

Effect of Ionic Liquids on Organic Reactions Based on Activity Coefficients at Infinite Dilution^{*}

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Abstract It is important to know how ILs (ionic liquids) influence organic reaction. In this paper, activity coefficients at infinite dilution of more than 80 organic compounds in ILs are collected and analyzed systematically. Through the study on typical organic reactions happened in ILs, such as Diels-Alder, esterification and Friedel-Crafts reaction, the ratio of activity coefficients at infinite dilution of products and reactants is employed to estimate different effects of different structural ILs on the rate and selectivity of reactions.

Keywords ionic liquid, activity coefficients at infinite dilution, organic reactions

1 INTRODUCTION

Room Temperature Ionic Liquids (RTILs), combination of organic cation and inorganic anion, are liquid in room temperature or at the temperature nearby [1]. RTILs, a type of solvents consist of only cations and anions, show their unique properties as solvents and catalysts in chemical industry and draw the attention of scientists. Many scientific research institutions and famous chemical companies, such as BP, IFP, BASF and CNPC have done much related researches. Nowadays, applications of ILs as solvents and catalysts to improve octane number of gasoline and to produce ethylbenzene have already been industrialized [2].

Ionic liquids with their physical properties become potential solvents for synthesis due to the following reasons: (1) They are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase; (2) They are often composed of poorly coordinating ions, so they have the potential to be highly polarized and non-coordinating solvents; (3) They are immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems; (4) Ionic liquids are nonvolatile. They do not evaporate, hence they may be used in high-vacuum systems and eliminate many containment problems; and (5) Another feature of ionic liquids is their ability to be reused many times [3–6].

Researching on how ILs influence the organic reaction is meaningful. Understanding these mechanisms can help researchers design special structure of IL for special reaction. However, direct researches need physical and material resources to do numerous experiments. By far, quantitatively relationship between structure of IL and rate or selectivity of reaction has

been reported rarely.

The activity coefficient at infinite dilution of a solute i , γ_i^∞ , is usually used as a parameter to choose solvents for separations [7]. At the same time, γ_i^∞ is also a measure of the solubility of solutes [8]. As we know, when the dissolution of a solute in a solvent reaches its equilibrium, the value of multiply of γ_i^∞ and concentration of the solute are constant. It implies that the larger the concentration is, the smaller the value of γ_i^∞ . Many kinds of reactions in ILs have something in common: reactants with high solubilities and products with low solubilities. Products are separated from ILs continuously because of their low solubilities, and then reactions in ILs are accelerated. Because γ_i^∞ is a measure for the solubility of solute, the ratio of γ_i^∞ between products and reactants is used to predict the effects on reaction by varying structures of ILs in this paper.

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The structure of ILs has an impact on the equilibrium concentration of solute and consequentially it change value of the γ_i^∞ . Hence, the effect of structure on γ_i^∞ instead of on reactions can be studied.

2.1 Effect of solute structure

Chemical potential of the solute i (μ_{il}) is defined in Eq. (1). The μ_{il} is the chemical potential of the solute i in pure liquid. Generally, $\gamma_i x_i$ is defined as activity of the solute i (a_i). In order to analyse the

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effect of ILs structure on γ_i^∞ , $RT \ln \gamma_{il} x_{il}$ is divided into two parts as shown in Eq. (2). In the ideal solution, $\gamma_{il} = 1$, and the value of excess free energy (G_{il}^E) of the solute i in IL represented by $RT \ln \gamma_{il}$ is 0. $\ln \gamma_{il}^\infty$ in Eq. (3) can be expressed in Eq. (4) in IL at infinite dilution. γ_i^∞ is short for γ_{il}^∞ .

$$\mu_{il} = \mu_{il}^* + RT \ln \gamma_{il} x_{il} \quad (1)$$

$$\mu_{il} = \mu_{il}^* + RT \ln x_{il} + RT \ln \gamma_{il} \quad (2)$$

$$G_{il}^E = RT \ln \gamma_{il}^\infty = H_{il}^E - TS_{il}^E \quad (3)$$

$$\ln \gamma_i^\infty = H_{il}^E / RT - S_{il}^E / R \quad (4)$$

According to Eq. (4), γ_i^∞ consists of two parts, entropic contribution (S_{il}^E / R) and enthalpic contribution (H_{il}^E / RT). The entropic contribution is related to the size and shape of the solute, while enthalpic contribution to the interaction between the solvent and the solute, such as non-specific force van der Waals and specific force H-bonding capacity *etc.* In order to calculate γ_i^∞ , the model for γ_i^∞ of a solute in water is employed (Eq. (5)) [9].

$$\ln \gamma_i^\infty = \frac{V_i}{RT} (\delta_i - \delta_{il})^2 + \ln \frac{V_i}{V_{il}} + 1 - \frac{V_i}{V_{il}} - e_0 V_i - e'_0 \quad (5)$$

where δ and V are the solubility parameter and the molar volume, respectively. Subscripts i and IL refer to the solute and the ionic liquid, respectively. The e_0 and e'_0 are the empirical parameters that correct the entropic contributions. However, as two empirical parameters being used to account for the uncertain effects, it is a simple but empirical model. The δ_{il} is defined using Eq. (6):

$$\delta_{il} = f_0 + f'_0 \frac{T_{mIL}}{V_{il}} \quad (6)$$

where f_0 and f'_0 are constants influenced by the structures of the IL. T_{mIL} is the melting point of IL and V_{il} is the molar volume of IL calculated from the molar mass and density of the IL [10].

The calculated and experimental γ_i^∞ of alkanes, alkylbenzenes and alcohols are compared in Figs. 1–3 (The γ_i^∞ calculated in various ILs: C₆mimPF₆, C₄-4-MePyBF₄, C₁mimTf₂N, C₂mimTf₂N, C₄mimTf₂N and C₂-2-MemimTf₂N [11–15]) with the deviations from experimental results being 1.4%, 0.5% and 1.16%, respectively. The results shown in Eq. (5) may also work well when IL is used as solvent.

Activity coefficient γ_i^∞ of alkanes, alkenes, alcohols, aldehydes and alkylbenzenes are calculated based on Eq. (5). The results are shown in Fig. 4, in which clear difference can be seen among different types of solute in the same IL. From the comparison of $\gamma_{i,entropy}^\infty$ with $\gamma_{i,enthalpy}^\infty$ of alkanes, it is found that

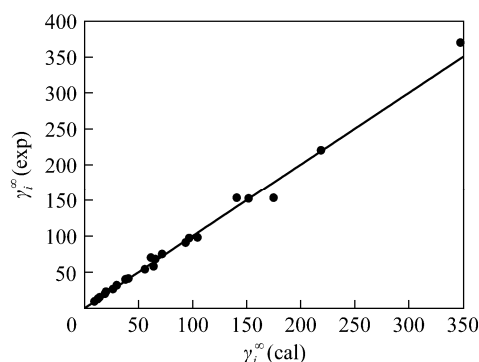


Figure 1 Comparison of calculated and experimental results for γ_i^∞ of alkanes

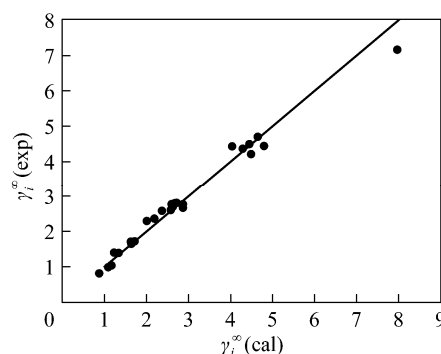


Figure 2 Comparison of calculated and experimental results for γ_i^∞ of alkylbenzenes

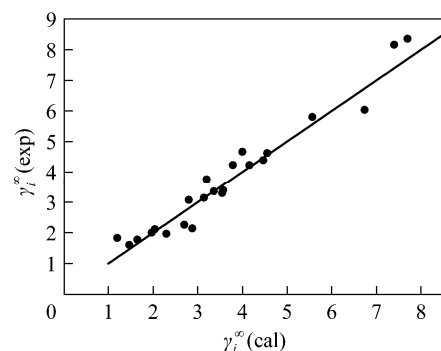


Figure 3 Comparison of calculated and experimental results for γ_i^∞ of alcohols

$\gamma_{i,entropy}^\infty$ plays the dominate role in influencing γ_i^∞ . Similar results are found in the cases of alkenes and alkylbenzenes. However, in cases of alcohols and aldehydes, the values of γ_i^∞ are contributed mainly by $\gamma_{i,enthalpy}^\infty$, because the specific interactions (H-bonding, n - π , π - π) are stronger than the effect of size or shape of solute. Because the interactions usually cause negative deviations, the γ_i^∞ values of alcohols and aldehydes are much smaller than those of alkanes, alkenes and alkylbenzenes.

However, no matter what kinds of solutes, the γ_i^∞ values increase with increasing carbon numbers.

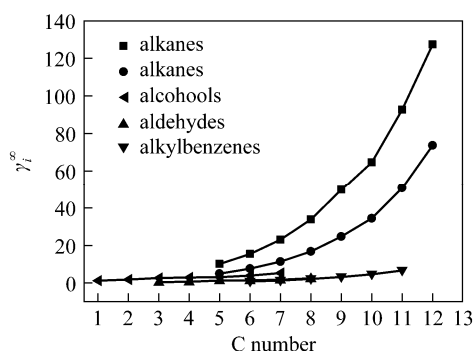


Figure 4 The γ_i^∞ variety with C number in $C_4\text{mimTf}_2\text{N}$ at 298K [14]

2.2 Effect of cation and anion

The relationship between IL structure and γ_i^∞ value is set up by Eqs. (5), (6). The effect of ionic structures on γ_i^∞ value can be calculated. For instance, the effect of methylation at the C(2)-position on imidazolium ring of ILs can be quantitatively described. The effect of enthalpy can be defined using Eq. (7):

$$\gamma_{i,\text{enthalpy}}^\infty = \frac{V_i}{RT} (\delta_i - \delta_{\text{IL}})^2 \quad (7)$$

while the effect of entropy can be calculated from Eq. (8):

$$\gamma_{i,\text{entropy}}^\infty = \ln \frac{V}{V_{\text{IL}}} + 1 - \frac{V}{V_{\text{IL}}} - e_0 V_i - e'_0 \quad (8)$$

In emimTf_2N and $\text{em}_2\text{imTf}_2\text{N}$, $\gamma_{\text{entropy}}^\infty$ and $\gamma_{\text{enthalpy}}^\infty$ value of hexane are 1.122 versus 1.126 and 24.72 versus 23.68 at 298.15 K, respectively, while the results for nonane become 1.035 versus 1.038 and 97.88 versus 94.97 at the same temperature, respectively. These imply that the effect of methylation at the C(2)-position on imidazolium ring on $\gamma_{\text{entropy}}^\infty$ is more noticeable than $\gamma_{\text{enthalpy}}^\infty$, and the γ_i^∞ value will reduce after methylating. The same trend is found in the cases of alkenes and alkylbenzenes. However, $\gamma_{\text{enthalpy}}^\infty$ and $\gamma_{\text{entropy}}^\infty$ values of methanol in the same ILs are 32.20 versus 32.49 and -31.93 versus -32.0 , respectively, implying that the effect of methylation on $\ln \gamma_{\text{enthalpy}}^\infty$ is more noticeable than $\gamma_{\text{entropy}}^\infty$, and the γ_i^∞ value will increase because of the loss of H-bonding capacity.

The anion also affects the γ_i^∞ value. Replacement of hydrophilic anion with hydrophobic anion significantly increases γ_i^∞ of aliphatic hydrocarbons. However, varying the anions does not change the general dependence of γ_i^∞ on chain length, cyclization, branching and polarity of the solutes [16]. Moreover, the γ_i^∞ of alkyl-benzenes in ILs with anions of PF_6^- , BF_4^- , Tf_2N^- and Cl^- are much smaller than that in ILs with other anions. This may be caused by liquid clathrate formation in those type of ILs [17]. The formation

of liquid clathrate is proportioned to the IL. Alkylbenzene molecules surrounded by anion-cation cages with strong interactions between the cation methyl groups and the π -system of the alkylbenzenes dramatically improve the solubilities of alkylbenzenes. That is why γ_i^∞ of alkylbenzenes behave as the opposite trend with increasing temperature [18–20].

3 EFFECT OF STRUCTURE ON REACTIONS BASED ON ACTIVITY COEFFICIENTS AT INFINITE DILUTION

3.1 Effect on esterification

Esterification in ILs belongs to acid-catalyzed reaction, ILs are used as both solvents and catalyst [21, 22]. The catalytic activity is influenced by two aspects. First, higher acidity has a better conversion. On the other hand, esterification is a kind of reversible reaction, so the different partial immiscibility of obtained esters in ILs might also affect the catalytic activity of ILs. Hence, choosing higher acidity IL or enlarging the differences between the γ_i^∞ value of reactants and products will enhance catalytic activity.

Based on analyzing a great deal of experimental data, combining with γ_i^∞ of reactants and products in different ILs, we found that γ_i^∞ of reactants decreased and γ_i^∞ of products increased when Brønsted acidic ILs were used instead of non-Brønsted acidic ILs.

In Figs. 5 and 6 red and blue points represent γ_i^∞ of alcohols or esters in non-Brønsted acidic ILs ($C_4\text{mimPF}_6$, $C_6\text{mimBF}_4$, $C_2\text{mimTf}_2\text{N}$, $C_4\text{mimTf}_2\text{N}$, $C_6\text{mimTf}_2\text{N}$, $C_2\text{-MemimTf}_2\text{N}$, $C_8\text{mimBF}_4$, $C_2\text{PyTf}_2\text{N}$, $C_4\text{mPyBF}_4$, PDmimBF_4 [11, 13–15, 18, 23–25, 26]), and black points represent those in Brønsted acidic ILs. It can be seen from Figs. 5 and 6 that γ_i^∞ of alcohols as reactants in

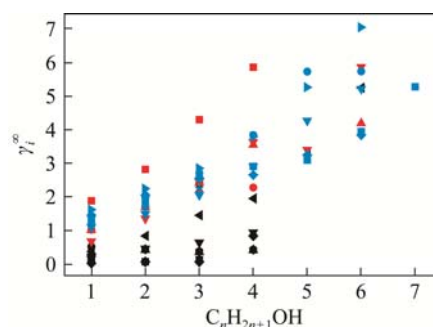


Figure 5 The γ_i^∞ of $C_n\text{H}_{2n+1}\text{OH}$ in Brønsted acidic and non-Brønsted acidic ILs

■ [mmim][(CH₃)₂PO₄]; ● [mmim][CH₃SO₄];
▲ [bmim][OcOSO₃]; ▼ [emim][CH₃C₆H₄SO₃];
◆ [mocim][Cl]; ◀ [emim][EtSO₄]; ▶ [omim][MDEGSO₄];
● [bmim][C₈H₁₇OSO₃]; ■ [bmim][PF₆]; ● [omim][BF₄];
▲ [bmPy][BF₄]; ▼ [bmim][BF₄]; ■ [bmim][Tf₂N];
● [em₂im][Tf₂N]; ▼ [emim][Tf₂N]; ◆ [hmim][Tf₂N];
★ [ePy][Tf₂N]; ▶ [Me₃BuN][Tf₂N]

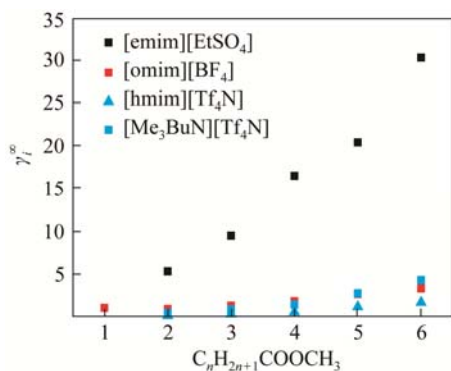


Figure 6 The γ_i^∞ of $C_nH_{2n+1}COOCH_3$ in Brønsted acidic and non-Brønsted acidic ILs

Brønsted acidic ILs are much smaller than non-Brønsted acidic ILs, while γ_i^∞ of esters as products are much larger. That is to say alcohols as reactants are soluble in Brønsted acidic ILs, while esters as products are insoluble in Brønsted acidic ILs. Esterification are accelerated with the gradual separation of esters as products out from reaction system. Based on numbers of γ_i^∞ of alcohols, acids and esters, theoretical relationships between γ_i^∞ and reaction rate constant may be set up. Through such comparison, the most proper structure of ILs can be found out or designed for esterifications.

3.2 Effect on Friedel-Crafts reactions

In Friedel-Crafts alkylation and acylation reactions, ILs are also used as both solvent and catalyst. The catalytic activity influenced strongly by varying the structure of ILs. For example, Friedel-Crafts alkylation reactions worked well in ILs with anion such as PF_6^- and SbF_6^- or other hydrophobic ILs at room temperature with 99% conversion after 12 hours, while no reactions occurred in hydrophilic ILs at all [27] (Table 1 [28]). The reason can be deduced from experiments. In hydrophobic ILs, catalyst existing in the interface between the IL and organic phases catalyze the reaction like a bridge, while completely dissolved catalyst in hydrophilic ILs seemed to be fixed. The loss of activity of catalyst is due to the lack of contact area with reactants.

It is reported that the rearrangement of alkene took place prior to the ring substitution, which indicated that the carbonium ion was formed first and the products were consist of the mixture of isomer.

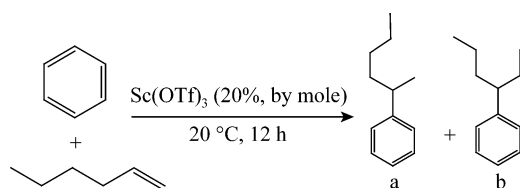


Table 1 Conversion rate and yield of reaction between benzene and 1-hexene in different solvents

Solvent	Conversion rate of hex-1-ene/%	Yield of monoalkylated product (mol ratio of a/b)
[C ₂ -mim][BF ₄]	0	0
[C ₂ -mim][TfO]	0	0
[C ₄ -mim][BF ₄]	0	0
[C ₄ -mim][TfO]	0	0
[C ₂ -mim][SbF ₆]	>99	96(1.5 : 1)
[C ₄ -mim][PF ₆]	>99	96(2 : 1)
[C ₄ -mim][SbF ₆]	~99	93(1.5 : 1)
[C ₅ -mim][PF ₆]	>99	95(1.6 : 1)
[C ₆ -mim][PF ₆]	>99	95(2 : 1)

Friedel-Crafts reaction is a kind of acid catalysis reaction. Acidity of ILs would be regulated by varying anion in order to improve conversion rate of the reaction. 1-alkyl-3-methylimidazolium chloride-aluminum (III) chloride which possessed Lewis acidity was employed to catalyze Friedel-Crafts reaction without any other catalysts. The yield of products increased with the content of aluminum (III) chloride varying from 48% to 51% [29]. When applying cation substituted by $-SO_3H$, $-RSO_3$ and $-COOH$, or anions of CF_3COO^- , $p-TSA^-$, HSO_4^- , $H_2PO_4^-$, CH_3COO^- , $MDEGSO_4^-$ and so on, ILs showed up its Brønsted acidity which had stronger catalytic activity [30]. The increasing positive charge H might be the reason why IL could stabilize the intermediate. It is static electric field of ILs which accelerates the catalytic rate by stabilizing the intermediate. However, alkenes of reactants would polymerize when the acidity of IL is too high. Double-acidic ILs such as $AlCl_3$ -EtPy- CF_3COO^- are also used in Friedel-Crafts alkylation and acylation reactions and performed well [31].

The influence of the cation is also important. For example, increasing carbon number of the alkyl group on cation, the solubility of reactant in IL increases remarkably, and then the reaction is accelerated.

Friedel-Crafts reaction of isobutene with 2-butene in $RmimCl-AlCl_3$ was studied. When R varied from C₄ to C₈, reaction rate and conversion rate increased with the γ_i^∞ ratio of products and reactants, Fig. 7 (reaction data [32]), in which γ_a , γ_b and γ_c represent γ of isobutene, 2-butene and alkylate respectively. The reaction rate or conversion rate of organic reaction in IL will increase when the γ_i^∞ of products are larger than those of reactants. Similar trends are found in reaction between benzene and 1-hexene in [C₄-mim][PF₆] and [C₆-mim][PF₆]. The γ_i^∞ of benzene, 1-hexene and alkylbenzene are 2.11, 11.14 and 23.10 in [C₆-mim][PF₆], respectively, while the γ_i^∞ ratio is about 1.0, affording a 95% yield. However, the γ_i^∞ ratio is 1.6 in [C₄-mim][PF₆], affording a 96% yield (reaction data [33]). Based on the conclusion above, the reaction trends of different reactions of the same kind can be estimated.

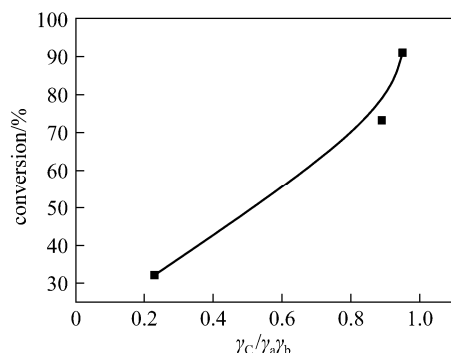


Figure 7 Friedel-Crafts reaction of isobutene and 2-butene in ILs with cations C_4 , C_6 , C_8

4 CONCLUSIONS

It was an innovation that the activity coefficients at infinite dilution was applied to judge the catalytic activity or conversion of organic reactions in ILs. The model for activity coefficients at infinite dilution of a solute in ILs was set up as follows:

$$\ln \gamma_i^\infty = \frac{V_i}{RT} \left(\delta_i - f_0 - f_0' \frac{T_{mIL}}{V_{IL}} \right)^2 + \ln \frac{V_i}{V_{IL}} + 1 - \frac{V_i}{V_{IL}} - e_0 V_i - e_0'$$

through which the effect of IL structure was analyzed quantitatively. The theory played very well in both the esterifications and Friedel-Crafts reaction.

NOMENCLATURE

e_0	empirical parameters
e_0'	correct the entropic contributions
f_0, f_0'	ionic liquid category specific constants
H_{iIL}^E	excess enthalpy of solute i in ionic liquid, J
R	ideal gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
S_{iIL}^E	excess entropy of solute i in ionic liquid, $\text{J} \cdot \text{K}^{-1}$
T	temperature, $^\circ\text{C}$
T_{mIL}	melting point of ionic liquid, $^\circ\text{C}$
V	molar volume, $\text{L} \cdot \text{mol}^{-1}$
γ_i^∞	activity coefficient at infinite dilution
$\gamma_{enthalpy}^\infty$	effect of enthalpy on activity coefficient at infinite dilution
$\gamma_{entropy}^\infty$	effect of entropy on activity coefficient at infinite dilution
δ	solubility parameter

Subscripts

i	solute i
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