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Detailed kinetic study of cumene isopropylation in a liquid–liquid biphasic system using acidic chloroaluminate ionic liquids

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ABSTRACT

A kinetic study of cumene isopropylation has been carried out using the acidic ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl)/$AlCl_3$ (molar ratio 1:2) as the catalyst phase in a semi-batch liquid–liquid biphasic reaction system. Kinetic models representing the alkylation reaction network have been established based on reaction temperature and propylene partial pressure variations. By comparing the results of the kinetic models with the measured concentrations in the liquid organic phase, the importance of the different product solubilities in the acidic ionic liquid became evident. Correction of the product concentrations in the organic phase based on a COSMO-RS calculation of the relative product solubilities in the acidic ionic liquid [EMIM][Al_2Cl_7] gave a remarkably good prediction of the reaction kinetics by the kinetic model. These findings demonstrate the suitability of COSMO-RS to predict the relative solubilities of different aromatic compounds in highly reactive catalytic systems.

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1. Introduction

Friedel–Crafts alkylation of aromatic substances is a major route of producing alkylated arenes at industrial scale. The reaction is catalysed by either Lewis or Brønsted acid catalysts and many applications still use homogeneous aluminium(III) chloride [1]. A major disadvantage of the current available homogeneous processes is the need to separate the reaction mixture from the catalyst through a hydrolysis step in which the catalyst is decomposed and extracted to the aqueous phase. Alkylations using heterogeneous catalysts mostly give quite low conversion and require relatively extreme reaction conditions. The latter often trigger oligomerisation [2] or even coke formation [3].

The application of acidic ionic liquids has opened the possibility to immobilise the acidic active species in an ionic phase, immiscible with the liquid product layer. The investigated reactions in such systems include the alkylation of benzene and toluene with alkyl halide [4,5], linear alkyl benzene production [6], alkylation of aromatics using alkenes [7] and alkylation of isobutene with 2-butene (refinery alkylation) [8]. Recent developments showed that ionic liquids of the type [cation][$(CF_3SO_2)_2N$]/$AlCl_3$ are able to dissolve significantly higher amounts of $AlCl_3$ than the conventional systems of type [cation][Cl]/$AlCl_3$ [9]. Furthermore, application of such system in a continuous loop reactor was demonstrated for toluene isopropylation and the catalyst was found to be active over more than 15 h time on stream [10].

Surprisingly, despite all the above mentioned progress in the use of acidic ionic liquid systems, there are—to the best of our knowledge—no detailed kinetic studies in the field of ionic liquid catalysed Friedel–Crafts alkylations. In this paper we present a first kinetic study of the isopropylation of cumene catalysed by Lewis-acidic imidazolium chloroaluminate melts. The aim of the study is to provide important information for the further optimisation of the reaction system towards a potential commercial application.

2. Experimental and methods

2.1. Chemicals

Cumene of 99.0% purity (Acros Organic) was applied as aromatic compound together with propylene 2.8 (99.8%) from Linde as alkylating agent. Water content of cumene was confirmed to be below 20 ppm.

1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) was purchased from Solvent Innovation GmbH, Cologne and used without further purification. Toluene (BASF) was used after reaction to dilute the samples for GC analysis. Aluminium(III) chloride was purchased from Merck and used without further purification.

For measuring the solubility of cumene (99% from Acros Organic), 1,3-diisopropylbenzene (96% from Alfa Aesar) and 1,3,5-triisopropylbenzene (>97% from Alfa Aesar) in the chloroaluminate ionic liquids by ^{1}H-NMR spectroscopy, deuterated dichloromethane from Fluka was applied as NMR solvent.

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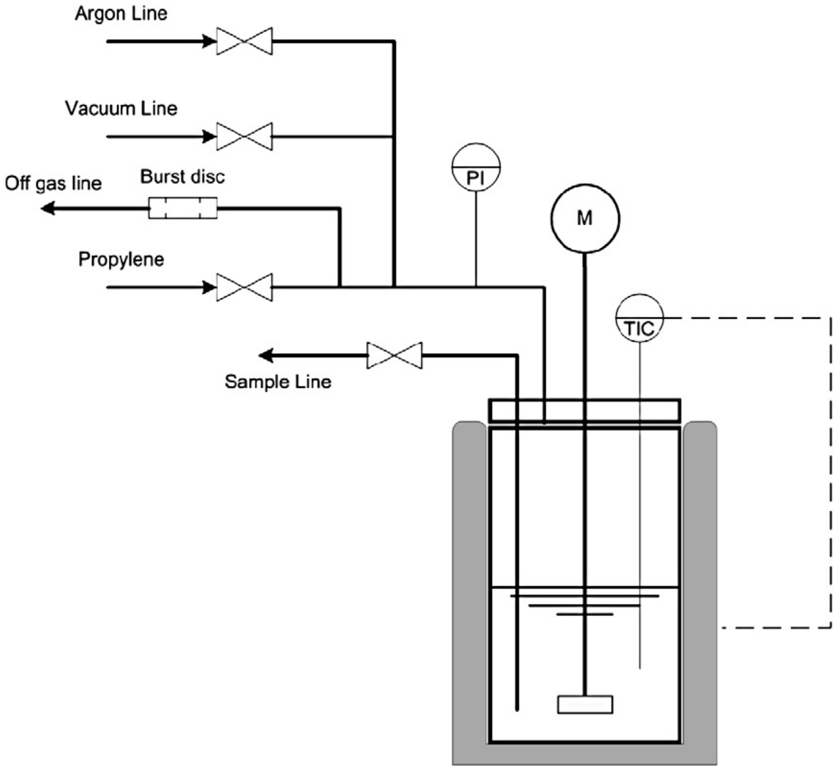


Fig. 1. Reactor set up for liquid–liquid biphasic isopropylation of cumene/meta-xylene using acidic ionic liquid.

2.2. Kinetic experiments

Experiments were carried out in a 600 mL Parr autoclave (see Fig. 1) equipped with a PARR four blade-gas entrainment stirrer of 3.2 cm diameter. Prior to the reaction, the autoclave was stored in an oven at 90 °C for 24 h to avoid any moisture contamination during reaction. The organic phase consisted at the beginning of the reaction of the extraction solvent and the aromatic substrate (in a molar ratio 9:1). The reaction was carried out in a glass liner placed into the autoclave. The glass liner was pre-heated before use in an oven (90 °C) and was filled previously with argon to avoid moisture contamination during weighing.

The catalyst was prepared by mixing a 2:1 molar ratio of $AlCl_3$ and [EMIM]Cl respectively at 70–80 °C in a Schlenk flask until complete dilution of $AlCl_3$ and a clear liquid was obtained. The desired amount of the catalyst phase was then placed into the glass liner using a syringe. Once the glass liner was placed inside the autoclave, the reactor was evacuated using a vacuum pump at room temperature for about two to three minutes followed by argon flushing. This procedure was repeated three times. The reactor was then heated up to the desired temperature using an external electrical heating jacket. Upon reaching the desired temperature, the reactor was connected to the propylene bottle with a defined outlet pressure and a sample was taken for reference. The propylene partial pressure was set in such way that approximately 20 mol% of propylene existed in the saturated organic phase at each temperature. The required propylene partial pressure can be seen from Table 1.

The reaction started ($t = 0$) when the gas entrainment stirrer was turned on. To achieve a good gas entrainment and saturation of the liquid phase the stirring rate was set to 1200 rpm. In order to get a first qualitative information on the reaction progress, an analytical balance was used to monitor the weight loss of the propylene bottle. Samples of 1 mL were taken through a capillary tube from the organic phase and since the total amount required for these GC analyses was very small compared to the volume of the organic phase, the total reaction volume was considered to be constant. Each sample taken from the reactor was further diluted with toluene and neutralised (using a mixture of solid magnesium sulphate and sodium carbonate) before being analysed by gas chromatography.

Table 1
Required propylene partial pressure for various reaction temperatures to adjust 20 mol% propylene in the organic phase

Temperature	Propylene partial pressure[a]
50 °C	3.6 bar
70 °C	4.7 bar
90 °C	6.3 bar
110 °C	8.5 bar

[a] Estimated using ASPEN PLUS simulator using NRTL thermodynamic model.

2.3. GC analysis

Samples were analysed by means of gas chromatography (Varian CP-3900) using a *WCOT* fused silica column (0.21 mm diameter and 50 m). The gas chromatograph was equipped with a Flame Ionisation Detector (FID) working at 270 °C.

The molar amount of each substance in the analysed reaction volume was calculated based on the mass fraction of each substance, the mass fraction of cyclohexane as standard multiplied by a correction factor as seen in Eq. (1) with C_F being the correction factor of the GC and M_w being the molecular weight of the analysed substance.

$$n_i = C_F \cdot \frac{\%m_i \cdot m_{\text{standard}}}{\%m_{\text{standard}} \cdot M_{w,i}}. \tag{1}$$

Since there were only negligible volumes of samples taken out of the reactor during the kinetic studies, the amount of standard substance in the reactor can be considered to be constant throughout the reaction.

2.4. Data processing

The kinetic model was fitted based on the molar amount/time profiles for each substance involved in the model. The modelled ordinary differential equations for the reaction network were solved using the explicit Runge–Kutta pair of Bogacki and Shampine [11]. The fitting procedure was carried out by iterating the reaction order and reaction rate constant in order to minimise the sum of square error between the calculated model and the experimental values. This was carried out using a non-linear optimisation algorithm as described in the literature [12].

2.5. NMR solubility experiment

Solubility measurements of aromatic compounds in chloroaluminate ionic liquids were carried out using ^{1}H NMR spectroscopy. The samples were prepared by mixing the aromatic compound under investigation (cumene, diisopropylbenzene or triisopropylbenzene, respectively) and cyclohexane in an equimolar amount. 5 g of each of these organic solutions were intensively mixed (24 h, 500 rpm to ensure equilibrium conditions) with 5 g of the chloroaluminate ionic liquid. After stirring, the ionic liquid phase was separated under inert atmosphere and analysed by ^{1}H NMR using a JEOL ECX400 spectrometer (400 MHz).

2.6. Diffusion coefficient measurements using NMR-diffusion ordered spectroscopy (DOSY)

The diffusion coefficients of cumene, 1,3-diisopropylbenzene and 1,3,5-triisopropylbenzene in the chloroaluminate ionic liquid were determined using NMR-Diffusion Ordered Spectroscopy (DOSY) technique. This method has been widely applied in determining diffusion coefficient of organic matters as well as self diffusion coefficient of ion-pairs in ionic liquids as described in various literatures [13]. For the DOSY measurements samples of 2.5 g of each of the aromatic substance with 2.5 g of the chloroaluminate ionic liquid were prepared. After stirring the mixture for 24 h the molecular diffusion of the investigated aromatic molecule was observed by applying magnetic field gradients. Based on the aromatic molecule movement from one magnetic field zone to another at a given temperature one can determine the diffusion coefficient of the observed aromatic substance in ionic liquid phase. For our DOSY measurements, 0.1 s and 0.003 s were used as diffusion time and gradient time respectively. Magnetic fields of 30–300 mT min^{-1} were applied.

3. Results and discussions

Kinetic investigation of cumene isopropylation was carried out in the temperature range between 50 °C and 110 °C. Based on the experimental protocol (see above), the following assumptions for the modelling were applied:

1. Propylene is assumed to reach its saturated concentration in the liquid organic phase due to the effectiveness of the gas entrainment stirrer and the applied high mixing rate.
2. Since propylene is present in excess in the liquid organic phase (in comparison to cumene) and it is fed continuously, all reactions are assumed to be not limited by propylene availability.
3. The amount of cumene is very low in comparison to the solvent so that the propylene concentration in the liquid organic phase can be assumed to be constant.

3.1. Kinetic model for the isopropylation of cumene

The reaction network of cumene isopropylation is described in Eq. (2) with k and ε being the reaction rates constant and the reaction coordinates, respectively. The first subscript refers to the isopropylation reaction of cumene (subscript = 1) while the second subscript refers to the single, double and triple alkylation reaction, respectively,

$$\begin{aligned}
&C_6H_5(C_3H_7) + C_3H_6 \xrightarrow{k_{1-1};\,\varepsilon_{1-1}} C_6H_4(C_3H_7)_2,\\
&C_6H_4(C_3H_7)_2 + C_3H_6 \xrightarrow{k_{1-2};\,\varepsilon_{1-2}} C_6H_3(C_3H_7)_3,\\
&C_6H_3(C_3H_7)_3 + C_3H_6 \xrightarrow{k_{1-3};\,\varepsilon_{1-3}} C_6H_2(C_3H_7)_4.
\end{aligned} \tag{2}$$

For simplicity sake let A = cumene, B = diisopropylbenzene (DIPB), C = triisopropylbenzene (TIPB) and D = tetraisopropylbenzene (TeIPB). The reaction rate expression for each reaction can now be written as follows:

$$\begin{aligned}
r_1 &= k'_{1-1}\cdot C_A^{nA} \quad \text{with } k'_{1-1} = k_1\cdot C_{\text{propylene}}^{np1},\\
r_2 &= k'_{1-2}\cdot C_B^{nB} \quad \text{with } k'_{1-2} = k_2\cdot C_{\text{propylene}}^{np2},\\
r_3 &= k'_{1-3}\cdot C_C^{nC} \quad \text{with } k'_{1-3} = k_3\cdot C_{\text{propylene}}^{np3}.
\end{aligned} \tag{3}$$

The modified reaction rate constant k' contains the propylene concentration term as it was fed continuously throughout the reaction and assumed to be constant over time. A mass balance of the liquid organic phase for a discontinuous system gives equation:

$$\begin{aligned}
\frac{dn_A}{dt} &= -r_1\cdot V_r,\\
\frac{dn_B}{dt} &= (r_1 - r_2)\cdot V_r,\\
\frac{dn_C}{dt} &= (r_2 - r_3)\cdot V_r.
\end{aligned} \tag{4}$$

Moreover the molar amount of each substance at a given time can be described as functions of reaction coordinate:

$$\begin{aligned}
n_A(t) &= n_{A0} - \varepsilon_{1-1}(t),\\
n_B(t) &= n_{B0} + \varepsilon_{1-1}(t) - \varepsilon_{1-2}(t),\\
n_C(t) &= n_{C0} + \varepsilon_{1-2}(t) - \varepsilon_{1-3}(t).
\end{aligned} \tag{5}$$

Substituting Eqs. (5) and (3) into Eqs. (4) gives a set of coupled differential equations as shown in Eq. (6):

$$\begin{aligned}
\frac{d\varepsilon_{1-1}}{dt} &= k'_{1-1}\cdot V_r^{(1-nA)}\cdot(n_{A,0} - \varepsilon_{1-1})^{nA},\\
\frac{d\varepsilon_{1-2}}{dt} &= k'_{1-2}\cdot V_r^{(1-nB)}\cdot(n_{B,0} + \varepsilon_{1-1} - \varepsilon_{1-2})^{nB},\\
\frac{d\varepsilon_{1-3}}{dt} &= k'_{1-3}\cdot V_r^{(1-nC)}\cdot(n_{C,0} + \varepsilon_{1-2} - \varepsilon_{1-3})^{nC}.
\end{aligned} \tag{6}$$

To get the activation energy and the reaction order of cumene isopropylation, the above mentioned model was fitted to the experimental results at reaction temperature of 50 °C, 70 °C, 90 °C and 110 °C. Interestingly, our experiments revealed a significant discrepancy between the molar amount of consumed cumene and the sum of all alkylated products analysed in the organic phase (for details see supporting information). When these experimental values were directly fitted to the model, noticeable "delay" behaviour was observed. This can be seen in Fig. 2 as the shaded area **I**, **II** and **III** for DIPB, TIPB and TeIPB, respectively.

We assumed that the delayed, S-shaped profile of the alkylated products can be explained by the fact that reaction products first accumulate in the acidic ionic liquid phase before they diffuse out into the liquid organic phase where samples were taken and analysed. The different behaviour for cumene would be explained—according to the same assumption—by the fact that cumene and the ionic liquid phase had been in contact during reaction start up and therefore considered to be in equilibrium with the ionic liquid phase right from the start of the reaction.

3.2. Experimental and COSMO-RS-based estimation of aromatic solubility in a non-acidic [EMIM]Cl/AlCl$_3$ mixture

To confirm our assumption we aimed to determine the solubility of all relevant aromatic compounds in the acidic chloroaluminate ionic liquid. As a suitable method to determine the solubility of organic substances in ionic liquids we chose ^{1}H NMR spectroscopy. The method allows to compare the signal intensity of a characteristic ionic liquid cation signal with a characteristic signal of the dissolved aromatic compound and to determine in this way the molar solubility.

However, in the case of acidic chloroaluminate ionic liquid, this procedure was impossible due to the fact that the acidic ionic liquid catalyst phase started to react with the aromatic substances under investigation during the time of the NMR solubility experiment. A typical ^{1}H NMR spectrum of the ionic liquid phase for a cumene/cyclohexane-acidic ionic liquid ([EMIM]Cl/AlCl$_3$ = 1:2) system is shown in Fig. 3c (spectrum was taken at 19 °C 30 min after addition of the ionic liquid to the organic mixture). Remarkably, almost no cumene could be detected in this spectrum as can be seen by the missing "fingerprint" of the tertiary carbon of the isopropyl group. Moreover, appearance of the single peak at 7.34 ppm

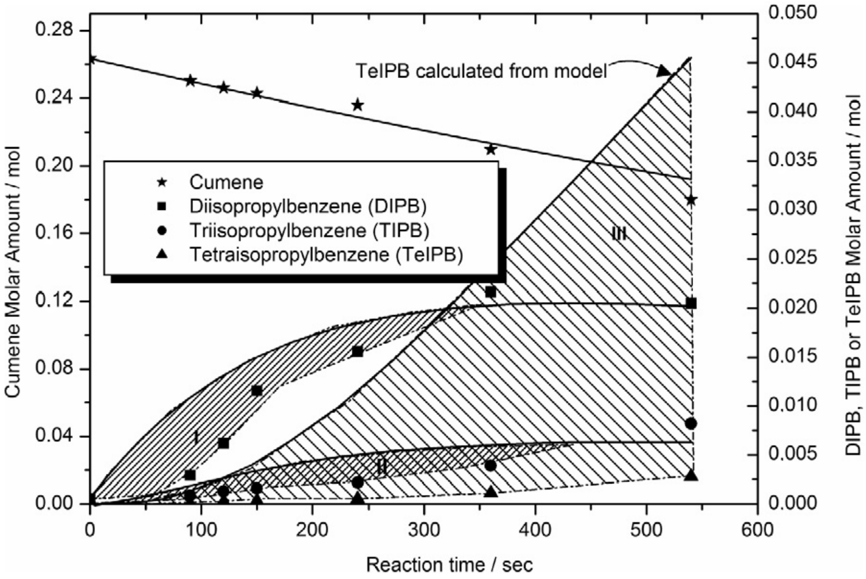
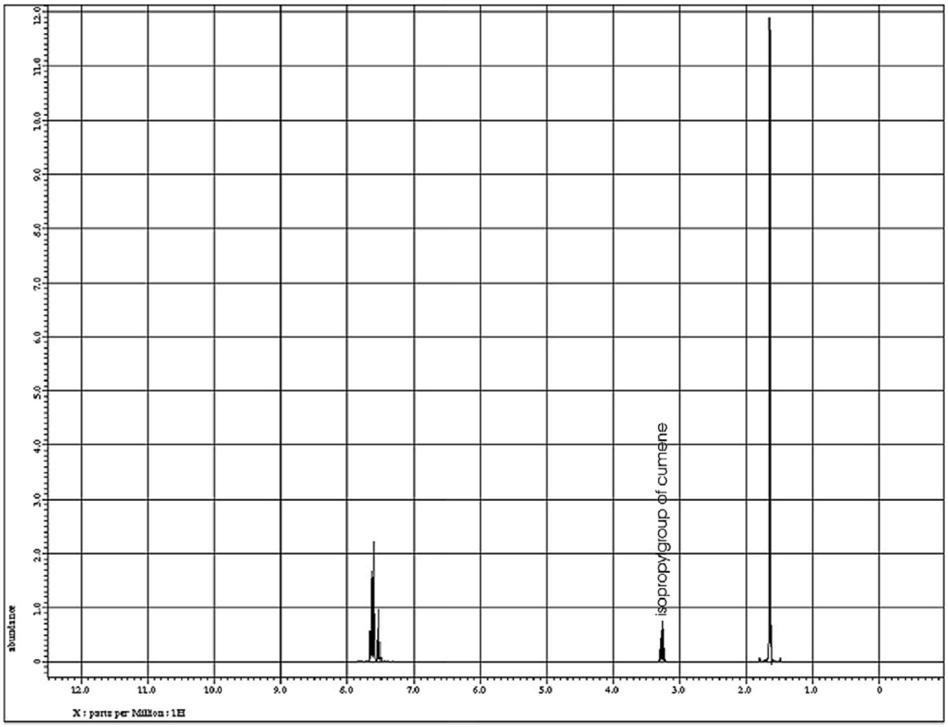
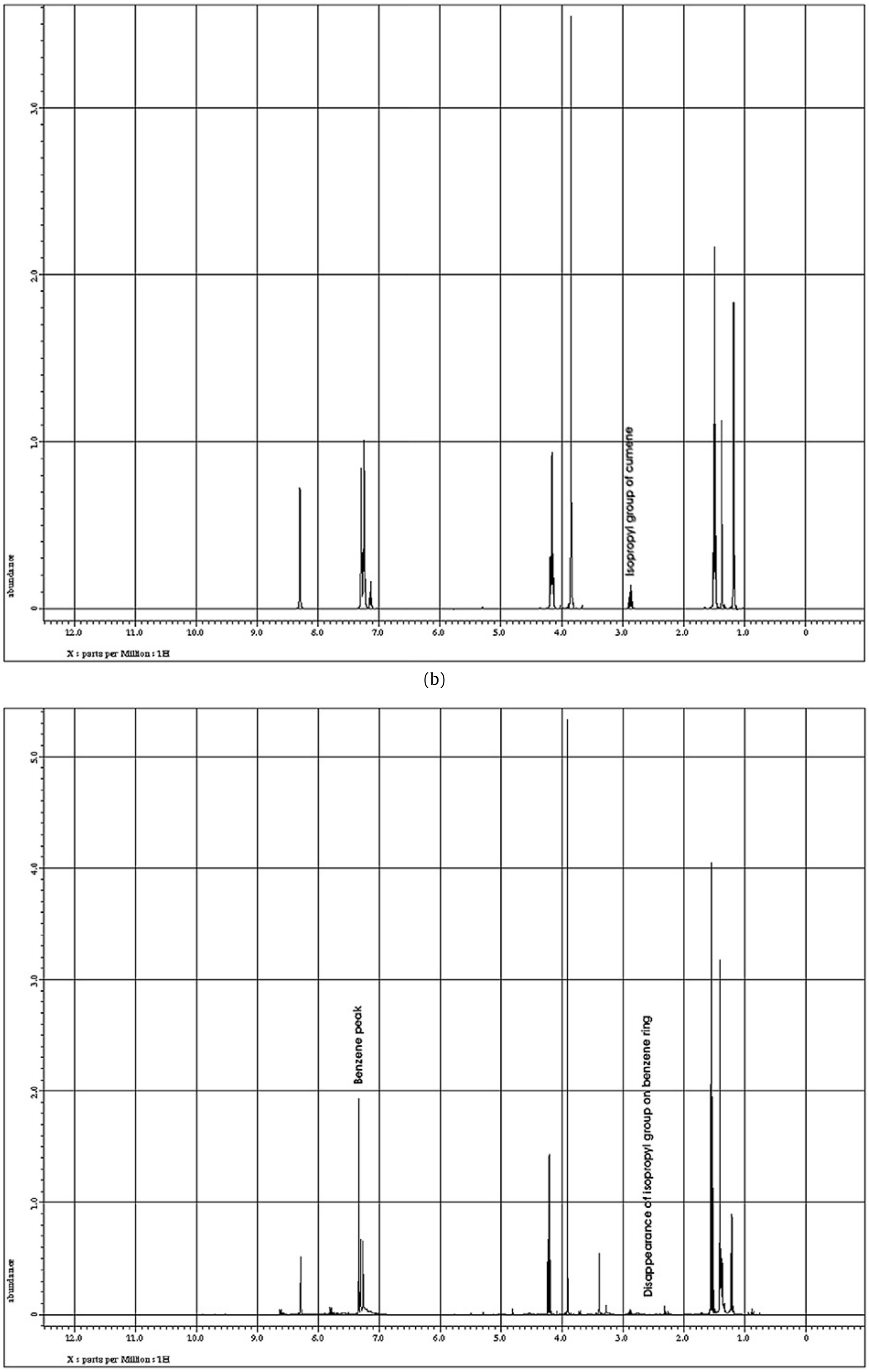


Fig. 2. Fitting result for cumene isopropylation at 50 °C taking only the products analysed from the liquid organic phase. $T_{react} = 50\,°C$; $p_{Tot} = 3.6$ bar; [EMIM]Cl/AlCl$_3$ = 1:2; [cumene] = 8.3×10^{-4} mol mL^{-1}; solvent = cyclohexane.



(a)

Fig. 3. Typical ionic liquid phase ^{1}H NMR of cyclohexane–cumene–ionic liquid system in equilibrium at room temperature: (a) cumene reference, (b) ionic liquid = [EMIM]Cl/AlCl$_3$ = 1:1, (c) ionic liquid = [EMIM]Cl/AlCl$_3$ = 1:2.



(b)

(c)

Fig. 3. (*continued*)

indicates benzene formation by cumene dealkylation. This result emphasizes the difficulty of solubility measurement in highly reactive systems.

It is important to note that the dealkylation reaction observed in these NMR solubility experiments does not play a significant role in the kinetic experiments. Almost no formation of benzene was observed in the kinetic experiments so that all reactions in the kinetic experiments can be assumed to be irreversible. The reason for this difference is that the NMR solubility measurements have been recorded in absence of propylene while all kinetic experiments have been carried out in the presence of excess propylene.

As one attractive possibility to overcome these practical difficulties of solubility measurements in highly reactive systems we identified the option to model the partition coefficient of each aromatic substance using the Conductor-like Screening Model for Real Solvent (COSMO-RS) [14].

However, there is—to the best of our knowledge—no report so far in the literature describing the usefulness of COSMO-RS to predict the solubility of organic substances in chloroaluminate ionic liquids. Therefore, we had to confirm in first place the reliability of this method for chloroaluminate ionic liquids.

Table 2
Comparison of COSMO-RS estimated partition coefficient with experimental results[a]

No.	Aromatic (Ar)	Experimental values						COSMO-RS estimation			
		$X_{\mathrm{Ar,org\ init}}$	$X_{\mathrm{Ar,org\ end}}$	$X_{\mathrm{Ar,IL\ end}}$	$X_{\mathrm{solvent,IL\ end}}$	P_i	S_i[b]	$\gamma_{\mathrm{Ar,org}}$	$\gamma_{\mathrm{Ar,IL}}$	P_i[c]	S_i
1	Cumene	0.502	0.465	0.210	0.089	0.453	1.000	0.090	2.338	0.039	1.000
2	1,3-diisopropylbenzene	0.502	0.504	0.067	0.073	0.134	0.296	0.035	4.087	0.009	0.223
3	1,3,5-triisopropylbenzene	0.500	0.511	0.020	0.059	0.039	0.087	0.014	5.731	0.003	0.065

[a] Solvent = cyclohexane; IL = [EMIM]Cl/AlCl$_3$ = 1:1; organic mixture: IL = 1:1 mass ratio.
[b] S_i = relative solubility based on individual partition coefficient = P_i/P_j.
[c] Estimated partition coefficient from COSMO-RS based on the activity coefficient according to thermodynamical equilibrium criteria where $x_{i,\mathrm{phase\,1}}/x_{i,\mathrm{phase\,2}} = \gamma_{i,\mathrm{phase\,2}}/\gamma_{i,\mathrm{phase\,1}}$.

$$[\mathrm{EMIM}]\mathrm{Cl} + \mathrm{AlCl_3} \rightleftharpoons [\mathrm{EMIM}][\mathrm{AlCl_4}]$$

$$[\mathrm{EMIM}][\mathrm{AlCl_4}] + \mathrm{AlCl_3} \rightleftharpoons [\mathrm{EMIM}][\mathrm{Al_2Cl_7}]$$

$$[\mathrm{EMIM}][\mathrm{Al_2Cl_7}] + \mathrm{AlCl_3} \rightleftharpoons [\mathrm{EMIM}][\mathrm{Al_3Cl_{10}}]$$

Scheme 1. Various ionic species present in an equilibrium condition of [EMIM]Cl/AlCl$_3$ mixture [16].

To achieve this, we decided to compare experimental NMR solubility data for neutral, non-reactive [EMIM][AlCl$_4$] with COSMO-RS derived partition coefficients for the same ionic liquid under the same conditions of the experiment (19 °C).

The COSMO-RS simulation incorporates two crucial assumptions. The first assumption is that the modelled ionic liquid phase consist of only [EMIM][AlCl$_4$] species, which is very well fulfilled for a [EMIM]Cl/AlCl$_3$ mixture in a 1:1 molar ratio [15,16]. The second assumption considers cyclohexane to be completely immiscible with the ionic liquid phase. Also this pre-condition can be regarded to be in good agreement with the experimental reality. Table 2 shows the results of our COSMO-RS modelling. It can be seen that COSMO-RS gives only a very crude estimation of the absolute experimental partition coefficient values. However, the relative partition coefficient values (P_i/P_{cumene}) given by COSMO-RS simulation represent the experimental values remarkably well.

This fit between the COSMO-RS predicted and the experimentally determined, relative partition coefficients of cumene, 1,3-diisopropylbenzene and 1,3,5-triisopropylbenzene in the neutral [EMIM][AlCl$_4$] ionic liquid, justified the next step in our study, namely the COSMO-RS simulation of the relative partition coefficients for an acidic, reactive ionic liquid. Using the COSMO-RS estimated, relative partition coefficients for the acidic ionic liquid system (which cannot be experimentally verified, see above) we aimed to support our hypothesis that the dissolved alkylation products in the acidic ionic liquid phase account for the unusual S-shaped product curves observed in the experiments.

3.3. COSMO-RS based partition coefficients estimation for highly acidic ionic liquid systems

Unfortunately, the situation in the acidic ionic liquid of interest, [EMIM]Cl/AlCl$_3$ (molar ratio: 1:2) is significantly more complex than in the case of the neutral ionic liquid. This is due to the fact that the acidic chloroaluminate system consists of a mixture of anions [15] (see Scheme 1).

For our COSMO-RS simulation we decided to simplify the complex ionic liquid anion mixture and considered the acidic ionic liquid to be pure [EMIM][Al$_2$Cl$_7$]. This simplification appeared acceptable as a 1:2 molar ratio of [EMIM]Cl and AlCl$_3$ (as used in our experiments) is known to contain almost 80 mol% of the anion [Al$_2$Cl$_7$]$^-$ and only 20 mol% of other anionic species [16].

Fig. 4 shows the key result of the COSMO-RS calculation, namely the fact that an increasing degree of alkylation at the aromatic ring decreases the solubility of that aromatic compound in the acidic ionic liquid drastically. Moreover, our calculations indicate that the solubility of each aromatic substance in the acidic ionic liquid phase increases slightly with temperature.

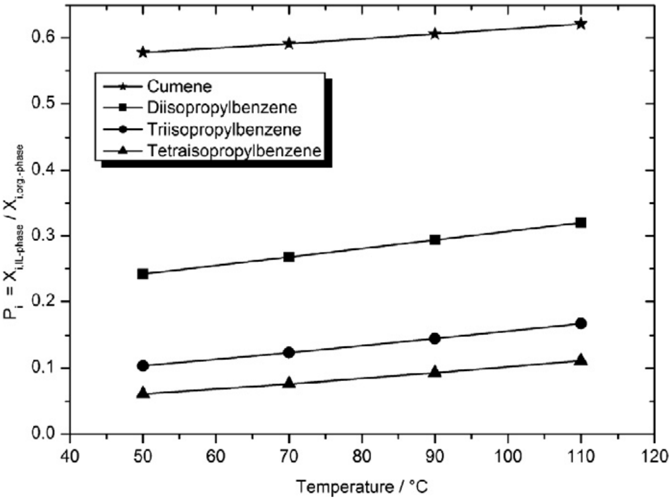


Fig. 4. Relative solubility of cumene, DIPB, TIPB and TeIPB in [EMIM][Al$_2$Cl$_7$] vs. cyclohexane as calculated at various temperatures using COSMO-RS. Solvent = cyclohexane; ionic liquid = [EMIM][Al$_2$Cl$_7$].

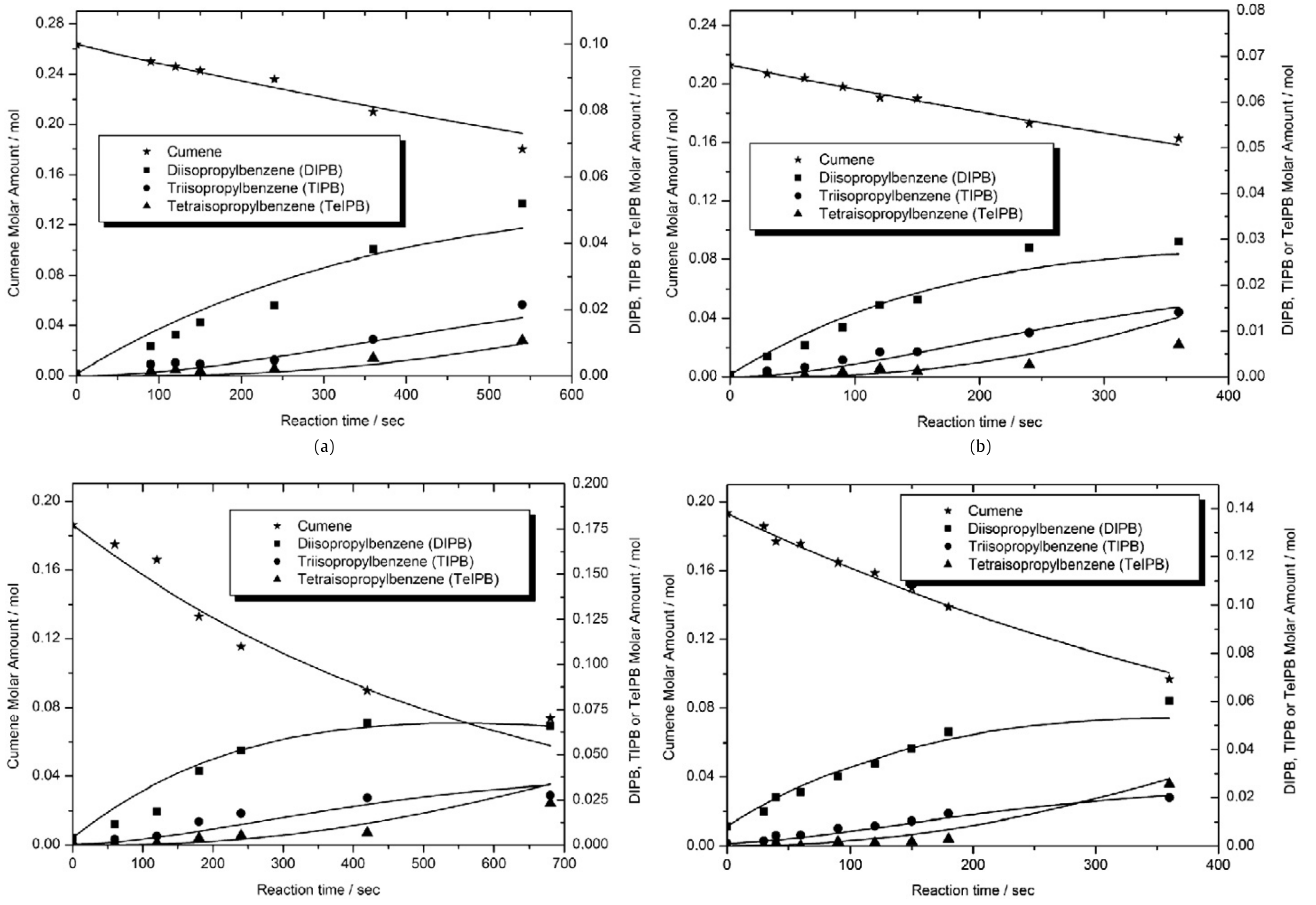
The relative solubility (S_i) of DIPB, TIPB and TeIPB in the acidic ionic liquid phase has been calculated using equation:

$$S_i = \frac{P_i}{P_{\mathrm{DIPB}} + P_{\mathrm{TIPB}} + P_{\mathrm{TeIPB}}}, \quad i = \mathrm{DIPB,\ TIPB\ or\ TeIPB}. \tag{7}$$

The next step in our efforts to explain the experimentally observed S-shape behaviour in the concentration/time plot was to use the calculated relative partition coefficients and relative solubilities to correct the product analyses from the organic phase during the kinetic experiments. The corrected molar amount of each alkylated product at each reaction temperature was obtained by proportionally distributing the observed missing molar amount of feedstock (cumene) using the relative solubility factors (S_i) calculated via the COSMO-RS method. The corrected molar amount of each substituted product for cumene isopropylation is provided in the supporting information.

It is important to point out that in such reacting system an equilibrium condition between organic phase and the ionic liquid phase is very unlikely to be reached. However, by implementing the relative solubilities as correction factors we estimate the relative driving forces for mass transfer of one specific aromatic compound from the reactive phase into the organic phase to be proportional to the distribution of this specific substance between the ionic liquid and the organic phase.

In fact, by applying the solubility corrected values for the formation of aromatic products in the cumene isopropylation system, the kinetic model (see Eq. (6)) shows a much better agreement than before (compare Figs. 2 and 5).



(a) (b)

(c) (d)

Fig. 5. Model-fitted results for cumene isopropylation reaction using corrected datasets based on proportionality factor estimated by COSMO-RS. [EMIM]Cl/AlCl$_3$ = 1:2; solvent = cyclohexane; [cumene] = app. 8.3×10^{-4} mol mL^{-1}; Cat:cumene = 1:25: (a) $T_{\text{react}} = 50\,^{\circ}\text{C}$, $p_{\text{Tot}} = 3.6$ bar; (b) $T_{\text{react}} = 70\,^{\circ}\text{C}$, $p_{\text{Tot}} = 4.7$ bar; (c) $T_{\text{react}} = 90\,^{\circ}\text{C}$, $p_{\text{Tot}} = 6.3$ bar; (d) $T_{\text{react}} = 110\,^{\circ}\text{C}$, $p_{\text{Tot}} = 8.5$ bar.

Table 3
Fitted kinetic parameters for cumene isopropylation[a]

	Cumene → DIPB	DIPB → TIPB	TIPB → TeIPB
Reaction order	0.99	1.04	1.05
Reaction rate constant (50 °C)	5.82×10^{-4} s^{-1}	1.91×10^{-3} s^{-1}	2.68×10^{-3} s^{-1}
Reaction rate constant (70 °C)	8.23×10^{-4} s^{-1}	4.65×10^{-3} s^{-1}	5.93×10^{-3} s^{-1}
Reaction rate constant (90 °C)	1.71×10^{-3} s^{-1}	1.92×10^{-3} s^{-1}	3.20×10^{-3} s^{-1}
Reaction rate constant (110 °C)	1.80×10^{-3} s^{-1}	3.49×10^{-3} s^{-1}	7.72×10^{-3} s^{-1}

[a] For reaction condition refer to Fig. 5.

The same correction procedure was therefore carried out for all other reaction temperatures. The results are also displayed in Fig. 5. By fitting the model to the COSMO-RS corrected values, the reaction order of cumene, diisopropylbenzene and triisopropylbenzene for the main, first consecutive and second consecutive alkylation reaction respectively was found to be first order (see Table 3).

For proper interpretation of the data in Fig. 5 it should be noted that the varying molar amounts of aromatic substances at initial condition ($t = 0$) are due to slightly varying reaction volumes in the individual experiments while concentrations and concentration ratios were kept constant in all experiments.

As expected, the observed reaction rate constants increase for higher consecutive alkylation reaction which is in agreement with the fact that the already alkylated products have a higher reactivity due to the higher electron density in their aromatic ring.

The formal activation energies for the reaction network were determined by plotting the logarithmic value of the reaction rate constant against $1/T$ in an Arrhenius diagram. It is important to note that the temperature dependency of propylene solubility is included in the here determined $E_{\text{A,eff}}$ value. Remarkably, all reaction steps show relatively low $E_{\text{A,eff}}$ values in the liquid–liquid biphasic system (see Fig. 6). Due to the fact that we consider a pseudo-one-component system (where propylene solubility and its temperature dependency are contained in the reaction rate constant of the model) the formal effective activation energy values of the biphasic alkylation reaction presented in this work cannot be directly compared to other published examples of homogeneous alkylation reactions [17a] and solid acid catalysed alkylation systems [17b] for which activation energies have been reported in the range of 40 to 90 kJ mol^{-1}.

In order to find out whether the observed, relatively low $E_{\text{A,eff}}$ values have to be attributed to mass transfer effects an estimation of Hatta number (Ha) [18] was carried out for our liquid–liquid biphasic alkylation catalysis. The mathematical form of the Hatta number for a first order reaction is given in Eq. (8). In our case,

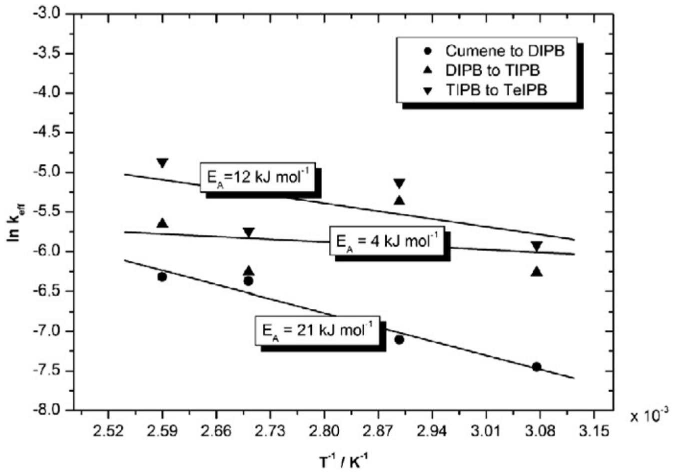


Fig. 6. Effective activation energy ($E_{A,\mathrm{eff}}$) for main, first and second consecutive alkylation for cumene isopropylation reaction.

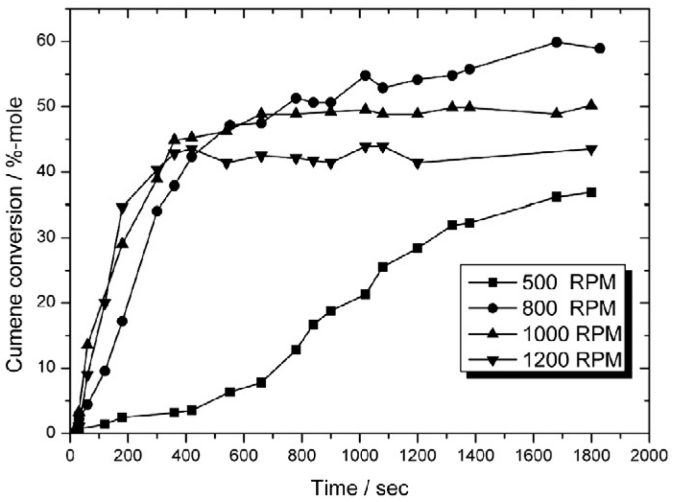


Fig. 7. Cumene conversion in strongly diluted reaction system at various stirring rate. $p_{\mathrm{Tot}} = 6.3$ bar; $T_{\mathrm{react}} = 90\,°\mathrm{C}$; [EMIM]Cl/AlCl$_3$ = 1:2; Cat:cumene = 1:50; [cumene] = 8.3×10^{-4} mol mL^{-1}.

the Hatta number represents the ratio of chemical reaction rate in the ionic liquid phase versus the rate of mass transport of the aromatic feedstock into the ionic liquid phase.

$$\mathrm{Ha} = \frac{1}{k_{i,\mathrm{IL}}} \cdot \sqrt{k \cdot D_{i,\mathrm{IL}}} \tag{8}$$

with $k_{i,\mathrm{IL}}$-mass transfer coefficient of aromatic component "i" in the ionic liquid phase ($\mathrm{m\,s^{-1}}$); k-intrinsic reaction rate constant of pseudo-first order reaction ($\mathrm{s^{-1}}$); $D_{i,\mathrm{IL}}$-diffusion coefficient of aromatic component "i" into the ionic liquid phase ($\mathrm{m^2\,s^{-1}}$).

Since intrinsic reaction rate constant is required for such estimation, additional experiments with highly diluted organic and catalyst phases were carried out at 90 °C. By varying the stirring rate of the gas entrainment stirrer (see Fig. 7) we could demonstrate that the reaction rate (i.e. cumene depletion rate) in these highly diluted systems are independent on stirring rate for rates greater than 800 rpm. Consequently, reaction rate constants determined under these conditions can be interpreted as intrinsic reaction rates that are not influenced by any mass transfer influence. The following intrinsic reaction rate constants were determined in this way: Isopropylation of cumene: $1.32 \times 10^{-3}\ \mathrm{s^{-1}}$, isopropylation of diisopropylbenzene: $2.01 \times 10^{-3}\ \mathrm{s^{-1}}$ and isopropylation of triisopropylbenzene: $2.17 \times 10^{-3}\ \mathrm{s^{-1}}$.

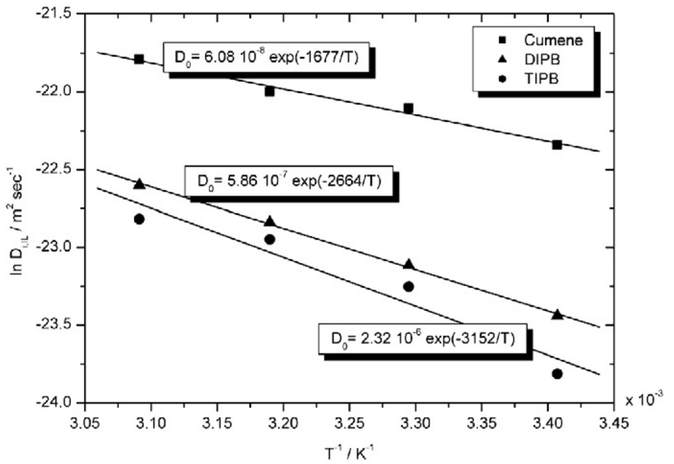


Fig. 8. Diffusion coefficient of cumene, DIPB and TIPB in chloroaluminate ionic liquid (EMIMCl:AlCl$_3$ = 1:1) at various temperature modelled as $D_{(\mathrm{T})} = D_0 \exp(-E_{\mathrm{D}}/RT)$.

Diffusion coefficients of the aromatic substances in the ionic liquid phase were measured using NMR-diffusion ordered spectroscopy (DOSY). Again, the DOSY measurements to determine the diffusion coefficients of the aromatic compounds in the ionic liquid were performed for the neutral ionic liquid ([EMIM]Cl/AlCl$_3$ = 1:1), since cumene reaction were inevitable during the time of the DOSY measurements in acidic systems.

Fig. 8 shows the diffusion coefficient of cumene, 1,3-diisopropylbenzene and 1,3,5-triisopropylbenzene in the neutral chloroaluminate ionic liquid as a function of temperature (with E_{D} being the activation energy of diffusion and D_0 being the maximum diffusion coefficient). Using this Arrhenius function, diffusion coefficients of the aromatic components were calculated for the relevant temperature of 90 °C. For cumene a $D_{\mathrm{cumene,IL,90\,°C}}$ of $6.1 \times 10^{-10}\ \mathrm{m^2\,s^{-1}}$ was obtained in this way.

The mass transfer constant ($k_{i,\mathrm{IL}}$) is strongly dependent on the ionic liquid's droplet size. This results from a complex interplay of reactor configuration (i.e. stirrer type and dimensions, reactor geometry, etc.) and physico-chemical properties of the ionic liquid itself (i.e. surface tension under reaction conditions). Newman correlation [19] as shown in Eq. (9) provides a rough estimation for $k_{i,\mathrm{IL}}$ assuming that there is no convective flow inside the ionic liquid droplets.

$$k_{i,\mathrm{IL}} = 6.58 \frac{D_{i,\mathrm{IL}}}{d_{32}}. \tag{9}$$

To estimate the mean sauter diameter (d_{32}) of a highly dispersed medium the empiric correlation of Shinnar [20] can be applied:

$$d_{32,\max} = 0.15 \cdot D_{\mathrm{stirrer}} \cdot \mathrm{We}^{-0.6} \tag{10}$$

with $d_{32,\max}$—maximum sauter diameter (mm); D_{stirrer}—stirrer diameter (mm); We—Stirrer's Weber number = $(\rho_{\mathrm{solvent}} \cdot N^2 \cdot D^3_{\mathrm{stirrer}})/\gamma_{\mathrm{interface}}$; ρ_{solvent}—dispersant's density ($\mathrm{kg\,m^{-3}}$); N—stirring rate (rps); $\gamma_{\mathrm{interface}}$—interfacial tension between dispersant (cyclohexane) and dispersed substances (ionic liquid) = $|\gamma_{\mathrm{solvent}} - \gamma_{\mathrm{IL}}|$ ($\mathrm{Nm^{-1}}$).

Properties values for cyclohexane were obtained from Perry's chemical engineering handbook [21]. The surface tension of the chloroaluminate ionic liquid was taken from a publication by Tong et al. [22]. With these data the calculated Sauter diameter according to Eq. (10) is in the range of 140–170 μm. Entering this value into Eq. (9) one obtains a mass transfer coefficient ($k_{i,\mathrm{IL}}$) of $2.37 \times 10^{-5}\ \mathrm{m\,s^{-1}}$ and together with the diffusion coefficient ($D_{i,\mathrm{IL}}$) and the reaction rate constant (k) the Hatta number can be calculated. The Hatta number calculated in this way for the conversion of cumene to diisopropylbenzene was found to be 0.03 to

0.05 showing that the reaction rate was not limited by mass transfer into the ionic liquid phase. This was also the case for the first and the second consecutive alkylation reaction.

Consequently, the observed, relatively low activation energy of the isopropylation reactions cannot be attributed to mass transfer influences on the observable reaction rate. A convincing explanation for the low formal activation energy arises from the fact that the temperature dependency of propylene solubility in the ionic liquid phase is included in the $E_{\mathrm{A,eff}}$ value in our case. Propylene pressure was adjusted to provide excess propylene in the organic and in the ionic liquid layer (for more information see supporting information), but temperature dependent propylene concentration in the ionic liquid will still have a strong influence on the reaction rate (in our model on the reaction rate coefficients k'_{1-x}). In former work by Eichmann [23], it was demonstrated that the propylene solubility in chloroaluminate ionic liquids can increase with decreasing temperatures and this effect was used in a similar argument to explain even the observed negative activation energies found for the Ni-catalysed dimerisation of propylene in slightly acidic chloroaluminate ionic liquids.

4. Summary

This work provides detailed kinetic information on liquid–liquid biphasic alkylation reactions catalysed by acidic ionic liquids. It was found that the model of pseudo first order consecutive reactions could be fitted satisfyingly to the experimental data only after taking into account the product share dissolving into the acidic catalyst medium. Since measuring the product solubility in the highly reactive catalyst phase was not possible in a direct manner, we calculated the product distribution in the acidic ionic liquid phase by estimating the partition coefficient using COSMO-RS model. Two major conclusions can be drawn from the good agreement that was found between the kinetic model and the corrected experimental data:

(a) COSMO-RS does indeed represent a useful tool to predict the relative solubilities of the different alkylated aromatic compounds in acidic chloroaluminate ionic liquids. The COSMO-RS calculations allow correcting the data from the experimental analysis of the organic product phase in a reasonable manner.
(b) The large difference in the solubilities of the alkylated aromatic compounds in the acidic chloroaluminate ionic liquid is indeed the major reason for the observed "delay behaviour" when taking into account only the product analyses from the organic phase. The COSMO-RS calculations showed a significantly lower solubility of aromatic compounds with increasing degree of alkylation thus providing a reasonable forecast for the experimentally observed enhanced selectivity to monoalkylated products in the liquid–liquid biphasic ionic liquid system.

Despite the fact that a low formal activation energy was observed for the investigated isopropylation reactions, mass transfer effects on the observed reaction rate can be ruled out for our experiments as the estimated Hatta number for the reaction system is significantly smaller than 0.3. A reasonable explanation for the observed low formal activation energies is given by the known fact that propylene solubility in acidic chloroaluminate ionic liquids increases with decreasing temperature [23].

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Supporting information

Supporting information for this article may be found on ScienceDirect, in the online version.

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