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# Reaction kinetics investigation of Malononitrile with substituted benzaldehydes in aqueous solutions of ethaline as deep eutectic solvent

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**Abstract**

Due to increasing demands for ecofriendly processes within the framework of green chemistry, and having shown substantial properties, especially in terms of toxicity, biodegradability, cost, and ease of preparation under ambient conditions, deep eutectic solvents (DESs) have become a suitable candidate as green solvents for reaction media in the past decade. In this work, condensation reaction of some para- and meta-substituted benzaldehydes and Malononitrile was kinetically investigated in ethylene glycol-choline chloride (ethaline) as a DES mixed with water, in the whole range of mole fractions, at room temperature. The correlation of second-order rate coefficients based on Hammett's substituent constants yield a linear straight line with positive slope in different mole fractions of ethaline–water mixtures. The measured second-order rate coefficients of the reaction showed a dramatic variation in ethaline–water mixtures with the increasing mole fraction of water.

**KEYWORDS**

binary solvent mixture, deep eutectic solvents, Hammett equation, preferential solvation, substituted benzaldehydes

## 1 | INTRODUCTION

Solvents have been known as important portion in many chemical and physical processes (solubility, reaction rates, selectivity, choosing the suitable solvent allows for thermodynamic and kinetic control on chemical reactions, chemical equilibria, position, and intensity of spectral absorption bands).[1–4] The understanding of solvent effects on chemical reactivity requires precise knowledge of various solute–solvent interactions. Due to the complexity of the solvation phenomena, there are no credible methods for a quantitative description and prediction of kinds of interactions. Solvent effects are mainly expounded as resulting from changes in media polarity, a general term that is related to the solvating ability of the solvent.[5]

During the past times, replacement reaction media for volatile organic compound, which has a negative impact on our body and ecosystem, have been marked by some environment friendly solvents and potential friendly solvents such as water,[6] supercritical water and carbon dioxide,[7,8] ionic liquids,[9–11] and deep eutectic solvents (DESs).[12–14]

DESs have been recently considered as ecofriendly solvents in chemical processing, due to their interesting physical and chemical properties.[15–18] Furthermore, DESs can be formed simply by mixing two or more components, a salt (eg, choline (2-hydroxyethyl-trimethylammonium) chloride) with a hydrogen bond donor compound (HBD), which are produced a composite with melting point (below 100°C) lower than that of each individual component. Therefore, many new DESs have been rapidly expanded as designer solvents. In addition, DESs, as the type of designer and green solvents, have some identified properties such as poor conduction, low vapor pressure, high viscosity, and high thermal stability.[19] These compounds have been applied as both solvent and

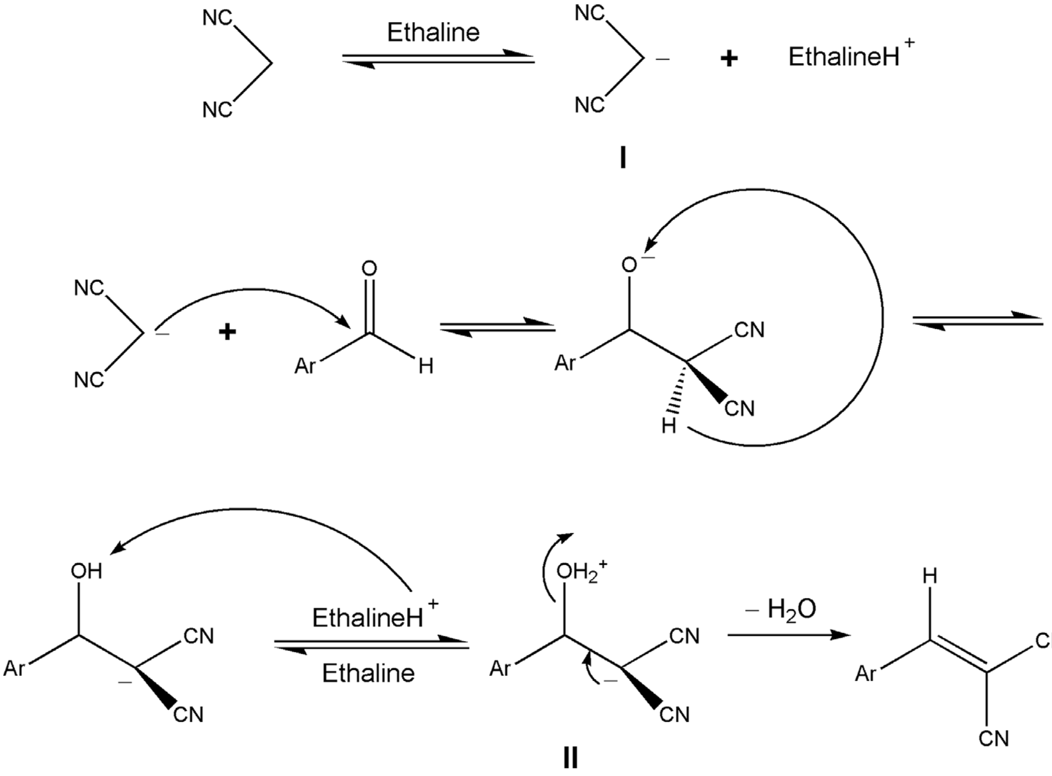

**FIGURE 1** The reaction mechanism of malononitrile and substituted benzaldehydes. The reaction begins by deprotonation of the activated methylene to give anion **I**. This anion reacts with the aldehyde that after protonation forms intermediate **II**. After elimination of water from this intermediate, the final product is formed

catalyst for condensation reactions, and it seems to be the excellent media for such reactions.[15]

One of the most important procedures for the formation of Carbon–Carbon bonds and unsaturated compounds is Knoevenagel condensation reaction.[20] Due to its importance and ability for the synthesis of pharmaceutical and biological active compounds, it has been used widely in organic synthesizes.[21] There are many methods for performing of Knoevenagel condensation reaction in organic solvents with catalyst.[22–24] Xu et al[25] accomplished Knoevenagel condensation reaction over microporous graphitic carbon nitride (CN-Mic) as an effective heterogeneous base catalyst. Recently, Liu et al[15] proceeded this reaction in choline chloride and urea based DESs as a reusable, non-toxic, biodegradable, easily available, and low cost catalyst.

In continuing our investigations on DESs,[26,27] in the present work, we report a kinetics study of the condensation reaction between substituted benzaldehydes and Malononitrile for the first time (Figure 1). The rate coefficient of the reaction was determined in various compositions of aqueous solution of ethylene glycol-choline chloride (ethaline), as a well-known DES, at 25°C. Moreover, the rate coefficient data variations were studied according to linear and nonlinear free energy relationship models such as Hammett equation and preferential solvation model. We should indicate that such studies are not aimed at developing an industrial process but expand the boundaries of knowledge and could be the beginning of the development of industrial applications in the future.

## 2 | EXPERIMENTALS AND METHODS

### 2.1 | Materials

Choline chloride (≥98%), ethylene glycol (≥99.8%), and Malononitrile were obtained from Merck. Also, benzaldehyde and its derivatives were purchased from Merck (all materials in high purity grade). Solid compounds were recrystallized from water/ethanol and water/acetone. Doubly distilled water was used in all solvent samples. Choline chloride was dried with a high-vacuum oven for 48 h at 313 K. Ethylene glycol was dried by 3 Å molecular sieve. The water content of the dried compound was determined by coulometric Karl Fischer titration yielding < 500 ppm. In order to obtain ethaline, choline chloride was mixed with ethylene glycol in a molar ratio of 1:2 and stirred under heating (near 353.15 K) until a homogeneous colorless liquid was formed. The mixtures of ethaline and water over the entire range of ethaline mole fractions were gravimetrically prepared. Each binary mixture was

**TABLE 1** The generality of the reaction of benzaldehydes with Malononitrile

| Entry | *R* | Yield (%)[a,b] | M.P.[c] (°C) | References M.P. (°C) |
|---|---|---|---|---|
| 1 | H | 91 | 83-85 | 82-84[28] |
| 2 | 3-$NO_2$ | 92 | 105-107 | 104[29] |
| 3 | 4-$NO_2$ | 98 | 160-162 | 158-159[28] |
| 4 | 4-Cl | 95 | 159-161 | 161-162[28] |
| 5 | 2-OH | 89 | 183-185 | 186-188[28] |
| 6 | 4-OMe | 90 | 111-113 | 113-114[29] |

[a] Isolated yield.

[b] Reaction conditions: Aromatic aldehyde (0.5 mmol), Malononitrile (0.5 mmol), DES (0.5 mL), 4 h, r.t.

[c] M.P. is melting point.

transferred to the quartz cuvette of a spectrophotometer before each kinetic run.

## 2.2 | Kinetic study procedure

The kinetics of Malononitrile with substituted benzaldehydes were investigated spectrophotometrically in different mixtures of ethaline with $H_2O$, by using a GBC UV–vis cintra 101 spectrophotometer coupled with a thermocell at 25°C. The kinetic runs were studied by measuring the product absorbance from 260 to 350 nm at constant concentration of substituted benzaldehydes ($10^{-5}$ mol dm$^3$) and Malononitrile ($10^{-2}$ mol dm$^3$). Other components, such as solvents, reactants, and intermediates, did not absorb in these wavelengths. Prior to kinetic runs, the stability of the products was tested in ethaline with $H_2O$ media for 24 h. The reaction kinetics of Malononitrile with substituted benzaldehydes were studied under pseudo-first-order conditions. All experiments were recorded at least in triplicate and averaged.

## 2.3 | Synthesis section

The products of the reaction were synthesized by addition of the equimolar amount of Malononitrile and each substituted benzaldehyde, directly. In order to enhance the efficiency, the reactions were performed in aqueous solution of ethaline as a DES.[15] The mixtures were stirred at room temperature for 4 h. Then water was added to the reaction mixture to precipitate the product of the reaction. The product was filtered and recrystallized in ethyl acetate. Final products were obtained in excellent yield, and results were summarized in Table 1.

# 3 | RESULTS AND DISCUSSION

The second-order coefficients of the reaction between Malononitrile with substituted benzaldehydes were determined under pseudo first-order conditions and over the whole range of mole fractions of water in ethaline. Data have been summarized in Table 2. In all reactions, reaction coefficients show a clear maximum around the mole fraction of 0.8 with respect to water.

## 3.1 | Preferential solvation

In the recent decades, studies of the preferential solvation model have increased noticeably in mixture of solvents.[30–33] This simple model as nonlinear equation has shown importance in describing the solute–solvent and solvent–solvent structural information. Preferential solvation model is based on two solvent exchange processes in the microsphere of the solvated molecule according to the following equations:

$$\mathrm{I(S1)_2 + 2S2 \rightleftharpoons I(S2)_2 + 2S1} \tag{1}$$

$$\mathrm{I(S1)_2 + S2 \rightleftharpoons I(S12)_2 + S1} \tag{2}$$

where I indicated the solute, S1 and S2 refer to the two pure solvents, and S12 represents a solvent formed by the interaction of solvents 1 and 2. The solvent S12 can have different properties from those of solvents 1 and 2. I(S1), I(S2), and I(S12) refer to solvation of the solute by solvents S1, S2, and S12, respectively. Equations 1 and 2 indicate the total exchange of solvent 1 by solvent 2 or mixed solvent in the solvation microsphere of the solute. Moreover, the constants $f_{2/1}$, $f_{12/1}$, and $f_{12/2}$ corresponding to the phenomena described by Equations 1 and 2 can be calculated using Equations 3–5:

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \tag{3}$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \tag{4}$$

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}} \tag{5}$$

where $x_i^s$ is the mole fraction of the solvent $i$ in the microsphere of the solvated solute, $x_i^0$ represent the mole fraction of solvent in the bulk solution. Thus, the physical property of a binary mixture ($Y$) can be calculated from those of pure solvents S1, S2, and S12 ($Y_1$, $Y_2$, and $Y_{12}$, respectively), according to Equation 6:

$$Y = \frac{Y_1(1-x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12} f_{12/1}(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \tag{6}$$

The solute–solvent interactions in terms of solvatochromic properties have been widely studied as the physical properties $Y$ in binary mixture.[26,27,30,33-35] Since there are reasonable correlations between activation free energy of the reaction and solvatochromic parameters, this model can be explained by

**TABLE 2** Second-order coefficients ($k_A$, $M^{-1}$ $s^{-1}$) for the reaction of substituted benzaldehydes with malononitrile in various mole fraction of water in ethaline at 25°C

| | Mole fraction of $H_2O$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Substituents in benzaldehyde** | **0** | **0.1** | **0.2** | **0.3** | **0.4** | **0.5** | **0.6** | **0.7** | **0.8** | **0.9** | **1** |
| p-OMe ($10^2 \times k_A$) | 0.55 | 0.81 | 2.1 | 4.6 | 5.7 | 6.4 | 9.4 | 10.2 | 11.5 | 8.75 | 4.8 |
| p-$CH_3$ ($10^2 \times k_A$) | 0.80 | 1.1 | 2.7 | 5.3 | 7.5 | 8.5 | 11.1 | 13.9 | 14.4 | 10.9 | 6.3 |
| None ($10^2 \times k_A$) | 1.2 | 1.5 | 3.0 | 7.1 | 9.1 | 11.3 | 16.2 | 18.4 | 25.3 | 19.2 | 9.2 |
| m-OH ($10^2 \times k_A$) | 1.4 | 2.0 | 4.2 | 8.4 | 13.2 | 15.1 | 18.3 | 25.1 | 31.5 | 23.2 | 10.0 |
| p-Cl ($10^2 \times k_A$) | 1.7 | 2.3 | 5.6 | 11.7 | 15.6 | 18.9 | 23.9 | 31.3 | 35.9 | 27.5 | 13.3 |
| m-Br ($10^2 \times k_A$) | 1.8 | 2.7 | 6.2 | 14.2 | 23.1 | 28.5 | 31.8 | 39.5 | 57.6 | 39.3 | 17.2 |
| m-$NO_2$ ($10^2 \times k_A$) | 2.5 | 3.3 | 8.9 | 22.2 | 31.2 | 35.0 | 57.9 | 68.7 | 82.8 | 63.1 | 32.1 |
| p-$NO_2$ ($10^2 \times k_A$) | 3.2 | 5.1 | 12.6 | 28.1 | 35.6 | 43.8 | 65.6 | 86.3 | 107.1 | 72.7 | 38.1 |

**TABLE 3** The preferential solvation parameters of water–ethaline mixtures calculated by fitting second-order rate coefficient of the reaction in Equation 6

| Substituents in benzaldehyde | $Y_1$ | $Y_2$ | $Y_{12}$ | $f_{2/1}$ | $f_{12/1}$ | $10^3 \times s$ | $r^2$ |
|---|---|---|---|---|---|---|---|
| p-OMe | −1.26 | −2.29 | −0.02 | 0.97 | 1.25 | 8.7 | 0.974 |
| p-$CH_3$ | −1.17 | −2.14 | −0.17 | 1.44 | 2.12 | 5.3 | 0.983 |
| None | −0.97 | −1.97 | 0.01 | 2.27 | 2.70 | 7.8 | 0.977 |
| m-OH | −0.96 | −1.89 | 0.03 | 2.63 | 6.29 | 7.1 | 0.979 |
| p-Cl | −0.86 | −1.82 | −0.004 | 2.82 | 4.95 | 5.9 | 0.982 |
| m-Br | −0.73 | −1.80 | 0.27 | 2.37 | 3.9 | 8.8 | 0.979 |
| m-$NO_2$ | −0.47 | −1.67 | 0.50 | 2.26 | 3.51 | 9.2 | 0.980 |
| p-$NO_2$ | −0.41 | −1.53 | 0.45 | 2.81 | 4.89 | 6.1 | 0.985 |

$Y_1$, $Y_2$, and $Y_{12}$ are $\log k_A$ in ethaline, water, and mixed solvents, respectively. $s$ and $r^2$ refer to the standard error and linear regression coefficient, respectively.

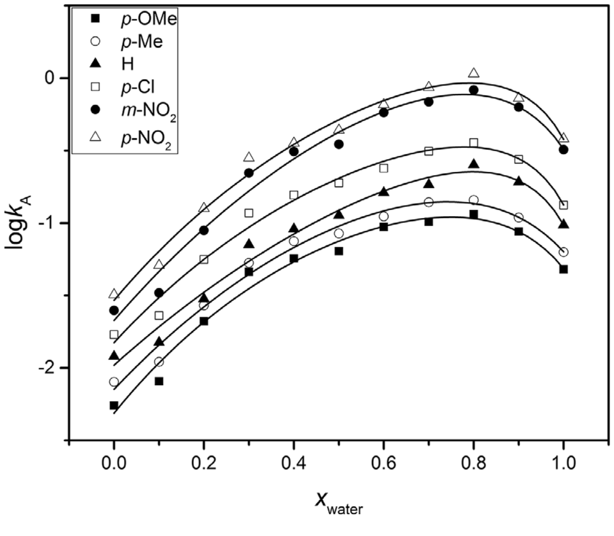

**FIGURE 2** The typical plot of log$k$ versus the mole fraction water. The solid curves have been calculated from coefficients of Equation 6 given in Table 3, and the points are experimental data

applying the log$k$ as a $Y$ parameter. Interesting results were observed, which are summarized in Table 3. The ability of Equation 6 in reproducing the reaction rate coefficients has been demonstrated in Figure 2. In the most of reactions, preferential solvation results reveal that $f_{2/1}$ values are more than the unit. It means that the solutes are preferentially influenced by water. Likewise, the $f_{12/1}$ parameter indicates that solutes are preferentially solvated by the mixed solvent in ethaline–water mixtures. The solvent–solvent interaction between ethaline and water can be result in the non-ideal behavior that was observed for log$k$ values. Complex molecules formed from two solvents, which are preferentially present in the microsphere solvation of the solutes, solvate the reactants and the transition state. Therefore, a positive deviation from ideal behavior is observed for log$k$. The ethaline as a protic DES has a high HBD interaction with Malononitrile. Therefore, it can affect the ability of the nucleophilicity of the Malononitrile.

## 3.2 | Structural LFER

The well-known Hammett correlation classically is applied to predict the effects of substituents and solvents on reaction-rate constants between organic compounds.[36] Some authors have investigated the effects of the chemical reactions in solution comprehensively since the proposal of Hammett's equation.[37–39] The Hammett equation is expressed by the following formula:

$$\log k = \log k_0 + \rho\sigma \tag{7}$$

**TABLE 4** Hammett's parameters for the reaction of Malononitrile with substituted benzaldehydes in the mixture of $H_2O$ and ethaline at 25°C

| $x_{H_2O}$ | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\rho$ | 0.631 | 0.656 | 0.687 | 0.736 | 0.750 | 0.767 | 0.806 | 0.841 | 0.886 | 0.854 | 0.822 |
| $r^2$ | 0.938 | 0.946 | 0.974 | 0.993 | 0.979 | 0.972 | 0.999 | 0.994 | 0.978 | 0.983 | 0.993 |

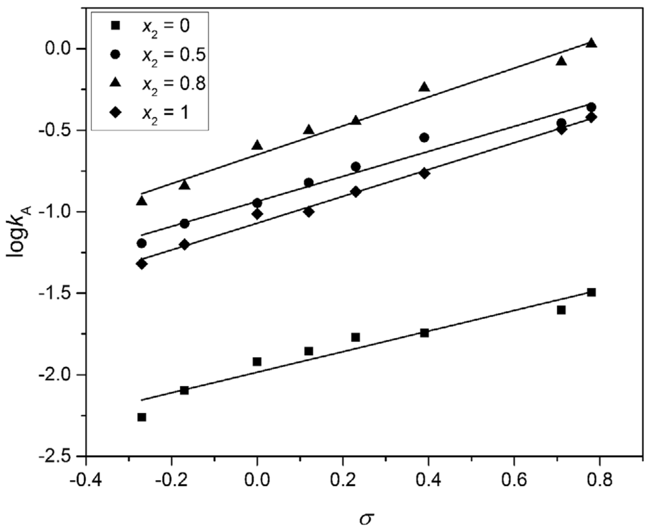

**FIGURE 3** Typical Hammett plot of log$k$ versus constant $\sigma$ for the reaction in the solvent mixtures ($x_2$ is the mole fraction of water)

where $k$ is the rate constant of the reaction. The symbol $k_0$ defines the rate coefficient corresponding to reaction of unsubstituted benzaldehyde with Malononitrile, $\sigma$ is a constant which demonstrates the characteristic of the substituent group. Its value indicates the resonance and inductive effects of substituent, simultaneously, when attached to a benzene ring. The electron-withdrawing substituents decrease the electron density of the aromatic ring whereas electron-donating substituents have an increasing effect. Values of $\sigma$ have been summarized in some reports.[40] Reactions with a negative $\rho$ are accelerated by electron-donating groups while the positive $\rho$ in a reaction shows that reaction rate decrease in the presence of an electron-donating group. The LFER investigations according to Hammett equation were performed in the solvent mixtures. Results have been summarized in Table 4 and show a good linear behavior with positive slope (Figure 3). The positive values of the Hammett slope imply that electron-withdrawing substituents accelerate the reaction rate. It can be attributed to the increasing electrophile characterization of substituted benzaldehydes and decreases the electron density on the C-atom of aldehyde of the transition state structure. In the other word, the electron-with drawing substituents amplify the possibility of nucleophilic attack on the carbon of the carbonyl group. This is an expectable result in condensation reactions. On the other hand, the low magnitude of $\rho$ values (less than unit) proposed that the electrophilicity of the substituted benzaldehydes is not a preferable effect on the reaction rate. The addition of water content in ethaline, both second-order rate coefficients and $\rho$ values increase slowly up to $x_{\text{water}} = 0.8$ then decrease to its corresponding value in the neat water. These variations demonstrate positive deviations from ideal behavior. It shows that the reaction has the highest rate and sensitivity about the characteristic of substituent.

## 4 | CONCLUSIONS

Both the solvent composition and the structure of reactants showed considerable changes in the reaction rate of Malononitrile with the substituted benzaldehydes. The second-order rate constant of the reaction represented an increase slowly to a maximum with adding the water, and then it decreased to its corresponding value in the neat water. The correlation of second-order rate coefficients based on Hammett's substituent constants yielded a linear line with positive slope. It can be attributed to the increasing electrophile characterization of substituted benzaldehydes and decrease the electron density on the C-atom of aldehyde of the transition state structure. The results obtained in the application of the preferential solvation model demonstrated that the non-ideal behavior of log$k$ in mixture of solvents can be related to the difference between the bulk composition of the solvents and the microsphere solvation of the solutes. As it mentioned, this paper is about fundamental chemistry and not with developing of a new industrial process but also, for industrial use, the reaction can be performed in the lower molar fraction of water like 0.2, or even in pure DES solvent as a green process. As the results show, the reaction can be carefully performed in this condition. Furthermore, DES can be easily recovered by addition of an organic solvent like dichloromethane, to the reaction media and separation of organic compounds and products.[41,42]

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## REFERENCES

1. Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. *Chem Soc Rev*. 2008;37:123-150.
2. Strawhecker KE, Kumar SK, Douglas JF, Karim A. The critical role of solvent evaporation on the roughness of spin-cast polymer films. *Macromolecules*. 2001;34:4669-4672.

3. Carlisle TK, Bara JE, Gabriel CJ, Noble RD, Gin DL. Interpretation of $CO_2$ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach. *Ind Eng Chem Res*. 2008;47:7005-7012.
4. Reichardt C. Solvatochromic dyes as solvent polarity indicators. *Chem Rev*. 1994;94:2319-2358.
5. Reichardt C. *Solvents and solvent effects in organic chemistry*. 3rd ed.. Wiley-VCH: Weinheim; 2003.
6. Capello C, Fischer U, Hungerbühler K. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem*. 2007;9:927-934.
7. Leitner W. Supercritical carbon dioxide as a green reaction medium for catalysis. *Acc Chem Res*. 2002;35:746-756.
8. Perrut M. Supercritical fluid applications: industrial developments and economic issues. *Ind Eng Chem Res*. 2000;39:4531-4535.
9. Hallett JP, Welton T. Room-temperature ionic liquids: solvents for synthesis and catalysis. *Chem Rev*. 2011;111:3508-3576.
10. Rogers RD, Seddon KR. Ionic liquids–solvents of the future?. *Science*. 2003;302:792-793.
11. Vekariya RL. A review of ionic liquids: applications towards catalytic organic transformations. *J Mol Liq*. 2017;227:44-60.
12. Smith EL, Abbott AP, Ryder KS. Deep eutectic solvents (DESs) and their applications. *Chem Rev*. 2014;114:11060-11082.
13. Zhang Q, De Oliveira Vigier K, Royer S, Jérôme F. Deep eutectic solvents: syntheses, properties and applications. *Chem Soc Rev*. 2012;41:7108-7146.
14. Dai Y, van Spronsen J, Witkamp GJ, Verpoorte R, Choi YH. Natural deep eutectic solvents as new potential media for green technology. *Anal Chim Acta*2013;766:61-68.
15. Liu S, Ni Y, Wei W, Qiu F, Xu S, Ying A. Choline chloride and urea based eutectic solvents: effective catalytic systems for the Knoevenagel condensation reactions of substituted acetonitriles. *J Chem Res*. 2014;38:186-188.
16. Gao G, Wang P, Liu P, Zhang W, Mo LP, Zhang ZH. Deep eutectic solvent catalyzed one-pot synthesis of 4, 7-dihydro-1H-pyrazolo [3, 4-b] pyridine-5-carbonitriles. *Chin J Org Chem*. 2018;38:846-854.
17. Liu P, Hao JW, Mo LP, Zhang ZH. Recent advances in the application of deep eutectic solvents as sustainable media as well as catalysts in organic reactions. *RSC Adv*. 2015;5:48675.
18. Zhang M, Liu YH, Shang ZR, Hu HC, Zhang ZH. Supported molybdenum on graphene oxide/$Fe_3O_4$: an efficient, magnetically separable catalyst for one-pot construction of spiro-oxindole dihydropyridines in deep eutectic solvent under microwave irradiation. *Catal Commun*. 2017;88:39.
19. Abbott AP, Barron JC, Ryder KS, Wilson D. Eutectic-based ionic liquids with metal-containing anions and cations. *Chem A Eur J*. 2007;13:6495-6501.
20. Gao Z, Zhou J, Cui F, Zhu Y, Hua Z, Shi J. Superparamagnetic mesoporous Mg–Fe bi-metal oxides as efficient magnetic solid-base catalysts for Knoevenagel condensations. *Dalton Trans*. 2010;3:11132-11135.
21. Tietze LF, Rackelmann N. Domino reactions in the synthesis of heterocyclic natural products and analogs. *Pure Appl Chem*. 2004;76:1967-1983.
22. Hruby SL, Shanks BH. Acid–base cooperativity in condensation reactions with functionalized mesoporous silica catalysts. *J Catal*. 2009;263:181-188.
23. Climent MJ, Corma A, Fornés V, etal. Aluminophosphates oxynitrides as base catalysts: nature of the base sites and their catalytic implications. *J Catal*. 1996;163:392-398.
24. Angeletti E, Canepa C, Martinetti G, Venturello P. Silica gel functionalized with amino groups as a new catalyst for Knoevenagel condensation under heterogeneous catalysis conditions. *Tetrahedron Lett*. 1988;29:2261-2264.
25. Xu J, Shen K, Xue B, Li YX. Microporous carbon nitride as an effective solid base catalyst for Knoevenagel condensation reactions. *J Mol Catal A Chem*. 2013;372:105-113.
26. Harifi-Mood AR, Sadrzadeh S. Dimethyl sulfoxide/deep eutectic solvents mixtures as media in the reation of 1-fluoro-2, 4-dinitrobenzene with piperidine: a solvent effect study. *J Phy Org Chem*. 2018;31.
27. Aryafard M, Abbasi M, Reha D, Harifi-Mood AR, Minofar B. Experimental and theoretical investigation of solvatochromic properties and ion solvation structure in DESs of reline, glyceline, ethalineand their mixture with PEG-400. *J Mol Liq*. 2019;284:59-67.
28. Kaupp G, Naimi-Jamal MR, Schmeyers J. Solvent-free Knoevenagel condensations and Michael additions in the solid state and in the melt with quantitative yield. *Tetrahedron Lett*. 2003;59:3753-3760.
29. Krishnan GR, Sreekumar K. First example of organocatalysis by polystyrene-supported PAMAM dendrimers: highly efficient and reusable catalyst for Knoevenagel condensations. *Eur J Org Chem*. 2008;2008:4763-4768.
30. Harifi-Mood AR, Khorshahi H. Binary mixtures of dimethyl sulfoxide with methanol, ethylene glycol, and glycerol as solvent: solvatochromism and chemical kinetics study. *J Mol Liq*. 2018;259:361-368.
31. Khupse ND, Kumar A. Delineating solute-solvent interactions in binary mixtures of ionic liquids in molecular solvents and preferential solvation approach. *J Phys Chem B*. 2010;115:711-718.
32. Moita MLCJ, Santos AFS, Silva JFCC. Lampreia IMS. Polarity of some [NR1R2R3R4]+[Tf2N]− ionic liquids in ethanol: preferential solvation versus solvent–solvent interactions. *J Chem Eng Data*. 2012;57:2702-2709.
33. Harifi-Mood AR, Abbasi M. Preferential solvation and solvatochromic parameters in mixtures of poly (ethylene glycol)-400 with some molecular organic solvents. *J Sol Chem*. 2018;47:1503-1513.
34. García B, Aparicio S, Alcalde R, Ruiz R, Dávila MJ, Leal JM. Characterization of lactam-containing binary solvents by solvatochromic indicators. *J Phy Chem B*. 2004;108:3024-3029.
35. Harifi-Mood AR, Habibi-Yangjeh A, Gholami MR. Solvatochromic parameters for binary mixtures of 1-(1-Butyl)-3-methylimidazolium tetrafluoroborate with some protic molecular solvents. *J Phy Chem B*. 2006;110:7073-7078.
36. Hammett LP. The effect of structure upon the reactions of organic compounds. Benzene derivatives. *J A Chem Soc*. 1937;59:96-103.
37. Heasley VL, Fisher AM, Herman EE, etal. Investigations of the reactions of monochloramine and dichloramine with selected phenols: examination of humic acid models and water contaminants. *J Env Sci Technol*. 2004;38:5022-5029.
38. Egorov AM, Matyukhova SA. Kinetics of reaction of copper with substituted benzyl chlorides in dipolar aprotic solvents. *In J Chem Kinet*. 2007;39:547-555.

39. Winkeljohn WR, Vasquez PC, Strekowski L, Baumstark AL. Oxidation of substituted pyridines by dimethyldioxirane: kinetics and solvent effects. *Tetrahedron Lett*. 2004;45:8295-8297.
40. Hansch C, Leo A, Taft R. A survey of Hammett substituent constants and resonance and field parameters. *Chem Rev*. 1991;91:165-195.
41. Smink D, Kersten SRA, Schuur B. Recovery of lignin from deep eutectic solvents by liquid-liquid extraction. *Sep Purif Technol*. 2020;235:116127.
42. Smith EL, Abbott AP, Ryder KS. Deep eutectic solvents (DESs) and their applications. *Chem Rev*. 2014;114:11060-11082.

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