Hydroformylation of Oct-1-ene in Novel Ionic Liquid Crystals

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Hydroformylation of oct-1-ene leading to nonanal (denoted by n) and 2-methyloctanal (denoted by iso), in a novel series of caprolactam-based and common imidazolium-based ionic liquid crystals (ILCs; see *Fig. 1*) carried out for the first time (caprolactam = hexahydro-2*H*-azepin-2-one) (*Scheme*). Variation of the chain length (n) of the alkyl substituent (C_n) at the caprolactam cation (CP^+) from $n = 12$ to 18 caused the n/iso ratios to vary from 1.7 to 2.9. Meanwhile, the TOF (turnover frequency) decreased from 148 to 122 mol mol^{-1} h^{-1}. Hydroformylation in the imidazolium-based ILCs revealed that $[C_{16}MIm]\cdot BF_4$ (n/iso 5.2, TOF 969 mol mol^{-1} h^{-1}) was more favorable than $[C_{16}MIm]\cdot MsO$ (n/iso 3.7, TOF 969 mol mol^{-1} h^{-1}) for the formation of the unbranched aldehyde. Although the n/iso ratio in caprolactam-based ILCs was lower than that in imidazolium-based ILCs, the conversions are higher in the former ILCs on the whole. It should be noted that the lamellar mesophase has a strong effect on the regioselectivity and TOF of the hydroformylation. Also, it is evident that the influences of different ILCs on the hydroformylation under the various reaction conditions are greatly different. The identification of the reaction products was established by GC and GC/MS analyses.

Introduction. – Hydroformylation of olefins catalyzed by homogeneous catalysts is one of the most important syngas-related reactions in industry [1]. Most of the traditionally used solvents, such as chlorinated hydrocarbons, MeCN, DMF, *etc.*, are not intrinsically environment-friendly. Thus, the use of a green solvent is highly desirable. In the past decades, ionic liquids (ILs), due to their peculiar physicochemical properties have attracted considerable attention as versatile media in various applications [2–4]. Particularly, ILs have been extensively investigated in catalytic processes; *e.g.*, ILs with the tetrafluoroborate anion have been successfully used in the rhodium-catalyzed hydroformylation of olefins [5]. Lactam-based *Brønsted*-acidic ILs were used as both potentially efficient catalysts and ionic media for esterifications, wherein the acidity and immiscibility of these ILs had a synergistic effect on the esterification performance [6]. Also, ILs can be used as solvents with significant effects [3][4][7]. Examples include the liquid–liquid extraction of the antibiotic erythromycin [3] and the hydrogenation of cyclohexene in $[C_4ClIm][BF_4]$ [4], where the ionic-catalyst solution could be effectively recycled after reaction.

Liquid crystals (LCs) are considered as the 'fourth state of matter' [8], and most of them are neutral organic compounds. Ionic liquid crystals (ILCs) are a class of liquid-crystalline compounds that possess the properties of liquid crystals and ILs, which means that some of the properties of ILCs differ significantly from those of neutral LCs. Typical for ILCs is the ion conductivity, and the ionic interactions tend to stabilize lamellar mesophases [9]. Based on this property, the orientation of the molecules

dissolved in the liquid crystals could be affected by this ordered media. Furthermore, the regio- and chemoselectivity of organic reactions in liquid-crystalline solvents are different from those observed in conventional organic solvents and in common ILs [10][11]. Hitherto, a great variety of ILCs have been synthesized [12], and the most widely investigated ILCs, without exception, are based on imidazolium salts [13], pyridinium salts [13a][14], phosphonium salts [15], or metal-containing salts [9]. Moreover, only a few studies have considered the use of ILCs as anisotropic solvents for organic reactions [11][16], such as the geometric isomerization of azobenzenes in the cholesteric phase of a 35:65 (*w*/*w*) mixture of cholesteryl chloride/cholesteryl nonanoate [17], and the stereoselectivity of *Diels–Alder* reactions in an *N*-alkylimidazolium ILC [16], *etc.*

Recently, a series of caprolactam-cation-based *Brønsted* acid ILs have been synthesized and characterized [18] (caprolactam = CP = hexahydro-2*H*-azepin-2-one). These ILs could be used as both effective catalysts and reaction media for the *Beckmann* rearrangement of cyclohexanone oxime to afford caprolactam [19]. In a following study, novel ILs based on *N*-alkylcaprolactam cations (C_n–CP^+; C_n = alkyl group with *n* C-atoms, *n* = 6, 12, 16, and 18) containing 4-methylbenzenesulfonate (TsO^-) and methanesulfonate (MsO^-) as anions were synthesized [20]. Characterization showed that, except for C_6–CP · TsO, the caprolactam-based ILs demonstrated an enantiotropic thermotropic liquid-crystalline behavior, an enantiotropic smectic A (SmA) mesophase, *i.e.*, those which owe their mesomorphism to thermally induced processes upon heating and cooling. In this work, we report, for the first time, the effect of the ordered solvents on the hydroformylation of oct-1-ene conducted in ILCs based on *N*-alkylcaprolactam and imidazolium cations.

Results and Discussion. – The structures of ILCs investigated in this work and the texture (lamellar SmA mesophase) of the novel caprolactam-based ILCs are shown in *Fig. 1* and *2*, respectively. For the purpose of comparison, general imidazolium-based ILCs, *i.e.*, $[C_{16}MIm] \cdot MsO$ and $[C_{16}MIm] \cdot BF_4$ [21], were chosen due to their known thermotropic ILC characters. The thermal properties of these ILCs are listed in *Table 1*.

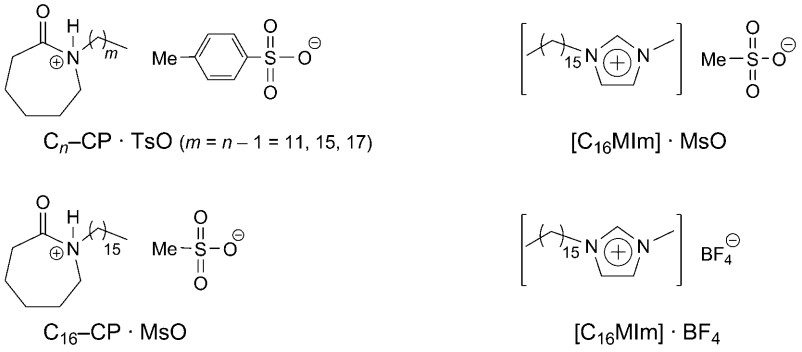


Fig. 1. *ILCs based on the caprolactam cation* (CP^+) *and imidazolium ion* (Im^+)

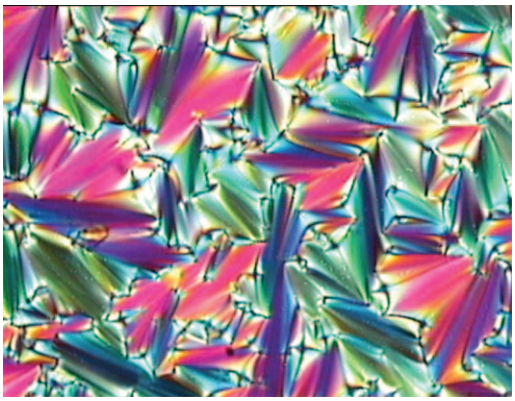


Fig. 2. *The focal conic fanlike texture – SmA of C_{18}–CP·TsO at 110° upon cooling from the isotropic liquid*

Table 1. *Transition Temperatures, Enthalpies, and Liquid-Crystalline Ranges of the C_n–CP·TsO ($n=6$, 12, 16, and 18), C_{16}–CP·MsO, [C_{16}MIm]·MsO, [C_{16}MIm]·BF_4, and [BMIm]·BF_4*[a])

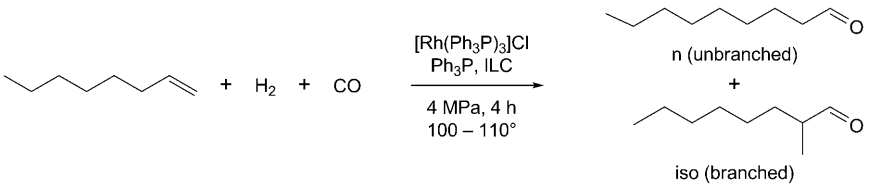
ILCs/ILs	$T_{Cr/SmA}$ [°][b])	ΔH_1 [kJ/mol][c])	$T_{SmA/I}$ [°][d])	ΔH_2 [kJ/mol][e])	ΔT [°][f])
C_6–CP·TsO	95[g])	21.7	–	–	–
C_{12}–CP·TsO	98	52.4	118	2.2	20
C_{16}–CP·TsO	104	70.8	129	1.9	25
C_{18}–CP·TsO	106	83.0	132	1.9	26
C_{16}–CP·MsO	113	38.5	135	0.7	22
[C_{16}MIm]·MsO	75	–	153	–	78
[C_{16}MIm]·BF_4	44	31.5	168	1.7	124
[BMIm]·BF_4	−87[h])	–	–	–	–

[a]) $[BMIm]^+$ = 1-Butyl-3-methyl-1*H*-imidazolium. [b]) $T_{Cr/SmA}$ = Transition temperature from crystal to SmA. [c]) ΔH_1 = Enthalpy from crystal to SmA. [d]) $T_{SmA/I}$ = Transition temperature from SmA to isotropic liquid. [e]) ΔH_2 = Enthalpy from SmA to isotropic liquid. [f]) $\Delta T = T_{Cr/SmA} - T_{SmA/I}$. [g]) Melting point. [h]) Glass transition temperature.

At the reaction temperature, the reaction mixture retained the lamellar mesophase structure, as observed with a polarizing microscope equipped with a temperature-control unit. This indicated that all ILCs were always ordered solvents in the hydroformylation of oct-1-ene to nonanal (n; unbranched) and 2-methyloctanal (iso; branched) in the presence of [$Rh(Ph_3P)_3$]Cl catalyst, independently of the addition of a triphenylphosphine (Ph_3P) ligand (*Scheme*).

The results of the catalytic hydroformylation of oct-1-ene in different ILCs are summarized in *Table 2*. Variation of the chain length (n) of the alkyl substituent (C_n) at the caprolactam cation from $n=12-18$ caused the n/iso (= unbranched/branched) product ratio to increase from 1.7 to 2.9 in the presence of the Ph_3P ligand, and to increase from 1.3 to 1.7 in the absence of the Ph_3P ligand (*Entries 2–4*). However, when these reactions were carried out in the C_6–CP·TsO medium (*Entry 1*), the regioselectivity of the n/iso products was 1.2 in the presence of Ph_3P, and 0.5 in the

Scheme. *Hydroformylation of Oct-1-ene in ILCs*



absence of Ph_3P. These results indicated that in the absence of Ph_3P ligand, the regioselectivity of unbranched to branched product in the longer-chain caprolactam-cation-based ILCs was markedly different from that observed in C_6–CP·TsO, *i.e.*, a shorter-chain ILC. The formation of the n/iso products in the lamellar mesophase was dependent on the chain length of the alkyl group at the caprolactam cation. With increasing the chain length of the alkyl group at the caprolactam cation, an enhancement of the regioselectivity towards the unbranched aldehyde was observed, no matter whether Ph_3P is added (*Entries 2–4*).

In C_{16}–CP·MsO, the catalytic hydroformylation showed a quite reverse performance, as shown by the dramatic change of the n/iso ratio of 1.3–2.9 in C_n–CP·TsO (*Entries 2–4*) to 0.8–0.3 (*Entry 5*) under the same conditions. This meant that, for the caprolactam-based ILCs, the anion exerted a strong influence on the regioselectivity of the products.

We then extended the hydroformylation to imidazolium-based ILCs to measure the catalytic impact on the regioselectivity of the product. As a result, these ILCs gave

Table 2. *Results of Hydroformylation of Oct-1-ene in the Presence of Different Thermotropic ILCs as Solvents* (Condition *A*, see *Fig. 3*)

Entry	ILCs/ILs	Ph_3P	n/iso	Conversion [%]	TOF [mol mol^{-1} h^{-1}][a])
1	C_6–CP·TsO	–[b])	0.5	95	559
		+[c])	1.2	95	744
2	C_{12}–C·TsO	–	1.3	95	168
		+	1.7	85	148
3	C_{16}–CP·TsO	–	1.5	98	172
		+	1.8	94	147
4	C_{18}–CP·TsO	–	1.7	80	79
		+	2.9	86	122
5	C_{16}–CP·MsO	–	0.8	98	500
		+	0.3	89	285
6	[C_{16}MIm]·MsO	–	2.5	96	121
		+	3.7	66	74
7	[C_{16}MIm]·BF_4	–	2.8	71	695
		+	5.2	67	969
8	[BMIm]·BF_4[d])	–	2.6	97	1112
		+	5.0	98	2503

[a]) TOF = turnover frequency. [b]) No Ph_3P ligand added. [c]) Ph_3P ligand added. [d]) $[BMIm]^+$ = 1-Butyl-3-methyl-1*H*-imidazolium.

better regioselectivity towards the unbranched aldehyde than caprolactam-based ILCs, no matter whether the Ph_3P ligand was added or not. Moreover, $[C_{16}MIm]\cdot BF_4$ was at an advantage over $[C_{16}MIm]\cdot MsO$ in the formation of the unbranched aldehyde under the same conditions (*Entries 6* and *7*): the n/iso ratios increased from 2.5 to 2.8 in the absence of Ph_3P and from 3.7 to 5.2 in the presence of Ph_3P. Although the n/iso ratio in caprolactam-based ILCs was lower than that in imidazolium-based ILCs, the conversions were higher in the former ILCs than in the latter on the whole, and no obvious trend in TOF (turnover frequency) was obtained among them. When the short-chain $[BMIm]\cdot BF_4$ was used as solvent, higher conversions and TOFs were obtained (*Entry 8*), despite regioselectivities similar to those of $[C_{16}MIm]\cdot BF_4$ (*Entry 7*).

Furthermore, the hydroformylation reactions of oct-1-ene were carried out in two media, $C_{12}-CP\cdot TsO$ and $[C_{16}MIm]\cdot MsO$, under different reaction conditions in comparison with the standard condition *A*, as shown in *Fig. 3*.

For $C_{12}-CP\cdot TsO$, the n/iso ratio changed largely from 1.7 to 0.3 upon increasing the reaction temperature from 105° (mesophase, condition *A*) to 135° (isotropic liquid phase, condition *B* (*Fig. 3*,*a* (left-hand side)). Meanwhile, the TOF increased from 148 to 206 mol mol^{-1} h^{-1} (*Fig. 3*,*b*), indicating that the isotropic liquid phase is liable to give 2-methyloctanal. Reducing, the reaction time from 4 h to 2 h (condition *C*) resulted in a large increase in the TOF (from 148 to 247 mol mol^{-1} h^{-1}) and a decrease in the conversion (from 85 to 51%). However, no significant change of the n/iso ratio was observed. A decrease of the total pressure from 4 to 2 MPa (condition *D*) caused a decrease of both the conversion and the TOF, and also, the regioselectivity of nonanal reduced to 0.6. From the above results, it can be concluded that in the mesophase, high pressure is favorable to form the unbranched nonanal, but high temperature (isotropic liquid phase) and low pressure are prone to form the branched 2-methyloctanal.

The same comparing experiments were performed in $[C_{16}MIm]\cdot MsO$. The n/iso ratios were slightly less influenced by the reaction temperature and time at high reaction pressure (4 MPa, CO/H_2 1:1; *Fig. 3*,*a* (right-hand side)), but led to an enlarged TOF (*Fig. 3*,*b*; conditions *B* and *C*). More noteworthy, a higher n/iso ratio of 6.8 was achieved at low reaction pressure (condition *D*) which improved the catalytic activity (TOF 255 mol mol^{-1} h^{-1}). Generally, in $[C_{16}MIm]\cdot MsO$, a high reaction temperature was favorable for hydroformylation, giving a relatively high conversion of oct-1-ene (95%) due to the isotropic liquid phase. On the other hand, the oriented long alkyl chain in $[C_{16}MIm]\cdot MsO$ had a highly positive effect on the formation of the unbranched aldehyde in the mesophase at low reaction pressure.

Conclusions. – In summary, hydroformylation of oct-1-ene was carried out in a series of *N*-alkylcaprolactam-based ILCs, as well as in general imidazolium-based ILCs. The results showed that the lamellar mesophase has a strong influence upon the regioselectivity of the reaction product, *i.e.*, the cation, the chain length of the substituent at the cation, and the anion of the ILCs make a full impact on the regioselectivity. On the whole, an imidazolium-based ILC medium is favorable for the formation of nonanal but gives a lower conversion than caprolactam-based ILCs. While $C_{12}-CP\cdot TsO$ has little influence on the formation of the unbranched nonanal in the mesophase under variable reaction conditions, $[C_{16}MIm]\cdot MsO$ as ordered solvent exhibits a much higher n/iso ratio under lower reaction pressure. It is evident that

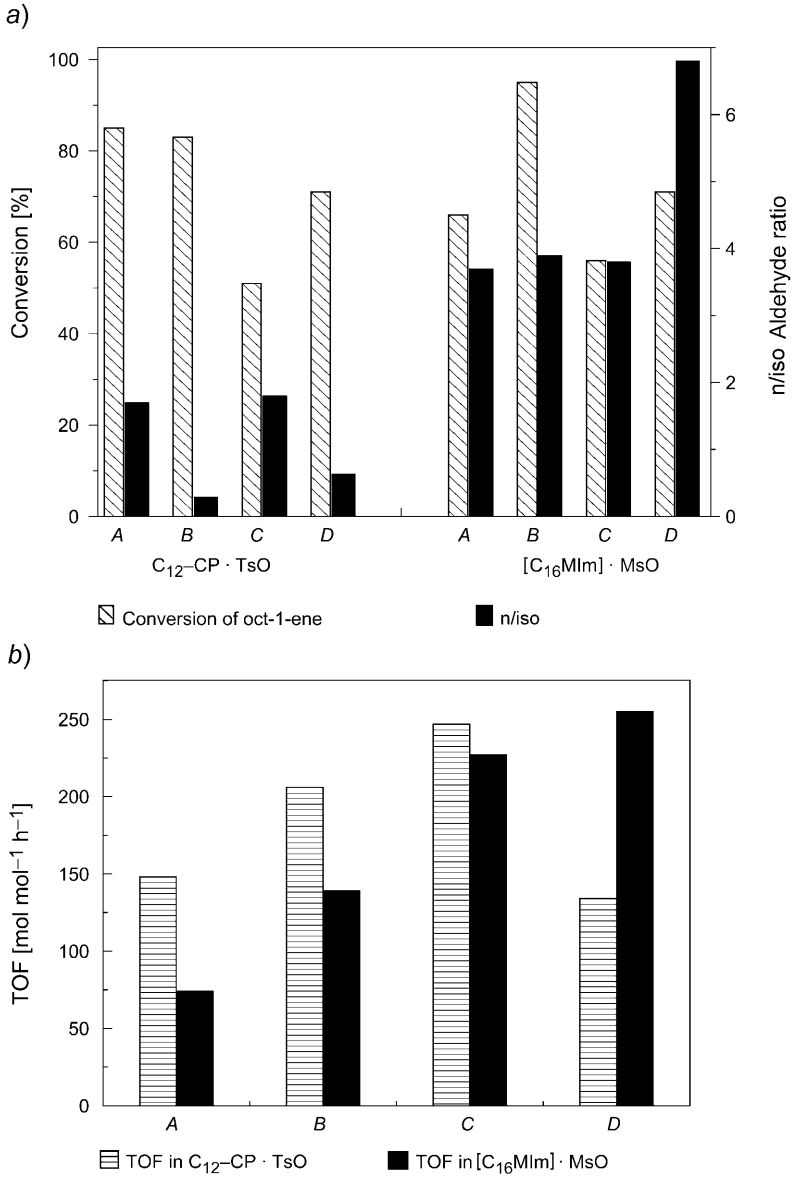


Fig. 3. a) *Conversion and n/iso aldehyde ratio, and* b) *TOF of the catalytic hydroformylation of oct-1-ene in the presence of* Ph_3P *in* $C_{12}-CP \cdot TsO$ *and* $[C_{16}MIm] \cdot MsO$ *under the various reaction conditions* A – D. *A:* At 105° (mesophase) and 4 MPa for 4 h; *B:* at 135° (isotropic liquid) and 4 MPa for 4 h; *C:* at 105° (mesophase) and 4 MPa for 2 h; *D:* at 105° (mesophase) and 2 MPa for 4 h; syngas CO/H_2 1:1.

changing the solvent from $C_{12}-CP \cdot TsO$ to $[C_{16}MIm] \cdot MsO$ as well as changing the other reaction conditions have significant effects on the hydroformylation of oct-1-ene.

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Experimental Part

General. All reagents used in this study were of anal. or chemical grade and were used without further purification, except that Ph_3P (*Shanghai Reagent Corporation Ltd.*) was recrystallized from $CHCl_3$/EtOH before use. The 4-methylbenzenesulfonyl chloride (TsCl) and methanesulfonyl chloride (MsCl), and all alcohols were purchased from the *Shanghai Reagent Corporation Ltd.* and *Taijin Reagent Corporation Ltd.*, resp. Caprolactam and $RhCl_3$ were purchased from the *Beijing Chemical Reagent Company* and *Shanghai New Metal Corporation Ltd.*, resp. The 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate ($[BMIm]\cdot BF_4$) was purchased from *Merck*. H_2 (99.99% pure) and CO (99.99% pure) were used directly from cylinders.

The alkyl sulfonates (alkylation reagents) [22], *N*-alkyl caprolactam-based ILCs [22] (*N*-alkylcaprolactam = 1-alkylhexahydro-2*H*-azepin-2-one), 1-hexadecyl-3-methyl-1*H*-imidazolium methanesulfonate [22] ($[C_{16}MIm]\cdot MsO$), 1-hexadecyl-3-methyl-1*H*-imidazolium tetrafluoroborate [21] ($[C_{16}MIm]\cdot BF_4$), and tris(triphenylphosphine)rhodium(I) chloride ($[Rh(Ph_3P)_3]Cl$) [23], were prepared according to the literature procedures with a slight modification.

Hydroformylation. All experiments were conducted in a 115 ml stainless-steel autoclave (35 mm diameter, 210 mm length) equipped with a 70 ml glass-lining cuvette and a magnetic stirrer. Typical experimental procedure: Oct-1-ene (0.1 g), $[Rh(Ph_3P)_3]Cl$ (0.0015 g), Ph_3P (0.134 g), and $C_{16}-CP\cdot TsO$ (1.2 g) were placed in the glass-lining cuvette. The autoclave was purged two times with H_2, pressurized with 4 MPa initial syngas mixture (CO/H_2 1:1) and then heated at 105° for 4 h. The autoclave was then cooled to r.t. and degassed. The resulting mixture was added to Et_2O (4 ml) and then subjected to centrifugation. The formed aldehydes were mainly in the Et_2O phase. The quant. and qual. analyses were determined by GC (*Agilent 6820*, FID detector, *o*-xylene as an internal standard) and by GC/MS (*HP 6890*/*5973*), resp.

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