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Novel Brønsted acidic deep eutectic solvent as reaction media for esterification of carboxylic acid with alcohols

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ABSTRACT

New halogen-free Brønsted acidic deep eutectic solvents (DES) have been prepared by mixing new quaternary ammonium methanesulfonate salts with *p*-toluenesulfonic acid (PTSA). They have been used as dual solvent-catalyst for esterification of several carboxylic acids with different alcohols with a reagent molar ratio of 1:1. The method is mild, safe, and simple. Ease of recovery and reusability of DES with high activity makes this method efficient and eco-friendly. The tunability of DES properties, attained by changes in the cation, was performed in order to achieve various esters in good yields.

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Synthesis of organic esters has a main role in organic synthesis from its infancy, due to the utility of esters as products or intermediates in diverse fields, both in the laboratory and in industry.¹ Most of the recent research work dealing with esterification has been associated with green chemistry: replacement of conventional organic solvents by new reaction media such as, for example, water or ionic liquids is often studied, as shown in the review of Otera and Nishikido.¹ Condensation between carboxylic acids and alcohols catalyzed by p-toluenesulfonic acid (PTSA) takes place smoothly in imidazolium ionic liquids, but only when using dried IL.² A new approach for esterification has involved the use of newly synthesized Brønsted acid ILs as dual solvent-catalysts.^{3–5} A high temperature (110 °C) has been often used, and a few of the ILs contain halogen atom which may cause serious concerns.⁶ Moreover, the preparation of ILs often requires the use of organic solvents, and heat supply,^{5,7} and cost can be high.

Deep eutectic solvents have recently appeared in the horizon as a new generation of ionic solvents of low cost; some authors refer to them as 'advanced ILs'.⁸ They are generally formed by the mixture of hydrogen bond donor (HBD) molecules with halide salts, which produces liquids with physical and solvent properties comparable to ILs.^{9,10} DES are easy to prepare in a pure state from low cost starting materials, and they should be tunable without organic synthesis of new compounds. The principle of 'creating' DES by complexing a halide salt was first demonstrated by Abbott for mixtures of quaternary ammonium salts with a range of amides⁹ and later extended to a wide variety of other HBD such as acids, amines, and alcohols, including glycerol.¹¹ Systems based on choline chloride (ChCl) have been shown to be good solvents for chemical and biochemical transformations^{12,13} and also to have practical use in several applications, such as metal oxide processing,¹⁴ electropolishing,¹⁵ and extraction of glycerol from biodiesel.¹⁶ Prasad and coworkers have recently used DES formed by ChCl + ZnCl₂ as a Lewis acid catalyst as well as reaction medium to prepare long chain wax esters in high yields, although they use high temperature (110 °C) with need of heat supply and the system contains several halogen atoms, and also metal atom, which can cause concerns.¹⁷

Here we report a novel class of DES that is designed to be a strong Brønsted acid. It is without any halogen or metal atom, and it is formed upon mixing a quaternary ammonium salt bearing methanesulfonate as the counterion, with *p*-toluenesulfonic acid (PTSA). Trimethylcyclohexyl ammonium methanesulfonate (TCy-AMsO), trimethylbenzyl ammonium methanesulfonate (TBn-AMsO), trimethylcyclohexyl ammonium methanesulfonate (TOAMsO), and trimethylcyclohexyl ammonium *p*-toluenesulfonate (TCyA-Tos), shown in Scheme 1, are the quaternary ammonium salts that were used.



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Scheme 1. Trimethylcyclohexyl ammonium methanesulfonate (TCyAMsO), trimethylbenzyl ammonium methanesulfonate (TBnAMsO), trimethylcyclohexyl ammonium *p*-toluenesulfonate (TCyATos).

They were prepared with a procedure that avoids several drawbacks often encountered in organic synthesis.[†] Our procedure is similar to the preparation of published 1,3-dialkylimidazolium methanesulfonate^{18,19} and gives high yield of product in short time in only one step, without any byproduct and without the need of energy supply since the reaction itself – exothermic – provides the necessary heat.

DES were simply prepared from TCyAMsO, TBnAMsO, TOAMsO or TCyATos, and *p*-toluenesulfonic acid monohydrate,[‡] and were used immediately after, without any treatment. The mixtures of TCyAMsO, TBnAMsO, TOAMsO, and TCyATos, with PTSA form eutectics at a molar ratio of ammonium salt/PTSA of 1. The melting points of some mixtures are reported in Figure 1. A significant depression of the melting point is observed

Viscosities of the eutectics were measured;²⁰ in fact viscosity is an important property of ionic liquids (and DES) and a relatively low viscosity is considered to be a distinctive property between ionic liquids and molten salts, which are highly viscous.²¹

Values of viscosity, η , at 80 °C are 95, 75, 65, and 170 cP for, respectively, TCyAMsO, TBnAMsO, TOAMsO, and TCyATos, with PTSA at a molar ratio of ammonium salt/PTSA of 1. These values are relatively low, considering that generally the viscosity values were found to cover the range 50–5000 cP for DES and for ionic liquids.¹⁰ These preliminary data relating to values of viscosity at

80 °C for our systems showed no significant change in viscosity with variations of the cation, but a relatively higher value was measured for TCyATos, indicating an effect of the anion. This can probably be related to the presence of an aromatic moiety in the anion of TCyATos, and its interaction with the same aromatic moiety of PTSA. For TBnAMsO, a liquid at room temperature, viscosity was measured over a range of temperatures and the profile is reported in Figure 2. The significant change of viscosity with temperature is also consistent with the data in the literature for DES.^{9,10,22}

Herein we show the use of our new DES as the dual solvent-catalyst in an efficient, simple, and clean method for esterification of carboxylic acids with alcohol, under mild conditions, with facile isolation of products and reuse of the reaction medium[§] (Scheme 2).

Table 1 shows the results of optimized conditions for the reaction of lauric acid with methanol, chosen as a model reaction (Table 1, entry 1). The ester methyl laurate was obtained quantitatively (97% by g.c.) in 2 h at 60 °C with the ionic eutectic solvent TCyAMsO-PTSA used as a minor component in the reaction mixture, that is, DES/acid = 1/3.3. In the absence of DES, and using a solution of PTSA in water as the reaction medium, the product yield was only 16% (Table 1, entry 3). On the other hand, the system DES formed by ChCl (choline chloride) and ZnCl₂, which was successful for long chain wax esters at 110 °C, gave no product under our milder conditions (Table 1, entry 2). The product was easily isolated: in fact DES and water remained in the lower phase while the ester product remained in the upper liquid phase and it was simply pipetted off using a Pasteur pipette. This phase separation shifts the equilibrium toward product formation in DES.

The procedure was tested with several other acids, also shown in Table 1. Yields reported are based on g.c. analysis but yields by weight were also evaluated in some cases, and were comparable with the g.c. data. Data in Table 1 show how the reaction becomes more difficult as the acid chain length increases (Table 1, entries 5,

[†] TCyAMsO was prepared from N,N-dimethylcyclohexylamine and methyl methanesulfonate, with ethyl acetate as the solvent. The reaction is exothermic and the mixture reached reflux without external energy supply. After cooling to r.t. a white solid formed, that was washed twice with diethyl ether, and dried in vacuum to give a white crystalline solid, with m.p. 224-225 °C. Yield is 95%. ¹H NMR (200 MHz, CD₃OD) $\delta = 1.1 - 2.3 (m, 10 H, 5 CH_2); 2.69 (s, 3 H, CH_3SO_3^{-}); 3.06 (s, 9 H, 3 CH_3 - N^+); 3.37 (m, 1)$ H, R-CH-N⁺). TOAMsO was prepared similarly from N,N-dimethyloctylamine. A white crystalline solid, with m.p. 178-180 °C was obtained in 94% yield. ¹H NMR (200 MHz, CD₃OD) δ = 0.88 (t, 3 H, R-CH₃); 1.33 (m, 10 H, 5 CH₂); 1.78 (m, 2 H, CH₂-C-N⁺); 2.69 (s, 3 H, CH₃SO₃⁻); 3.11 (s, 9 H, 3 CH₃-N⁺); 3.31 (m, 2 H, R-CH₂-N⁺). TBnAMsO was prepared from dimethylbenzylamine and methyl methanesulfonate; the white solid, with m.p. 222-223 °C, was formed in a yield of 93%. ¹H NMR (200 MHz, CD₃OD): δ = 2.69 (s, 3 H, CH₃SO₃⁻); 3.10 (s, 9 H, 3 CH₃-N⁺); 4.52 (s, 2H, CH₂-Ar); 7.56 (s, 5H, Ar). TCvATos was prepared similarly from N.N-dimethylcyclohexylamine and methyl ptoluenesulfonate. The white solid with m.p. 241-243 °C was obtained in a yield of 92%. ¹H NMR (200 MHz, CD₃OD) δ = 1.1-2.3 (m, 10 H, 5 CH₂); 2.36 (s, 3H, CH₃Ar); 3.06 (s, 9H, 3CH₃); 3.37 (m, 1H, CH-N⁺); 7.23 (d, 2H, Ar); 7.70 (d, 2H, Ar).

[‡] Equimolar amounts of quaternary ammonium salt (1.5 mmol) and *p*-toluenesulfonic acid monohydrate (Sigma–Aldrich, 98,5+% used as received) were mixed in a screw-capped 3 ml vial. The mixture was magnetically stirred and heated to 60 °C until a clear colourless liquid was obtained (about 10 min).

[§] DES was used right after its preparation. Equimolar amounts (4.5 mmol) of acid and alcohol were added, and the resulting mixture, was heated to 60 °C (or 80 °C if specified) and magnetically stirred for the specified amount of time. Initially the reaction mixture is homogeneous and fluid, and then a heterogeneous system formed as reaction proceeded, due to insolubility of the esters produced in the DES. For the g.c. analysis further elaboration was as follows. At the end of the reaction, 'butylbenzene was added, as the internal standard, to the mixture, which was then extracted with diethyl ether. Organic layer was washed with NaHCO₃, dried over Na₂SO₄ and analyzed by g.c.



Figure 1. Variations in melting points with composition for mixture of the various ammonium salts with PTSA: TCyAMsO (\triangledown); TOAMsO (\bigcirc); TCyATos (\square); TBnAMsO (\blacksquare).



Figure 2. Variations in viscosity with temperature for TBnAMsO/PTSA 1:1. The line is drawn to guide the eye.



Scheme 2. Esterification reaction.

7). Attempts to increase the yield were carried out: an increase in reaction time (Table 1, entry 8) and an increase in temperature up to 80 °C (Table 1, entry 9) were useful, but yields became quantitative in 2 h and 60 °C using DES formed by a more hydrophobic quaternary ammonium salt, showing how useful is the tunability of the DES. The use of TOAMsO is shown in entries 6 and 10 of Table 1.

The method was extended to the use of different alcohols. Primary alcohols gave good yields: as already observed for the acids, also for alcohols an increase in the chain length, from methanol to ethanol, *n*-butanol, and *n*-octanol, leads to more difficult reactions. Anyway the use of TCyAMsO-PTSA gave generally good yields (>75%) in 2 h and at 60 °C, as shown in Table 1, entries 11, 12, 13. For secondary alcohols the Fischer reaction is generally more difficult due to steric hindrance²³ and yields were no higher than ca. 50% for the reaction of lauric acid with cyclohexanol or isopropanol (Table 1, entries 14, 17). In these cases we attempted to accelerate the reaction and improve the yield both increasing the reaction time and rising the temperature. We got yields >75% in 6 h and at 80 °C, as shown in entries 16 and 19 of Table 1. We tried to extend the method to hindered acids, and tried the reaction of *n*-octanol with isobutyric acid and trimethylacetic acid, using the reaction with acetic acid for comparison. We got good yields also with hindered acids in 2 h with a temperature of 80 °C (Table 1, entries 20–22).

The Fischer esterification rate for reaction of benzoic acid with methanol is known to be lower than reaction of aliphatic acid. due to electronic effects.²³ In fact it gave a yield of only 40% in TCy-AMsO-PTSA in 2 h at 60 °C. The yield was 55% raising the temperature to 80 °C, as shown in Table 2, entries 1, 2. As for esterification of lauric acid, also for benzoic acid in the absence of DES, and using a solution of PTSA in water as the reaction medium, the product yield was low, only 22% (Table 2, entry 3). The use of the longer alcohol *n*-octanol gave even worse yields (Table 2, entry 8, 9), as expected because methanol is generally the most reactive alcohol. Attempts to improve yields of the reaction of benzoic acid were carried out. The use of longer reaction times at 80 °C gave interesting results. In the case of reaction with methanol, data in Table 2 show the existence of an optimum reaction time, that is at 4 h, (yield 69%, Table 2, entry 4), because for both shorter and longer reaction time the yield decreased (Table 2, entries 2, 5, 6). On the other hand, for n-octanol the yield monotonically increased with reaction time, and the best yield obtained is 86% at 17 h (Table 2, entries 9-12). Experiments carried out to verify the extent of the reverse reactions showed that in the case of methyl benzoate the hydrolysis significantly occurred. In fact if methyl benzoate was added to a system containing DES (formed by TCyMsO/PTSA) and water in equimolar amounts with the ester (water is a Fischer esterification product) the methyl ester content decreased by 15% in 2 h.

For reaction of benzoic acid with both methanol and *n*-octanol yields were improved using DES formed by ammonium salts bearing an aromatic moiety. For the reaction with *n*-octanol, the use of DES formed by TBnAMsO gave a good yield of octyl benzoate, 72%, at 80 °C in 4 h (Table 2, entry 13), and the use of DES formed by TCyATos was even better, leading to an yield of 88% at 80 °C in 4 h (Table 2, entry 14). Also in this case, we can see how useful the tunability of DES is. The use of DES formed by TCyATos was also tried to improve the reaction of benzoic acid with methanol, and the yield does not vary significantly with respect to reaction in TCyAOMs (Table 2, entry 7). No attempt of yield improvement, with variation of reaction times, was investigated.

The method was extended to the reaction in which both the acid and the alcohol are solids, and the reaction of benzoic acid and 2-(4-hydroxyphenyl)-ethanol was carried out. The reaction medium TCyAMsO-PTSA worked well, became homogeneous and limpid at 80 °C and the product formed. Anyway the yield (determined by weight) is not high (Table 2, entry 15) although 17 h of reaction time were used. Furthermore, in this case the use of DES bearing an aromatic moiety, TCyATos-PTSA, led to a decreased yield (Table 2, entry 16), meaning that the effect of changes in the DES structure on the reaction yield is dependent on the reagent structures. The method was also extended to aliphatic acid bearing an aromatic moiety. Reaction of phenylacetic acid with methanol was carried out. Results were rather good with TCyAMsO-PTSA (Table 2, entry 17), and were further improved using TCyATos-PTSA with a 82% yield (Table 2, entry 18).

Table 1

Fischer esterification of aliphatic acids with alcohols in DES formed by PTSA and various quaternary ammonium salts^a

Entry	Acid	Alcohol	Quaternary Ammonium salt in the DES	Time (h)	Temperature (°C)	Yield ^b (%)
1	Lauric	MeOH	TCyAMsO	2	60	97 (94) ^c
2	Lauric	MeOH	ChCl ZnCl ₂	2	60	
3	Lauric	MeOH	d	2	60	16
4	Octanoic	MeOH	TCyAMsO	2	60	90 (85) ^c
5	Palmitic	MeOH	TCyAMsO	2	60	77
6	Palmitic	MeOH	TOAMsO	2	60	93
7	Stearic	MeOH	TCyAMsO	2	60	55
8	Stearic	MeOH	TCyAMsO	4	60	54
9	Stearic	MeOH	TCyAMsO	2	80	71
10	Stearic	MeOH	TOAMsO	2	60	97
11	Lauric	EtOH	TCyAMsO	2	60	81
12	Lauric	n-BuOH	TCyAMsO	2	60	78
13	Lauric	n-OctOH	TCyAMsO	2	60	74
14	Lauric	Cyclohexanol	TCyAMsO	2	60	42
15	Lauric	Cyclohexanol	TCyAMsO	2	80	59
16	Lauric	Cyclohexanol	TCyAMsO	6	80	85
17	Lauric	Isopropanol	TCyAMsO	2	60	50
18	Lauric	Isopropanol	TCyAMsO	2	80	66
19	Lauric	Isopropanol	TCyAMsO	6	80	72
20	Acetic	n-OctOH	TCyAMsO	2	60	96
21	Isobutyric	n-OctOH	TCyAMsO	2	80	85
22	Trimethylacetic	n-OctOH	TCyAMsO	2	80	73

^a 4.5 mmol of acid; carboxylic acid: alcohol: DES = 1:1:0.3.

^b Yield in mol % by gc, i.s. ^tButylbenzene.

^c Yield by weight in parentheses.

^d The reaction medium is a solution of PTSA (1.5 mmol) in water (0.70 ml).

Table 2

Fischer esterification of acids bearing aromatic moiety with alcohols in DES formed by PTSA and various quaternary ammonium salts^a

Entry	Acid	Alcohol	Quaternary ammonium salt in the DES	Time (h)	Temperature (°C)	Yield ^b (%)
1	Benzoic	МеОН	TCyAMsO	2	60	40
2	Benzoic	MeOH	TCyAMsO	2	80	53
3	Benzoic	MeOH	d	2	80	22
4	Benzoic	MeOH	TCyAMsO	4	80	69
5	Benzoic	MeOH	TCyAMsO	6	80	58
6	Benzoic	MeOH	TCyAMsO	17	80	59
7	Benzoic	MeOH	TCyATos	4	80	65
8	Benzoic	n-OctOH	TCyAMsO	2	60	19
9	Benzoic	n-OctOH	TCyAMsO	2	80	41
10	Benzoic	n-OctOH	TCyAMsO	4	80	55
11	Benzoic	n-OctOH	TCyAMsO	6	80	64
12	Benzoic	n-OctOH	TCyAMsO	17	80	86
13	Benzoic	n-OctOH	TBnAMsO	4	80	72
14	Benzoic	n-OctOH	TCyATos	4	80	88
15	Benzoic	2-(4-Hydroxyphenyl)-ethanol	TCyAMsO	17	80	60 ^c
16	Benzoic	2-(4-Hydroxyphenyl)-ethanol	TCyATos	17	80	49 ^c
17	Phenylacetic	MeOH	TCyAMsO	2	80	65
18	Phenylacetic	MeOH	TCyATos	4	80	82

^a 4.5 mmol of acid; carboxylic acid:alcohol:DES = 1:1:0.3.

^b Yield by gc, i.s. ^tButylbenzene.

^c Yield by weight; identification of ester produced by comparison with ¹H NMR in the literature.²⁴

^d The reaction medium is a solution of PTSA (1.5 mmol) in water (0.70 ml).

Table 3

Recycling	of	TCyAMsO-PTSA	system	in	the
preparatio	n o	f methyl laurate ^a			

Cycle	Yield ^b (%)
1	95
2	97
3	94
4	98
8	92°
8	36

^a 4.5 mmol of acid; lauric acid: alcohol: DES = 1:1:0.3.

^b Yield by gc, i.s. ^tButylbenzene.

^c After water removal from DES in vacuum at 60 °C.

Last but not least, we used our model reaction for reusability tests. It was possible to conduct the esterification of lauric acid with methanol in TCyAMsO-PTSA for more consecutive cycles.[¶] Results reported in Table 3 show no loss of the dual catalyst-solvent

¹ For the test of reusability, as the reaction time was reached, the mixture was decanted while hot. As two clearly separated phases are formed, the upper liquid layer was spilled off with a Pasteur pipette and weighted, then analysed by gc, after addition of the internal standard. The lower layer formed by DES and water was used for 4 consecutive cycles without any treatment. A drying in vacuo at 60 °C overnight was carried out on DES for further cycles. Tests for reagent/product entrapment in DES were carried out: after the ester had spilled off, DES was extracted with petroleum ether and thereafter with diethyl ether and extracts analysed by gc after addition of the internal standard. Analysis evidenced no presence of the reagent lauric acid, and small amounts (2–5%) of the ester methyl laurate produced.

functions of the DES for 4 consecutive cycles, with no treatment on DES.

For further cycles the yield remained high only with a simple treatment on DES consisting in water elimination from DES in vacuo at 60 °C. In fact after 8 cycles the yield was still good, 92%, but a test showed that the yield was quite lower (36%) if DES had no treatment.

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