Thermodynamics of Ionic Liquids Based on Transitional Metal
- Giauque Travel Award Presentation -

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The Ionic liquid systems based on transitional metal chloride: $FeCl_3$/BMIC (1-methyl-3-butylimidazoliumchloride), $FeCl_3$/EMIC(1-methyl-3-ethylimidazolium chloride) and $ZnCl_2$/BMIC were prepared by directly mixing anhydrous $FeCl_3$ (or $ZnCl_2$) and EMIC(or BMIC) with molar ratio 1/1 under dry argon atmosphere. The densities and surface tension of the ionic liquids (ILs) were determined in temperature range of 278.15 K to 343.15 K.

According the Glasser's theory[1], standard entropies, S^0 (298)/（$J{\cdot}K^{-1}{\cdot}mol^{-1}$）＝ 1246.5($V_m/nm^3$) +29.5, and crystal energies, U_{poT} (298)/ (kJ/mol)= $1982.1\times(\rho/M)^{1/3}+103.8$, of the ILs were calculated and are listed in Table 1, where V_m, M and ρ are molecular volume, molar mass and density of the ILs. In general, surface tension, γ, of the ILs almost linearly decreases while temperature elevates and the relationship is expressed in Eötvös equation [2]: $\gamma V^{2/3} = k\,(T_C - T)$, where V is molar volume of ILs(see Fig. 1). The magnitude of the slope, k, can represent the polarity of ionic liquids. In terms of the new theory of ILs—"interstice theory"[3], the average interstice volume: $v = 0.6791(k_b/\gamma T)^{3/2}$ and the thermal expansion coefficient, α, of ILs were calculated and are also listed in Table 1. The magnitude order of thermal expansion coefficient α (calculated) is in good agreement with α (experimental) so that this result means that the interstice theory is reasonable.

Table 1. Thermodynamic properties of the ILs

	$FeCl_3$/BMIC	$FeCl_3$/EMIC	$ZnCl_2$/BMIC
S ($10^{-6}J/K{\cdot}m^2$)	55.76	62.76	89.23
Ea ($10^{-3}J/m^2$)	62.60	60.16	85.45
S^0 ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	540.2	469.1	477.4
α(exp.) ($10^{-4}K^{-1}$)	4.73	5.96	3.9
α(cal) ($10^{-4}K^{-1}$)	4.57	5.03	5.37
v ($10^{-24}cm^3$)	18.15	20.49	12.55
k ($10^{-7}J/K$)	1.63	1.67	2.3
U_{poT} (kJ/mol)	420	436	434

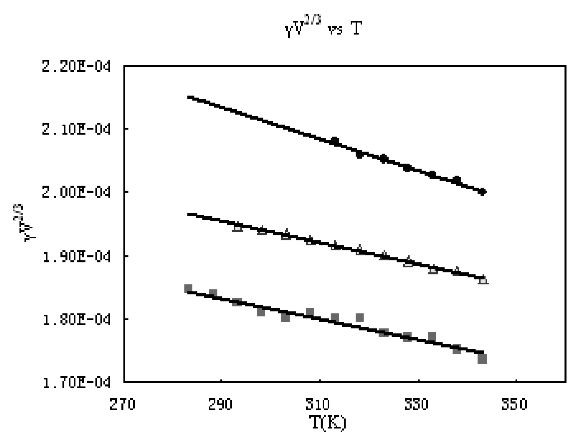

Fig. 1 Plot of γ $V^{2/3}$ vs T
(■$FeCl_3$/BMIC ; ▲$FeCl_3$/EMIC; ●$ZnCl_2$/BMIC)

[1] Glasser, L. Thermochim. Acta. 2004, **421:** 87-93.
[2] Adamson, A. W., Physical chemistry of surfaces,3rd Edn., John-Wiley,1976, New York, translated by Gu, T. R. Science Press, 1986, Beijing.
[3] Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Xu, W.-G. *Green Chem.*, **2004**, 6: 541-543.