	488.14	815.26	1.777	−301.4	[16]
[C$_2$Py][NTf2]	19.85	9.10	20.34	−1.1046	545.43	935.70	1.789	−283.4	[16]
[C$_3$Py][NTf2]	30.12	12.30	17.9	−0.8906	548.62	921.41	1.771	−297.6	[16]
[C$_4$Py][NTf2]	27.70	11.70	17.87	−0.8036	564.29	960.39	1.771	−300.5	[16]
[C$_5$Py][NTf2]	51.55	22.50	15.33	−0.9399	589.42	1002.25	1.781	−303.5	[16]
[N$_{1114}$][NTf2]	16.15	6.40	16.58	−1.0480	519.52	892.48	2.074	−292.6	[16]
[N$_{1123}$][NTf2]	54.50	21.60	18.32	−1.1450	519.29	863.03	1.774	−278.4	[16]
[N$_{1134}$][NTf2]	36.52	15.50	17.38	−1.0100	545.91	940.48	1.813	−286.3	[16]
[MEA][BF$_4$]	57.87	8.50	10.82	−0.1428	286.25	391.96	1.921	−386.6	This work
[DEA][BF$_4$]	37.63	7.26	11.54	−0.2383	328.29	503.06	1.735	−374.1	This work
[TEA][BF$_4$]	65.00	15.41	11.58	−0.4495	365.71	593.37	2.031	−264.2	This work

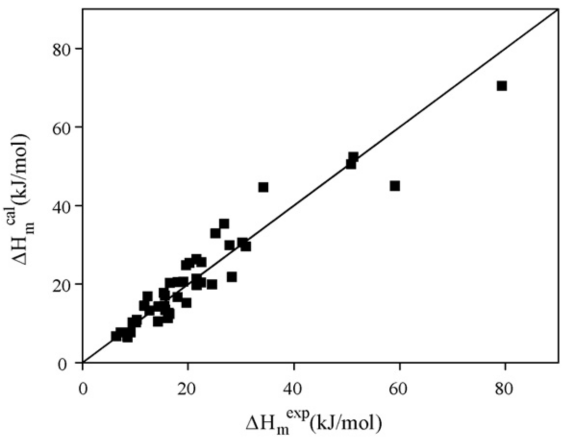


Fig. 3. Linear relationship between experimental and calculated heats of fusion.

and heat transfer fluids, their heat capacities have been determined and the results are presented in Fig. 2 and Table 2.

According to the DSC figure, [C_{16}MIM]Br remains stable to 370 K. There is no phase transition in the solid-phase zone and no association or decomposition in the researched liquid-phase zone. The only endothermic peak in the range of (329–339) K corresponds to fusion of the sample. The peak temperature is 335.15 K, close to above mentioned melting point 337.06 K. [C_{16}MMIM]Br is in the condensed state until 350K. The peak temperature is 368.15 K, agreeing with the measured result 371.7 K. In general, heat capacities of [C_{16}MIM]Br and [C_{16}MMIM]Br are a little greater than those for molecular liquids because of ion–ion interactions.

Heats of fusion for ionic liquids, used here as the basis for the construction of the QSPR model, were taken from previous studies concerning the thermodynamical properties of ionic liquids [13–15] and the International Union of Pure and Applied Chemistry (IUPAC) database [16]. Heats of fusion for all ionic liquids collected in this study are summarized in Table 3. The quantum chemistry computation was carried out using Gaussian03 software. PM3 semi-empirical method with unrestricted spin in ground state was adopted. The geometrical structure of ionic liquids was optimized to a minimum energy. After optimizing calculation, the stabilized geometrical structures and corresponding structure parameters of ionic liquids were obtained. The calculated results of the molecular orbital (i.e., dipole moment μ and lowest unoccupied molecular orbital (LUMO) level E_{LUMO}), the geometric parameters (i.e., surface area S, volume V and the shortest hydrogen bond distance L_{H}) and the cation-anion interaction energy E_i were applied as the descriptors of ionic liquids for the determination of the correlating equation. The cation–anion interaction energy of ionic liquids is defined as the difference between the energy of the ion pair and the sum of the energies of the purely cationic and anionic species, which directly indicates the strength of cation–anion interaction. The descriptors of ionic liquids for QSPR model were also listed in Table 3.

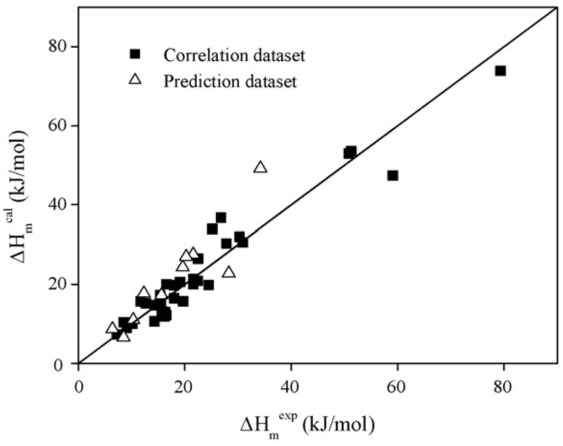


Fig. 4. Correlation and prediction for heats of fusion.

The measured heats of fusion data were regressed with six descriptors and the multiple regression results for 44 ionic liquids are as follows:

$$\begin{aligned}\Delta H_{\mathrm{m}}(\mathrm{kJ/mol}) = {} & 112.82 - 3.1925 \times \mu - 7.3247 \times E_{\mathrm{LUMO}} \\ & + 0.49747 \times S - 0.23304 \times V - 28.552 \times L_{\mathrm{H}} \\ & + 0.17797 \times E_i \end{aligned} \tag{1}$$

The correlation $R^2 = 0.9047$, $F = 58.54$, standard deviation (S.D.) = 4.797. The most important descriptor used is the cation–anion interaction energy of ionic liquids E_i. The comparison of the calculated heats of fusion with experimental data is shown in Fig. 3.

As seen in Fig. 3, a good agreement between experimental and calculated values is obtained. Then 10 different kinds of ionic liquids were randomly selected as the prediction sets, and the rest of the experimental data were regressed as training sets in regressing the QSPR models. Then the model was checked against the prediction sets. The comparisons of the correlated and predicted values with the experimental results are shown in Fig. 4.

It can be seen from Fig. 4 that the experimental data are in consistent with the correlated and predicted results using this six-descriptor QSPR model.

4. Conclusions

Melting points, heats of fusion and heat capacities for a series of imidazolium-based ionic liquids or ethnolamine tetrafluoroborates have been measured by differential scanning calorimeter. The experimental results indicate that long-chain alkylimidazolium bromides [C_{16}MIM]Br and [C_{16}MMIM]Br are suited for use as PCMs. A six-descriptor QSPR model for heat of fusion was developed and the calculated results show that it can give reasonable correlation and prediction accuracy for 44 ionic liquids with different kinds of cations and anions.

Acknowledgment

The financial supported by the National Scientific Funding of China (No. 20706005) are gratefully acknowledged.

References

[1] H. Marco, R. Anders, Hydroformylation in room temperature ionic liquids (RTILs): catalyst and process developments, Chem. Rev. 108 (2008) 1474–1497.
[2] A. Arce, H. Rodríguez, A. Soto, Purification of ethyl *tert*-butyl ether from its mixtures with ethanol by using an ionic liquid, Chem. Eng. J. 115 (2006) 219–223.
[3] J.Q. Zhu, J. Chen, C.Y. Li, W.Y. Fei, Centrifugal extraction for separation of ethylbenzene and octane using 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid as extractant, Sep. Purif. Technol. 56 (2007) 237–240.
[4] J.Q. Zhu, J. Chen, C.Y. Li, W.Y. Fei, Study on the separation of 1-hexene and trans-3-hexene using ionic liquids, Fluid Phase Equilib. 247 (2006) 102–106.
[5] B.Q. Wu, R.G. Reddy, R.D. Rogers, Novel ionic liquid thermal storage for solar thermal electric power systems, in: Proceedings of the International Solar Energy Conference, Washington, USA, 2001, p. 445.
[6] M.E.V. Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochemistry of ionic liquid heat-transfer fluids, Thermochim. Acta 425 (2005) 181–188.
[7] D.R. MacFarlane, P. Meakin, N. Amini, M. Forsyth, Structural studies of ambient temperature plastic crystal ion conductors, J. Phys. Condens. Mat. 13 (2001) 8257–8267.

[8] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, Pyrrolidinium imides: a new family of molten salts and conductive plastic crystal phases, J. Phys. Chem. B 103 (1999) 4164–4170.
[9] R.L. Gardas, J.A.P. Coutinho, Applying a QSPR correlation to the prediction of surface tensions of ionic liquids, Fluid Phase Equilib. 265 (2008) 57–65.
[10] N. Sun, X.Z. He, K. Dong, X.P. Zhang, X.M. Lu, H.Y. He, S.J. Zhang, Prediction of the melting points for two kinds of room temperature ionic liquids, Fluid Phase Equilib. 246 (2006) 137–142.
[11] K. Tochigi, H. Yamamoto, Estimation of ionic conductivity and viscosity of ionic liquids using a QSPR model, J. Phys. Chem. C 111 (2007) 15989–15994.
[12] G.V.S.M. Carrera, L.C. Branco, J. Aires-de-Sousa, C.A.M. Afonso, Exploration of quantitative structure property relationships (QSPR) for the design of new guanidinium ionic liquids, Tetrahedron 64 (2008) 2216–2224.
[13] U. Dománska, P. Morawski, Influence of high pressure on solubility of ionic liquids: experimental data and correlation, Green Chem. 9 (2007) 361–368.
[14] E.A. Turner, C.C. Pye, R.D. Singer, Use of ab initio calculations toward the rational design of room temperature ionic liquids, J. Phys. Chem. A 107 (2003) 2277–2288.
[15] U. Dománska, Thermophysical properties and thermodynamic phase behavior of ionic liquids, Thermochim. Acta 448 (2006) 19–30.
[16] NIST Standard Reference Database #147, http://ilthermo.boulder.nist.gov.