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Solvent effects in liquid-phase dehydration reaction of ethanol to diethylether catalysed by sulfonic-acid catalyst

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ABSTRACT

The liquid-phase dehydration of ethanol to diethylether over heterogeneous sulfonic-acid catalysts was carried out in a stirred batch reactor. The different Amberlyst catalysts were found to have similar activities for this reaction; even though Amberlyst 70 showed a lower acid capacity compensated by a higher specific activity. By comparing the conversion of ethanol as a function of reaction mixture composition, it was found that reaction rates greatly depended on ethanol concentration but also on reaction mixture polarity. The swelling of the used resins could not explain the observed variations of initial reaction rate since this effect was observed both with resins and with homogeneous catalyst, i.e. p-toluenesulfonic acid. The initial ethanol concentration has a complex effect on initial reaction rates that could not be correlated by usual kinetic models. Taking account of the intrinsic reactivity trends of the SN_2 etherification reaction, a strong dependence was found between solvent properties and initial reaction rate.

1. Introduction

The intermolecular reaction of primary alcohols gives ethers, which are important high value oxygenated compounds. Among them, dimethyl ether appears to be a promising alternative compression ignition fuel with reduced NO_x, SO_x, and particulate matter emissions [1]. Catalytic dehydration processing of methanol has been successfully industrialized since the last decade and uses solid acid catalyst in a fixed [2,3] or fluidized-bed reactor [4] and is still a current subject of research interest [5].

It is also well known that the addition of oxygenated additives to gasoline and diesel fuels represents a promising method of enhancing the combustion efficiency in internal combustion engines with an equally significant reduction of pollutant emissions [6]. In comparison with short and branched ethers used in gasoline such as MTBE (methyl tert-butyl ether) or ETBE (ethyl tert-butyl ether), ethers for diesel have to be linear with a relatively long chain [7–13]. Dehydration of linear primary alcohols to dialkyl ethers is performed in the liquid phase over solid acid catalysts below 433 K to limit the formation of alkene [12,14]. Experiments were performed in pure alcohols and ether selectivity and yields higher than 90% were obtained [10,15]. Langmuir–Hinshelwood or Eley–Rideal kinetics models have been used to represent rate data of liquid-phase dehydration of alcohols to ethers [10,15–17]. However, some discrepancy was observed for sulfonic styrene–divinylbenzene copolymer catalysts because of complex interactions between reactants, by-products, reaction medium and heterogeneous catalyst [10,16]. Water formed during alcohol etherification reaction is known to strongly adsorb on solid catalyst and to strongly inhibit the etherification reaction [9,16]. Furthermore, the solvent can have a dramatic effect on the acid strength of solid acid catalysts [18,19] and on the accessibility of active sites [8,10,18].

This work presents the study of solvent composition on reaction kinetic of liquid-phase dehydration reaction of linear alcohol to dialkyl ethers. Specifically noteworthy is the observation that the composition of the bulk solvent properties during dialkyl ether synthesis dramatically change from protic solvent (i.e. linear alcohol) to aprotic solvent (i.e. dialkyl ethers) and water. This paper presents the results obtained in our investigations on the preparation of diethylether from ethanol over a series of sulfonic styrene-divinylbenzene copolymers. More precisely our efforts have been dedicated to the analysis of the influence of liquid phase composition on the initial rate data.

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2. Experimental

2.1. Chemicals

Ethanol, 1-butanol, dimethylsulfoxide, heptane, toluene, sulfolane, were supplied by Aldrich (analytical grade, 99%) and used as received.

2.2. Catalysts

Dry Amberlyst-15 (A15), Amberlyst-35 (A35), Amberlyst-36 (A36) were provided by Rohm and Haas, France and used as received. Amberlyst-70 (A70), kindly provided wet by Rohm and Haas France, was washed with water, 1 N HCl, water and then dried under vacuum. Particles with diameters between 0.3 and 1.2 nm were used. p-Toluenesulfonic acid monohydrate (p-TSA) was supplied from Aldrich and used without further purification. Characteristics of catalysts are shown in Table 1.

2.3. Apparatus

The experiments were carried out in a stainless steel 125 mL autoclave operating in batch mode. The reaction medium was stirred at 600 rpm by a Rushton turbine and mixing baffles on the reactor walls were used to improve the mixing. An internal thermocouple coupled with heating resistor allows measurement and control of the reaction mixture temperature with an accuracy of ±1 K. A pressure transducer was used to measured reactor pressure.

2.4. Procedure

The reactor was filled at 80 vol.% by different concentration mixtures of ethanol and solvent. Catalyst concentration was fixed to 30 mmol $H^+ L^{-1}$ for both heterogeneous and homogenous catalysts. The reactor was closed and then pressurised to 5 bar with N_2 at room temperature. Then, the reaction mixture was then heated to 433 K and an internal pressure up to 15 bar was obtained. It typically takes 6–8 min to reach this working temperature. To follow the concentration variation of compounds with time, 0.25 mL liquid samples were periodically sampled from the reactor, precisely weighted, mixed with known amount of 1-butanol (used as an external standard) and analyzed by an 6890 Agilent GC equipped with a DB-Wax column and a FID detector. Initial rates were deduced from the linear plot of diethylether concentration as a function of time in between the first sample taken when the reaction mixture reach 433 K and the last sample taken with a conversion lower than 5 mol%. Some conversion of ethanol to diethylether was observed until the temperature of the reactor reach 433 K, less than 1 mol%. Thus, the composition of the bulk solution at 433 K was used as reference.

The error in the mass balance for all the experiment was less than the average experimental error and no ethylene was detected in the gas chamber for temperature below 433 K.

Table 1
Characteristics of the catalysts as provided by the supplier.

Catalyst	Acidity (eq./kg)	Pore diameter (Å)	Specific area (m^2/g)
A15	4.7	300	53
A35	5.2	300	50
A36	5.4	240	33
A70	2.6	220	36
p-TSA	5.25	n.a.	n.a.

2.5. Estimation of ethanol activity

The non-random two liquids (NRTL) theory was used to estimate compounds activity coefficient in mixture and equilibrium properties. This theory introduced by Prausnitz et al. [20] allows to calculate activity coefficient (γ_i) (Eq. (1)) with the use of binary interactions coefficients C_{ij}^0, $C_{ij}^T \alpha_{ij}^0$, α_{ij}^T

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ij} G_{ij} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{n} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k} \right) \qquad (1)$$

with

$$\tau_{ij} = \frac{C_{ij}^0 + C_{ij}^T (T - 273.15)}{RT}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\alpha_{ij} = \alpha_{ij}^0 + \alpha_{ij}^T (T - 273.15)$$

Calculation were made by the used of process simulation software (ProsimPlus) [21] in with interaction parameter are already implemented.

2.6. Composition of the gas phase

To check the fulfillment of mass balance, the volatile compounds mole in gas phase were estimated using NRTL theory [20,21]. The volume of gas phase was very small compared to the liquid phase and it was essentially composed by nitrogen. For experiments with toluene or heptane, less than 5 mol% of ethanol and diethylether were in the gas phase.

3. Results and discussion

3.1. Catalytic activity

Since water is known to decrease the activity of etherification catalysts, all solvents and catalysts were used dried with the exception of p-TSA, which was used as a monohydrate. In this particular case, the initial water concentration was equal to 30 mmol L^{-1} (540 mg L^{-1}). Toluene was chosen as diluent for the comparison of the catalytic activity of homogenous and heterogeneous catalyst because of the lack of solubility of p-TSA in aliphatic solvent. The concentration of ethanol was arbitrarily set to 3.3 mol L^{-1} and reaction temperature was set to 433 K for the reaction to be as fast as possible avoiding ethylene formation [22]. It should be noticed here that the reaction temperature was higher than the maximum operating temperature recommended by the supplier (393 K for A15, 423 K for A 35 and A36 and 463 K for A70). However, fresh resins were used for each experiment and the experimental data point used to determined initial reaction rate were obtained in less than 30 min. Fig. 1 compares the reactivity of the catalyst for the same concentration of acidic sites, i.e. 30 mmol $H^+ L^{-1}$.

We have previously checked that, for both homogeneous and heterogeneous catalyst, the reaction rate was proportional to the amount of catalyst at least until a concentration of 120 mmol $H^+ L^{-1}$. Under our conditions, the heterogeneous sulfonic-acid catalysts were found to be more active than the homogeneous acid catalyst. The yield of diethylether was higher than 10% after 60 min with heterogeneous sulfonic acid catalyst whereas a conversion of less than 0.5% was obtained using p-TSA (Fig. 1). The initial reaction rate difference between resins and p-TSA can be explained by: (i) an initial water concentration equal to 30 mmol L^{-1} when monohydrate p-TSA was used as catalyst and (ii) an increase of acidity strength due to higher acid density in

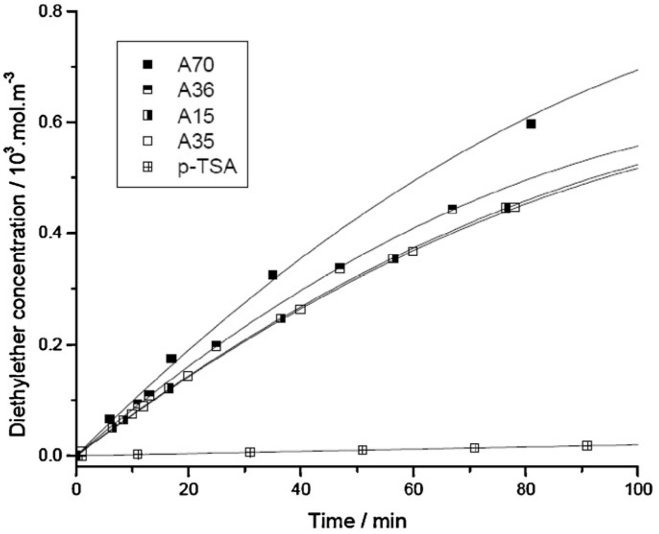

Fig. 1. Reaction profile of ethanol dehydration 3.3 mol L^{-1} in toluene at 433 K as a function of catalysts (30 mmol H$^+$ L^{-1}).

resins [23] and by a “confinement” effect [18,24], ethanol being much more concentrated in the solid catalyst due to a higher affinity of ethanol for the resin. Initial reaction rate data are given in Table 2. Among the sulfonic-acid catalysts, and for an equivalent proton loading, A70 was found to have the highest initial reaction rate. It should be noted that 1 kg of A70 contained only 2.6 mol of acid group whereas A36, A35 and A15 contained twice this amount of acid group (Table 1). Therefore, using the same weight loading of catalyst, A70 was the less active catalyst.

3.2. Influence of the ethanol concentration.

Fig. 2 shows the evolution of the initial reaction rate versus initial ethanol concentration in toluene. For A15, the initial reaction rate increases when the ethanol concentration increases. A plateau was reached for a concentration of 6 mol L^{-1} of ethanol and could be explained by the saturation of the reactive acidic centers of the catalyst by the ethanol [25–27]. Furthermore, an inflexion of the initial reaction rate was observed for a concentration of ethanol of 3 mol L^{-1}. We have carefully checked these points and the profiles observed in Fig. 2 were confirmed. Since the mixture ethanol–toluene is a non-ideal system, the ethanol activity has been calculated for the binary system of solvent using NRTL theory [20,21]. Fig. 2 shows the evolution of the initial reaction rate versus initial ethanol activity in toluene and the same profile were noticed.

The role of the solvent in controlling the swelling of the resin and on the acid strength of solid acid catalyst has already been described and could explain such a profile [10,19]. For example, one could imagine a catalyst with acid sites having different activities and accessibilities. The swelling of the resin as the function of initial ethanol concentration could give access to new acidic sites.

Table 2
Initial reaction rate data for the liquid-phase dehydratation reaction of ethanol (3.3 mol L^{-1}) to diethylether at 433 K in toluene, catalyst loading of 30 mmol H$^+$ L^{-1}.

Catalyst	r_i^0 (mol (min mM$_{\mathrm{H}^+}$)$^{-1}$)$^{\mathrm{a}}$	r_i^0 (mol (min g)$^{-1}$)$^{\mathrm{a}}$
A70	0.025	0.065
A36	0.019	0.10
A35	0.017	0.09
A15	0.017	0.08
p-TSA	0.00044	0.0026

[a] Experimental error ±5%.

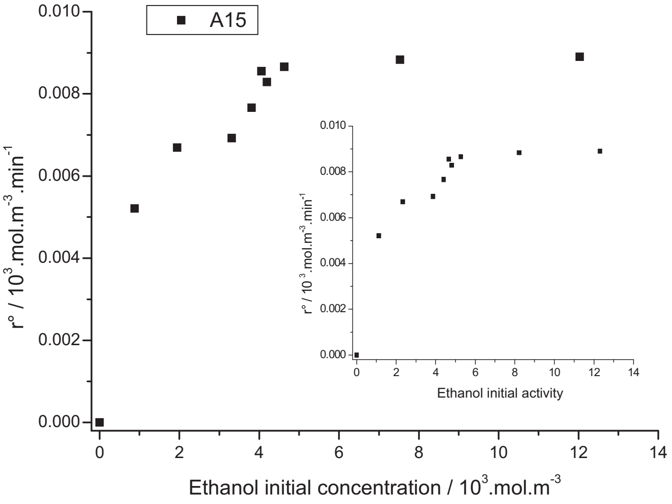

Fig. 2. Initial reaction rate of etherification of ethanol as the function of initial ethanol concentration in toluene (A15, 433 K, catalyst loading of 30 mmol H$^+$ L^{-1}).

Thus, we decided to further study this reaction using homogeneous catalyst, i.e. p-TSA (Fig. 3).

As expected (Fig. 1), the initial reaction rate for p-TSA was significant lower due to the presence of one equivalent of water but, as expected with homogeneous catalyst, an increased of the initial reaction rate with increasing concentration of ethanol was observed (Fig. 3). However, an inflexion of the initial reaction rate was observed again, but for a concentration of ethanol of 8 mol L^{-1}. Thus, the inflexion observed with the resin (Fig. 2) could not be explained by the swelling of the resin as the function of bulk solvent properties. Moreover, the inflexion is observed at higher ethanol concentration. Such difference between homogeneous and heterogeneous catalyst could be explained because ethanol strongly bound by polar interaction to resin A15. Since ethanol is strongly chemisorbed on the resin, the inflexion is believed to occur at lower ethanol initial concentration while the local concentration in the catalyst is much higher. We decided to further study this effect in heptane. Fig. 4 shows the evolution of the initial reaction rate of etherification of ethanol as the function of initial ethanol concentration in heptane for solid acid catalyst A36 and A15.

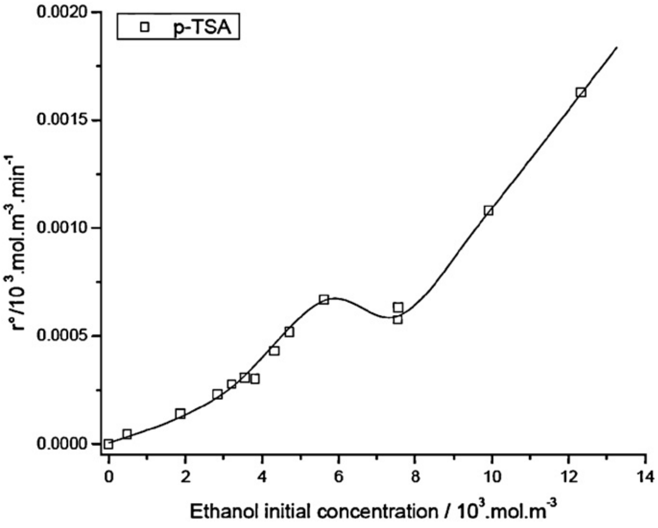

Fig. 3. Initial reaction rate of etherification of ethanol as the function of initial ethanol concentration in toluene (p-TSA, 433 K, catalyst loading of 30 mmol H$^+$ L^{-1}).

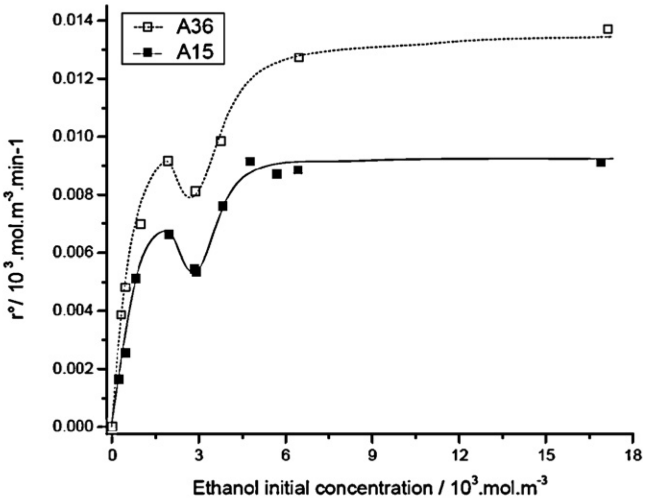

Fig. 4. Initial reaction rate of etherification of ethanol as the function of initial ethanol concentration in heptane (433 K, catalyst loading of 30 mmol H$^+$ L^{-1}).

Reaction rate was shown to be slightly faster than in toluene. Moreover, it increased when increasing the concentration of ethanol. As expected, for a concentration above 6 mol L^{-1} of ethanol, complete adsorption of ethanol on the reactive acidic centers of the catalyst limit the reaction for both resins and resin A36 has the higher activities. Furthermore, the same inflexion of initial reaction rate as the function of the ethanol concentration was observed for both resins and for the same ethanol initial concentration, i.e. 3 mol L^{-1} (Fig. 4). In order to explain this inflexion, we have checked the influence of solvent composition on activation energy of etherification of ethanol. The activation energy for diluted and pure ethanol were determined from the Arrhenius plots of initial reaction rate versus reciprocal temperature and are shown in Fig. 5, with the activation energies obtained from the slope. Activation energies of 121 ± 10 kJ mol^{-1} and 117 ± 10 kJ mol^{-1} for pure ethanol and 0.8 mol L^{-1} ethanol in heptane, respectively, were obtained. These values are comparable to previously reported literature data, in the range 100–120 kJ mol^{-1} [8,11,15,17,23].

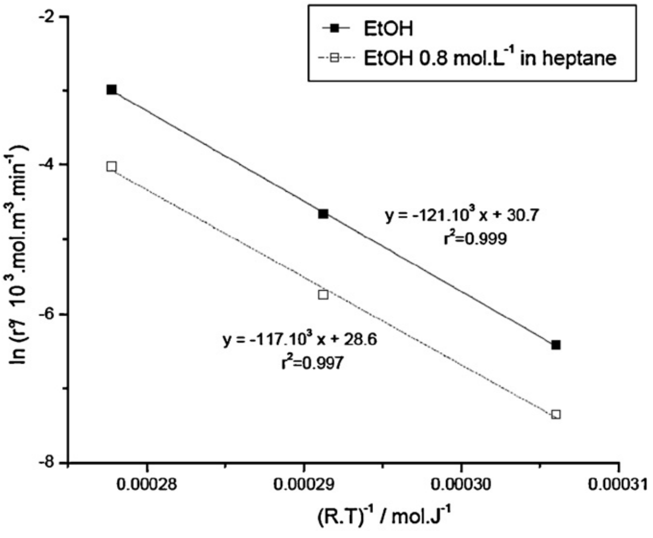

Fig. 5. Arrhenius plot for ethanol dehydration in heptane, in presence of A15 for both pure ethanol and ethanol diluted in heptane (0.8 mol L^{-1}), catalyst loading of 30 mmol H$^+$ L^{-1}.

Table 3
Initial reaction rate of etherification of ethanol as a function of solvent, solvent dielectric constant (ε_r) and scale of solvent hydrogen-bond acceptor (β) (ethanol (1 mol L^{-1}) 433 K, A15 catalyst loading of 30 mmol H$^+$ L^{-1}).

Solvent	r_i^0 (mol m^{-3} min^{-1})	ε_r[a]	β[a,b]
Heptane	7.3	1.92	0
Chlorobenzene	6.9	7	7
Toluene	6.8	2.38	11
Sulfolane	3.3	44	39
THF	0.82	7.58	55
DMSO	0.0074	46.45	76

[a] See [28].

[b] See [29].

As both activation energies are similar it appears that no difference of mechanism can explain the unexpected inflexion observed while plotting reaction rates versus ethanol concentration (Fig. 4).

3.3. Solvent effect in etherification of ethanol

The inflexion observed in the initial reaction rate of etherification of ethanol as a function of initial ethanol concentration (Fig. 4) couldn't be explained by the swelling of the resins or by a modification of activation energy. However, a change on the acid strength of catalyst could be suspected. Furthermore, it is known that surface-catalysed coupling of alcohols to ethers proceeds by the SN$_2$ pathway [28]. The strong dependence of the activation-free energy of SN$_2$ reactions on the solvent is well known [29–31] and could explain the effect observed. Thus, we decided to study the activities of acid catalyst A15 for ethanol dehydration in different solvents. Initial reaction rate as the function of solvent are reported in Table 3.

The results obtained at constant ethanol concentration (Table 3) clearly show a strong influence of the solvent on the initial reaction rate of etherification of ethanol. The general trend is the diminution of the catalyst activity with an increase of solvent dielectric constant, but a much better fit is observed (Fig. 6) using a β scale of solvent hydrogen-bond acceptor (HBA) from Kamlet–Taft [32].

The results obtained are in good accordance with the common mechanistic study and kinetic model proposed in the literature for dehydration reaction of alcohols catalysed by ion-exchange resins (Fig. 7). It is assumed that the dehydration of alcohols to ethers involves the in situ formation of an oxonium ion at the surface of the ion-exchange resin follow by a nucleophilic bimolecular sub-

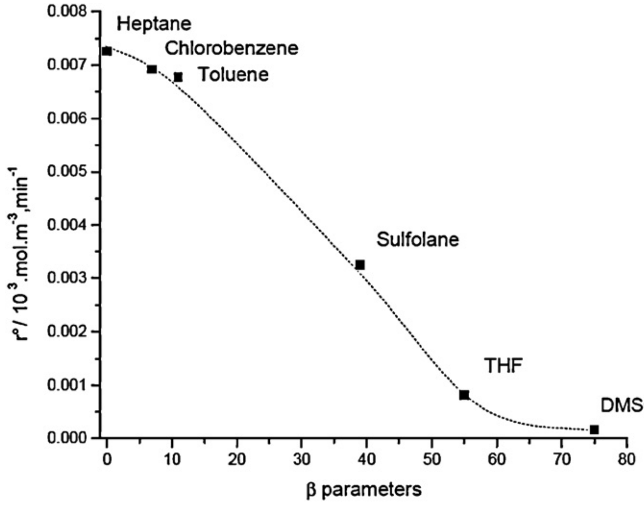

Fig. 6. Initial reaction rate of etherification of ethanol as the function of β parameters (ethanol concentration: 1 mol L^{-1}, 433 K, A15 catalyst loading of 30 mmol H$^+$ L^{-1}).

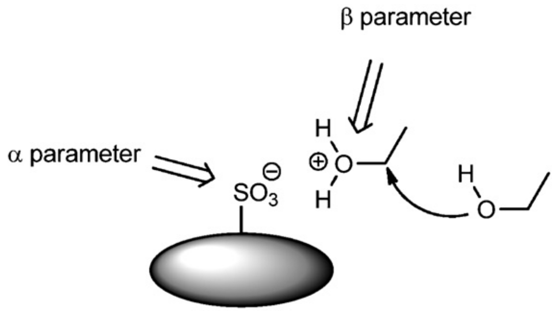

Fig. 7. Influence of solvent properties on kinetic model (Eley–Rideal).

stitution (SN_2). Thus, a decrease of reaction rate (Fig. 6) is observed when the β parameter increases, a high β value involving a better stabilisation of the oxonium ion [31].

Moreover it is also known that the acidity of the sites of the catalyst can be increased by interaction with solvent capable of forming strong hydrogen bonds with the anion of the catalytic site [33]. Such properties can be evaluated using an α scale of solvent hydrogen-bond donor (HBD) [31,32]. In our case, among the solvents used only ethanol has an α parameter different than 0 ($\alpha = 0.83$). In our experiments, the amount of ethanol adsorb on the resin is believed to decrease from alcanes to DMSO. A decrease of the local concentration of ethanol and should decrease the strength of the catalyst. Thus, ethanol concentration has a very complex effect on the reaction rate: it increase the reaction rate by an increase of reactant concentration and by an improvement of acid strength of the catalyst (HBD parameter) but in the same time it slow down the reaction rate as oxonium ion stabiliser (HBA parameter). The function, which results of these antagonist parameters, is reported indirectly in Figs. 2–4.

4. Conclusion

The influence of the liquid phase composition on the initial reaction rate of ethanol etherification has been investigated using different sulfonic acid catalyst. For both heterogeneous and homogeneous sulfonic-acid catalysts it was observed that the initial ethanol concentration has a complex effect on initial reaction rates. Initial reaction rates depend on ethanol concentration but also on bulk solvent properties.

From the data, we could conclude that the observed inflexion of the initial reaction rate of the liquid phase dehydratation of ethanol to diethylether in non polar solvents as the function of ethanol concentration could be explain by the formation of a new liquid phase around the acid site. The composition of this liquid phase greatly depends on bulk solvent properties. This study suggests that solvent effect should be take into account in the modelling of etherification and could explain the discrepancy observed between models and experimental data obtained during liquid-phase formation of ethers.

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