Hydrodynamic and mass transfer performance of a hydrophobic deep eutectic solvent in extracting phenol from aqueous phase

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Abstract. Hydrophobic deep eutectic solvents (HDESs), due to many advances, have found profound applications in many fields including the extraction process. This study delves into the drops behavior of a green HDES, synthesized from dodecanoic acid and octanoic acid precursors (1:3 molar ratio) in separation of phenol from aqueous phase. The solvent has the desired properties of low interfacial tension with water and low viscosity. Based on various relevant criteria, the generated drops in a pilot column were in circulating mode and the terminal velocities were close to the Klee-Treybal model. In mass transfer study, as the key factor in evaluating the HDES performance, extraction fractions were found within (0.13−0.19) and the overall mass transfer coefficient within (12.48−24.09) μm/s, comparable with imidazolium-based ionic liquids as alternatives of DESs. For the aim of modelling, the mass transfer coefficient data were precisely reproduced according to the modified Newman's equation, taking into account the local continuous phase mass transfer resistance and an effective molecular diffusivity. A maximum deviation of 9.3% was relevant to the experimental data compared with the model predicted values. The results highlight industrial scale application of HDESs for extracting pollutants.

Keywords: Deep eutectic solvent; Phenol; Drop hydrodynamic; Extraction fraction; Mass transfer coefficient

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1. Introduction

Water pollution poses a widespread threat to all living organisms. Phenolic compounds, in particular, are widely recognized as hazardous materials in water due to their vast biological

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activity and toxicity [1]. Phenolic compounds may generate harmful compounds during disinfection and oxidation processes, necessitating substantial methods for their removal from aqueous solutions [2]. This issue is a crucial matter in various industries dealing with phenol including those of producing pharmaceuticals, polymers, rubbers, paints, fertilizers, surfactants, explosives, textiles, pulp and papers, iron and steel, and in petroleum industries [3-5].

For the aim of separation, liquid−liquid extraction process is a preferred operation in different chemical and allied industries. The basis is transferring one or more solutes from a feed to solvent due to different chemical potential and reaching ultimately to equilibrium conditions, if relevant. This technique is known economy for cases in petrochemical, hydrometallurgy, food, pharmaceutical and biochemistry as well as removing pollutants from aqueous media. However, noteworthy, the major challenge for this process relies on the solvent issues like volatility, toxicity, large scale demands. Therefore, use of alternative solvents has been always interested.

Green solvents have emerged as a pivotal material in development of sustainable chemical processes, offering alternatives to traditional solvents, among them, deep eutectic solvents (DES) and ionic liquids (ILs) are with unique properties [6]. The latter are salts that exist in a liquid or semi-liquid state at room temperature, characterized by their low volatility, high thermal stability, and tunable solubility. They are composed entirely of ions and have the ability to dissolve a variety of substances, making them profound materials for various applications in extraction, catalysis and electrochemistry [7]. DESs, on the other hand, have been identified as the attractive green alternatives since they are often formed by materials that are capable to become assimilated by the environment. DESs are frequently formed by binary or ternary mixtures that associate via hydrogen bonds and give a product with significant depression in melting point compared to the individual constituents. In fact, interactions in ILs differ from those in DESs corresponding to the electrostatic-type in the former and hydrogen bond-type in the latter. To form a DES, one or more hydrogen bond donor (HBD) and one or more hydrogen bond acceptor (HBA), should contribute [8]. Though both the ILs and DESs exhibit favorable characteristics, DESs offer several advantages over ILs in the views of:

- Cost effectiveness: DESs are generally produced less expensive than ILs, making them more accessible for various applications [9].
- Simplicity of preparation: The synthesis of DESs typically requires fewer steps and less stringent conditions, often involving simple mixing of readily available compounds [10,11].
- Biodegradability: Many DESs are composed of naturally occurring substances, which can lead to better environmental outcomes compared with the IL synthetic compounds [12].
- Low Toxicity: By selecting suitable precursors, safe solvents could be prepared and incorporating natural components significantly reduces the level of toxicity. Key natural ingredients including organic acids, organic bases, and amino acids are recently involved in DES preparation [13,14].
- Enhanced solvating properties: DESs can offer superior solvation capabilities for specific solutes, beneficial in extraction and separation processes [15].
- Low viscosity: DESs could be with significantly low viscosity compared to many ILs, favoring solute transfer [16].

Relevantly, hydrophobic deep eutectic solvents (HDESs), are immiscible or partial soluble in aqueous media, which makes them distinct for extracting organic pollutants like phenol from aqueous solutions [17,18]. So far, numerous studies have been devoted to extraction of phenol from aqueous solutions with HDESs derived from monoterpenoids-fatty acids [19,20] and menthol-fatty acids [21]. However, mixer-settlers have been used in these studies and no assessment has been made on the drops hydrodynamic and mass transfer coefficient. It is while majority of extraction processes relies on the contact of phases in columns in which one phase is dispersed drop-wise through the continuous phase, providing a large surface area for mass transfer [22]. Thus, for evaluating new generation of solvents, hydrodynamic and mass transfer performance of drops have to be determined prior to large scale applications.

Present study focuses on the drops behavior of a benign HDES, synthesized from dodecanoic and octanoic acids, in extracting phenol from aqueous phase. The corresponding physical and equilibrium properties of the HDES, have been recently reported [23,24]. This solvent originates from naturally occurring fatty acids which often demonstrate minimal toxicity and are considered as environmentally friendly compounds [25]. Deep eutectic solvents from fatty acids preserve their inherent advantages of non-corrosiveness, cost-effectiveness and non-toxicity [26].

Hydrodynamic behavior of the HDES drops, moving steadily in the aqueous phase, is ascertained and the phenol overall mass transfer coefficient is determined for mass transfer direction of continuous to dispersed phase. Results are compared with the previous studies in extracting phenol from aqueous phase using conventional and ionic liquid solvents [27,28]. Accordingly, the overall mass transfer coefficient are calculated form the modified Newman's equation, which takes into account the local mass transfer coefficient of the continuous phase in a direct calculation as well as the equilibrium distribution of the solute and the effective diffusivity. This study helps to develop an efficient and environmental-friendly strategy for large-scale operations.

2. Materials and methods

2.1. Materials

The octanoic acid (purity over 98%) and dodecanoic acid (purity 98%), as the precursors of the deep eutectic solvent were sourced from Sigma-Aldrich, and phenol was the product of Merck (purity over 99%). All chemicals were used without any purification. Fresh deionized water (conductivity about 8 µS/cm) was prepared by means of a deionizing system from Hastaran Company.

Each solution was prepared with respect to the required mass of solute using an Ohaus balance (Adventurer Pro AV264, Switzerland), measuring samples with accuracy of 0.0001 g. The corresponding physical properties of the dispersed and continuous phases of the HDES–phenol–water system are given in Table 1. Densities were determined precisely by using an automatic densimeter (Anton Paar DMA 4500, Austria, uncertainty of 0.01 kg/m^3) which works based on oscillating of the U-tube. Deionized water and dry air were used for calibration of this equipment prior to measurements. Viscosity measurements were conducted using an Ubbelohde viscometer (uncertainty of 2×10^{-3} kg/m·s) attributed to the equation $\mu = \rho(kt - c/t)$ in which μ, ρ, and t refer to viscosity, density, and efflux time, respectively. Parameters k and c represent viscometer constants. The viscometer temperature was controlled via the thermostat. Interfacial tensions were measured using a tensiometer (FARS EOR Tech) which works on pendant-drop analysis and consisted of an image processing system coupled with a MLH-10X high zoom camera lens. To analyze phenol concentration in HDES samples, an Abbe refractometer (AR4, Kruss, Germany, accuracy of 0.00005) was used while temperature was set at 25 °C using a thermostat with external circulation (Julabo, Germany, uncertainty of 0.1 °C).

Molecular diffusivity of phenol in the HDES (dispersed phase) was calculated from the well-known Wilke and Chang correlation, modified by Reddy and Doraiswamy [29]. For this aim, the molecular weight, normal boiling point, critical temperature and pressure were estimated as 158.24 g/mol, 278 °C, 464.6 °C and 2516.9 kPa, respectively; obtained based on a previously introduced method [30]. To determine the required molar volume of the solvent at normal boiling point, the Rackett equation [31], modified by Spencer and Danner [32] was used, resulting in molar volume of 222.1 cm^3/mol. The group contribution method proposed by Schotte [33] was employed to estimate the molar volume of phenol at the normal boiling point as 98.15 cm^3/mol.

The utilized HDES was synthesized from dodecanoic and octanoic acids with molar ratio of 1:3 and prepared according to the procedure detailed in the literature [35,36]. Briefly, different compounds, with specified mole ratios, were stirred and gradually heated in a glass vessel to about 70 °C obtaining a clear solution. The HDES product was found with melting point of 8.3 °C. The melting point of a solvent indicates the lower threshold of its liquid state. This temperature not only marks the transition from solid to liquid but also determines the thermal stability i.e. remaining in the liquid state at room temperature and facilitating its use in various processes and reactions with no need of heating [37-39].

2.2. Experimental setup and procedures

For conducting experiments, a Pyrex glass column measuring 11.4 cm diameter and 51 cm height (Figure 1) was utilized to assist phase contact [40,41]. The continuous aqueous phase solution was with 2 wt% phenol and the column was filled with about 4 L of this solution. HDES drops were conducted into the continuous aqueous phase by means of a syringe pump (JMS SP-500, Japan), to drive a glass syringe and through various glass nozzles positioned at the bottom of the column. The steady movement of drops was achieved after about 6.5 cm travelling above each nozzle tip. To accurately measure the initial concentration at this point, a separate short column similar to the main one was utilized equipped with the same nozzles. For measuring drop diameter, the pump flow rate was adjusted so that the spacing between the generated drops was 5 to 6 cm. Under this condition, the required time to generate a specific number of drops (about 10 drops) was recorded and based on the calibrated flow-rate of the syringe pump, the volume of each drop and diameter were calculated.

To determine the contact time and terminal velocity, the time of traveling from the point 6.5 cm above the nozzle tip to the level of continuous phase (spanning a distance of 33 cm) was measured by means of a stopwatch and, after that, the drop terminal velocity was easily obtained. Each experiment was conducted at least three times for each nozzle and the average values were considered for the analysis. For determining initial and final concentrations, a minimum number of drops were collected above the small and large columns, followed by immediate analysis using the refractometer. All experiments were performed at the laboratory temperature ($25 \pm 1\ ^{\circ}$C).

3. Results and discussion

3.1. Hydrodynamic study

Based on the internal flow pattern, drops in contact with liquid continuous phase are generally classified into three categories of rigid, circulating and oscillating. Specifically, the criteria for ascertaining the internal circulating pattern are as following:

- Dimensionless group H, defined by the Grace model [42] as:

  $$\mathrm{H} = (4/3)\mathrm{E\ddot{o}}\ \mathrm{M}^{-0.149}\,(\mu_c/\mu_w)^{-0.14} \qquad (1)$$

  in which Eötvös ($\mathrm{E\ddot{o}}$) and Morton (M) dimensionless numbers are as $\mathrm{E\ddot{o}} = g\,\Delta\rho d^2/\gamma$ and $\mathrm{M} = g\,\mu_c^4\Delta\rho/\rho_c^2\gamma^3$ in which d, g, γ, ρ_c and μ_c are, respectively, drop size, gravitational acceleration, interfacial tension, continuous phase density and viscosity. The parameter $\Delta\rho$ represents the density difference of the phases. Subscripts *c* and *w* relate to the continuous phase and pure water.
- Reynolds number of drops in the continuous phase, $\mathrm{Re}_c = \rho_c u_t d/\mu_c$, in which u_t is the drop terminal velocity.

- Weber number, $\mathrm{We} = \rho_c u_t^2 d / \gamma$, indicating the ratio of the drop inertia to the interfacial tension.
- The ratio of $\mathrm{Re}_c / \mathrm{N}_{PG}^{-0.15}$ in which N_{PG} is the inverse of Morton number.
- Critical diameter, introduced by Klee and Treybal [43] as:

$$d_c = 0.33 \rho_c^{-0.14} \Delta\rho^{-0.43} \mu_c^{0.30} \gamma^{0.24} \quad \text{(in c.g.s. units)} \qquad (2)$$

Tables 2 and 3 list the size of drops generated from various nozzles and the corresponding criteria values related to the drop circulating. As is represented, all drops exhibit a circulating flow pattern. The measured terminal velocity and the terminal velocity based on the Grace [42], the Klee and Treybal [43] and Vignes [44] models in relation to drop size are presented in Figure 2. There is a better agreement between the terminal velocity values and the Klee and Treybal model. The difference between the data and the predicted values by the Vignes model is significant. A rather poor agreement with the Grace model is also relevant arising from the high viscosity ratio and low interfacial tension between aqueous and organic phases. This discrepancy has been discussed by Saien and Asrami [27] and Bäumler et al. [45].

3.2. Mass transfer study

Based on mass balance around drops over a short time interval of steady movement, the overall mass transfer coefficient (K_{od}) can be determined after integrating. The terms involved are the initial and final concentrations and contact time [46]:

$$K_{od} = -\frac{d}{6t} \ln(1 - E) \qquad (3)$$

$$E = \frac{C_{df} - C_{di}}{C_d^* - C_{di}} \qquad (4)$$

where E stands for the extraction fraction, t contact time, and d drop diameter. The extraction fraction is defined based on the drops initial (C_{di}) and final (C_{df}) concentrations in drop phase and C_d^* as the drop corresponding equilibrium concentration of phenol in the continuous phase (14.6 wt%) The equilibrium data for the utilized HDES−phenol−water chemical system have been properly reported in a previous study [23]. The direction of mass transfer in all the experiments was from continuous to dispersed phase.

With the employed experimental set-up, the obtained extraction fraction and overall mass transfer coefficient were within (0.13−0.19) and (12.48−24.09) μm/s, respectively. As illustrated in Figure 3, the extraction fraction exhibits a positive variation with drop size, attributed to the intensified internal circulation within the drops. The figure further demonstrates that K_{od} increases consistently with drop size; hence, it is influenced by both the extraction fraction and key hydrodynamic parameters, including drop size and contact time. Prolonged contact times results in a decrease in K_{od}. The observed variations in K_{od} are aligned closely with the findings reported by Sun et al. for single drops [28].

Table 4 provides a summary of the various methods and solvents used in the phenol extraction from aqueous phase. As is observed, HDES drops, despite smaller size, due to the low interfacial tension, exhibit higher overall mass transfer coefficients when compared with an imidazolium-based ionic liquid solvent [27]. Noteworthy, as indicated by Eq. (3), the overall mass transfer coefficient is inversely dependent on the contact time, shorter for the larger drops. The higher overall mass transfer coefficient values, compared with conventional solvents of methyl isobutyl ketone (MIBK) and cumene (rather volatile and hazardous nature) can be attributed to the low level viscosities (5.7×10^{-4} and 7.3×10^{-4} kg/m·s at 25 $^{\circ}$C), as well as high interfacial tension in contact with water, consistent with generating big drops. It is worth to mention that salty aqueous solutions often raise the interfacial tension between organic and aqueous phases.

3.3. Mass transfer coefficient modeling

Analysis of mass transfer between the involved phases, grounded in Whitman's two-film theory, reveals the mass transfer resistance to be mainly in the continuous phase. It is due to the relatively high slope of the solute equilibrium curve (about 7.1 at 25 °C), in the chemical system of HDES−phenol−water system.

There are two frequent methods to calculate the overall mass transfer coefficient: i) adding resistances based on the Whitman two film theory and ii) mathematical solution of the diffusional mass transfer in drops while passing steadily through a continuous phase with a certain level of mass transfer resistance [49]. Considering these alternatives and the mass transfer resistance in the continuous phase, the second method, proposed by Stainer [50] and for instance used by Ghalehchian and Slater [51] was employed. Accordingly, the modified Newman's equation is expressed as:

$$K_{od} = \frac{-d}{6t} \ln\left[\sum_{n=1}^{\infty} \frac{1}{\beta_n^2[\beta_n^2 + \mathrm{L}(\mathrm{L}-1)]} \exp\left(\frac{-4\,D_{\mathrm{d}}\,\beta_n^2\,t}{d^2} \right) \right] \qquad (5)$$

where eigenvalues β_n , n = 1, 2, 3, …, are derived from the equation:

$$\beta \cot \beta + \mathrm{L} - 1 = 0 \qquad (6)$$

in which, L is defined as $\mathrm{L} = k_c d / 2m\, D_d$, analogous to a Sherwood number. Here k_c is the continuous phase mass transfer coefficient, m represents the slope of the equilibrium line at the corresponding temperature (25 °C), and D_d is the molecular diffusivity in the dispersed phase (HDES). Thus, it is needed to determine the continuous phase mass transfer coefficient from

$k_c = \mathrm{Sh}_c D_c / d$, and contributed in K_{od} via L and β. The parameter D_c stands for the molecular diffusivity of phenol in the water continuous phase. Accordingly, the Sherwood number of continuous phase, Sh_c, is calculated based on following equation, proposed by Steiner for continuous phase Sherwood number, taking into account experimental data for a wide range of 10 < Re_c < 1200 and 190 < $\mathrm{Sc}_c = \mu_c / (\rho_c D_c)$ < 241000, collected from eight groups of investigators [50]:

$$\frac{\mathrm{Sh}_c - \mathrm{Sh}_{c,rigid}}{\mathrm{Sh}_{c,circ} - \mathrm{Sh}_{c,rigid}} = 1 - \exp\left[-4.18 \times 10^{-3} \mathrm{Pe}_c^{0.42}\right] \quad (7)$$

It has been expressed that according to the model, k_c changes gradually within the limits corresponding to rigid drops, relevant to low Peclet numbers ($\mathrm{Pe}_c = \mathrm{Re}_c \times \mathrm{Sc}_c$) and drops with potential-flow conditions with high Peclet numbers. The continuous phase Sherwood number corresponding to rigid drops, $\mathrm{Sh}_{c,rigid}$, was proposed by Steiner [50] as:

$$\mathrm{Sh}_{c,rigid} = 2.43 + 0.77\, \mathrm{Re}_c^{1/2} \mathrm{Sc}_c^{1/3} + 0.0103\, \mathrm{Re}_c \mathrm{Sc}_c^{1/3} \quad (8)$$

whereas Sherwood number for drops with perfect internal circulating, $\mathrm{Sh}_{c,circ}$, was introduced from the Boussinesq equation [52] as:

$$\mathrm{Sh}_{c,circ} = \frac{2}{\sqrt{\pi}} \mathrm{Re}_c^{1/2} \mathrm{Sc}_c^{1/2} \quad (9)$$

With respect to applicability of Eq. (5) for rigid drops; it is reasonable to substitute an effective diffusivity for the molecular diffusivity coefficient. In the method which was proposed by Sherwood [53] for the first time, $\Re$ is nominated as the “enhancement factor”. Steiner [50,54] evaluated this method by utilizing a wide range of experimental data with various physical properties and mass transfer resistance as well as different interfacial tensions.

Here, the provided overall mass transfer coefficient data and the appropriate drop size as well as the physical properties were introduced to the above model including Eqs. (5-9) together with the effective diffusivity as $D_{oe} = \Re D_d$. Accordingly, the values of the enhancement factor, $\Re$, were obtained within the range of (4.35−16.52) for different drops. This range is close to that reported by Sun et al. [28] for single drops using methyl isobutyl ketone−phenol−water chemical system.

The enhancement factor, $\Re$, is closely related to drops Reynolds number ($\mathrm{Re} = \rho_c u_t d / \mu_c$), within (202.62−247.11), corresponding to the impact of drop size, as well as the Eötvös number ($\mathrm{E\ddot{o}} = g \Delta\rho d^2 / \gamma$), within (1.51−1.89), indicating the ratio of gravitational to interfacial tension forces. Previously, these dimensionless numbers were used for correlating $\Re$ in accordance to the data obtained from a Hanson mixer settler as well as from pulsed disc and doughnut columns [55,56]. Rahbar Kelishami et al. [57] introduced an effective diffusivity as a function of Reynolds number and the height of the packings in a packed column. Here, the enhancement factor values were precisely reproduced by the following equation:

$$\Re = a_0 + a_1 (\mathrm{Re})^{a_2} (\mathrm{E\ddot{o}})^{a_3} \quad (10)$$

in which a_0 to a_3 are the equation parameters. The optimized values for these parameters as well as the regression coefficient are listed in Table 5. Based on the above correlation, the enhancement factor ($\Re_{\mathrm{cal}}$) values were within (3.24−15.21). By applying the introduced effective diffusivity to the model, the overall mass transfer coefficients were with a maximum relative deviation of 9.3% compared to the experimental data.

4. Conclusions

In this study, a green hydrophobic deep eutectic solvent was synthesized from fatty acids and was explored with desired performance in extraction of phenol from aqueous phase. Results confirmed the superior performance of the solvent. The hydrodynamic studies indicated circulating drops within the size range of (2.77−3.10) mm, and terminal velocities revealed in better agreement with the Klee−Treybal model. The relevant overall mass transfer coefficients, within (12.48−24.09) µm/s, were comparable with other solvents like ionic liquids. The obtained data could be precisely predicted by the model developed for rigid drops passing through the continuous phase with a level of mass transfer resistance by incorporating an effective diffusivity. The corresponding enhancement factor was expressed as a function of involved parameters.

The results underscore the potential of a deep eutectic solvent as an economy and environmentally friendly option in the extraction of phenol. Future studies may focus on the extraction efficiency of the deep eutectic solvent on diverse phenolic compounds with various concentrations or in contact with real wastewaters. The effects of different operating parameters such as temperature, pH and presence of salts could be investigated. Further, solvent regeneration in multiple extraction cycles and assessment of the life cycle would be beneficial.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

c	viscometer constant (–)

C	solute concentration (wt%)
d	drop diameter (mm)
D	diffusivity (m^2/s)
E	extraction fraction (–)
Eö	Eötvös dimensionless number ($g\Delta\rho d^2/\gamma$) (–)
H	dimensionless group in the Grace model (–)
k	viscometer constant (–) and local mass transfer coefficient (μm/s)
K_{od}	overall mass transfer coefficient (μm/s)
L	dimensionless group defined for Newman's equation ($L = k_c d / 2mD_d$) (–)
m	solute distribution coefficient (–)
M	Morton dimensionless number ($g\mu_c^4\Delta\rho/\rho_c^2\gamma^3$) (–) and molecular weight (g/mol)
$\mathrm{N_{PG}}$	inverse of Morton dimensionless number (–)
Pe	Peclet number (Re. Sc) (–)
Re	drop Reynolds number ($\rho_c u_t d / \mu_c$) (–)
Sc	Schmidt number ($\mu/\rho D$)
Sh	Sherwood number (–)
T	temperature (°C)
t	drops contact time and efflux time in viscometer (s)
u_t	terminal velocity (m/s)
We	drop Weber number ($\rho_c u^2 d / \gamma$) (–)

Greek symbols

β	eigenvalue (–)
$\Re$	enhancement factor for diffusivity (–)
γ	interfacial tension (mN/m)
μ	viscosity (kg/m·s)
ρ	density, (kg/m^3)
Δ	difference (–)

Subscripts

c	continuous phase
cr	critical size
d	dispersed phase
f	final value
i	initial value
m	molecular
oe	overall effective
od	overall dispersed value
t	terminal
w	water
cal	calculated
exp	experimental

Superscripts

*	equilibrium

References

1. Haydari, I., Aziz, K., Kaya, S., et al. “Green synthesis of reduced graphene oxide and their use on column adsorption of phenol from olive mill wastewater”, *Process Saf. Environ. Prot.*, **170**, pp. 1079–1091 (2023). https://doi.org/10.1016/j.psep.2022.12.086
2. Busca, G., Berardinelli, S., Resini, C., et al. “Technologies for the removal of phenol from fluid streams: A short review of recent developments”, *J. Hazard. Mater.*, **160**(2-3), pp. 265–288 (2008). https://doi.org/10.1016/j.jhazmat.2008.03.045
3. Candan, E., and Ayten, G. “Review of treatment technologies for the removal of phenol from wastewaters”, *J. Water Chem. Technol.*, **43**(2), pp. 145–154 (2021).
4. Pavithra, K.G., Rajan, P.S., Arun, J., et al. “A review on recent advancements in extraction, removal and recovery of phenols from phenolic wastewater: Challenges and future outlook”, *Environ. Res.*, **237**, 117005 (2023). https://doi.org/10.1016/j.envres.2023.117005
5. Raza, W., Lee, J., Raza, N., et al. “Removal of phenolic compounds from industrial waste water based on membrane-based technologies”, *J. Ind. Eng. Chem.*, **71**, pp. 1–18 (2019). https://doi.org/10.1016/j.jiec.2018.11.024
6. Prabhune, A., and Dey, R. “Green and sustainable solvents of the future: deep eutectic solvents”, *J. Mol. Liq.* **379**, 121676 (2023). https://doi.org/10.1016/j.molliq.2023.121676
7. Singh, S.K., and Savoy, A.W. “Ionic liquids synthesis and applications: An overview”, *J. Mol. Liq.*, **297**, 112038 (2020). https://doi.org/10.1016/j.molliq.2019.112038
8. Guo, Z., Ling, Z., Wang, C., et al. “Integration of facile deep eutectic solvents pretreatment for enhanced enzymatic hydrolysis and lignin valorization from industrial xylose residue”, *Bioresour Technol.*, **265**, pp. 334–339 (2018). https://doi.org/10.1016/j.biortech.2018.06.027
9. Paiva, A., Craveiro, R., Aroso, I., et al. “Natural deep eutectic solvents–solvents for the 21st century”, *ACS Sustain. Chem. Eng.*, **2**(5), pp. 1063–1071 (2014). https://doi.org/10.1021/sc500096j
10. Xue, K., Liu, H., Fan, D., et al. “Selective recovery of lithium from aqueous solution with hydrophobic deep eutectic solvent based on quantum chemical calculations and experimental investigation”, *Process Saf. Environ. Prot.*, **192**, pp. 1566–1575 (2024). https://doi.org/10.1016/j.psep.2024.11.040
11. Chen, Y., and Mu, T. “Revisiting greenness of ionic liquids and deep eutectic solvents”, *Green Chem. Eng.*, **2**(2), 174–186 (2021). https://doi.org/10.1016/j.gce.2021.01.004
12. Płotka-Wasylka, J., De la Guardia, M., Andruch, V., et al. “Deep eutectic solvents vs ionic liquids: similarities and differences”, *Microchem. J.*, **159**, 105539 (2020). https://doi.org/10.1016/j.microc.2020.105539
13. Nie, F., Feng, C., Ahmad, N., et al. “A new green alternative solvent for extracting echinacoside and acteoside from cistanche deserticola based on ternary natural deep eutectic solvent”, *J. Ind. Eng. Chem.*, **118**, pp. 499–510 (2023). https://doi.org/10.1016/j.jiec.2022.11.033
14. Vanda, H., Dai, Y., Wilson, E.G., et al. “Green solvents from ionic liquids and deep eutectic solvents to natural deep eutectic solvents”, *CR Chim.*, **21**(6), pp. 628–638 (2018). https://doi.org/10.1016/j.crci.2018.04.002

15. Yang, J., Wang, Y., Zhang, W., et al. “Alkaline deep eutectic solvents as novel and effective pretreatment media for hemicellulose dissociation and enzymatic hydrolysis enhancement”, *Int. J. Biol. Macromol.*, **193**, pp. 1610–1616 (2021). https://doi.org/10.1016/j.ijbiomac.2021.10.223

16. Ribeiro, B.D., Florindo, C., Iff, L.C., et al. “Menthol-based eutectic mixtures: Hydrophobic low viscosity solvents”, *ACS Sustain. Chem. Eng.*, **3**(10), pp. 2469–2477 (2015). https://doi.org/10.1021/acssuschemeng.5b00532

17. Sadrmousavi-Dizaj, A., Xu, D., Zhang, L., et al. “Liquid–liquid equilibria and intermolecular interactions for extraction of 2-methyl phenol, 3-methyl phenol and phenol from water by a ternary hydrophobic deep eutectic solvent”, *J. Taiwan Inst. Chem. Eng.*, **167**, 105845 (2025). https://doi.org/10.1016/j.jtice.2024.105845

18. van Osch, D.J., Zubeir, L.F., van den Bruinhorst, A., et al. “Hydrophobic deep eutectic solvents as water-immiscible extractants”, *Green Chem.*, **17**(9), pp. 4518–4521 (2015). https://doi.org/10.1039/C5GC01451D

19. Jiang, Z., Wang, X., Deng, H., et al. “Study of the experimental and microscopic mechanism of the removal of phenolic compounds from wastewater based on hydrophobic deep eutectic solvents”, *J. Mol. Liq.*, **406**, 125055 (2024). https://doi.org/10.1016/j.molliq.2024.125055

20. Maletta, A., Gutiérrez, A., Tan, P.J., et al. “Separation of phenolic compounds from water by using monoterpenoid and fatty acid based hydrophobic deep eutectic solvents”, *J. Mol. Liq.*, **381**, 121806, (2023). https://doi.org/10.1016/j.molliq.2023.121806

21. Cheng, H., Huang, Y., Lv, H., et al. “Insights into the liquid extraction mechanism of actual high-strength phenolic wastewater by hydrophobic deep eutectic solvents” *J. Mol. Liq.* , **368**, 120609, (2022). https://doi.org/10.1016/j.molliq.2022.120609

22. Mazzola, P.G., Lopes, A.M., Hasmann, F.A., et al. “ Liquid–liquid extraction of biomolecules: an overview and update of the main techniques”, *J. Chem. Technol. Biotechnol.*, **83**(2), pp. 143–157 (2008). https://doi.org/10.1002/jctb.1794

23. Saien, J., Bahiraei, M., and Jafari, F. “A green hydrophobic deep eutectic solvent for extraction of phenol from aqueous phase”, *Sci. Rep.*, **13**(1), 17449 (2023). https://doi.org/10.1038/s41598-023-44600-x

24. Bahiraei, M., Saien, J., and Jafari, F. “Salting-out effects in extraction of phenol from aqueous solutions using a hydrophobic deep eutectic solvent based on dodecanoic and octanoic acids: experimental study and comparison”, *J. Chem. Eng. Data.*, **69**, pp. 4019–4028 (2024). https://doi.org/10.1021/acs.jced.4c00570

25. Kudłak, B., Owczarek, K., Namieśnik, J. “Selected issues related to the toxicity of ionic liquids and deep eutectic solvents: A review”, *Environ. Sci. Pollut. Res.*, **22**, pp. 11975–11992 (2015). https://doi.org/10.1007/s11356-015-4794-y

26. Florindo, C., Romero, L., Rintoul, I., et al. “From phase change materials to green solvents: Hydrophobic low viscous fatty acid–based deep eutectic solvents”, *ACS Sustain. Chem. Eng.*, **6**(3), pp. 3888–3895 (2018). https://doi.org/10.1021/acssuschemeng.7b04235

27. Saien, J., and Asrami, M.R. “Comparative studies on the performance of ionic liquid and conventional solvent drops in extraction of phenol from water”, *Chem. Eng. Res. Des.*, **166**, pp. 259–266 (2021). https://doi.org/10.1016/j.cherd.2020.12.014

28. Sun, Y., Zhao, Q., Zhang, L., et al. “Measurement and correlation of the mass transfer coefficient for the methyl isobutyl ketone–water–phenol system”, *Ind. Eng. Chem. Res.*, **53**(9), pp. 3654–3661 (2014). https://doi.org/10.1021/ie4036862

29. Reddy, K., and Doraiswamy, L. “Estimating liquid diffusivity”, *Ind. Eng. Chem. Fundam.*, **6**(1), pp. 77–79 (1967). https://doi.org/10.1021/i160021a012

30. Mirza, N.R., Nicholas, N.J., Wu, Y., et al. “Estimation of normal boiling temperatures, critical properties, and acentric factors of deep eutectic solvents”, *J. Chem. Eng. Data.*, **60**(6), pp. 1844–1854 (2015). https://doi.org/10.1021/acs.jced.5b00046

31. Rackett, H.G. “Equation of state for saturated liquids”, *J. Chem. Eng. Data.*, **15**(4), 514–517 (1970). https://doi.org/10.1021/je60047a012

32. Spencer, C.F., and Danner, R.P. “Improved equation for prediction of saturated liquid density”, *J. Chem. Eng. Data.*, 17(2), pp. 236–241 (1972). https://doi.org/10.1021/je60053a012

33. Schotte, W. “Prediction of the molar volume at the normal boiling point”, *Chem. Eng. J.*, **48**(3), pp. 167–172 (1992). https://doi.org/10.1016/0300-9467(92)80032-6

34. Niesner, R., and Heintz, A. “Diffusion coefficients of aromatics in aqueous solution”, *J. Chem. Eng. Data.*, **45**(6), pp. 1121–1124 (2000). https://doi.org/10.1021/je0000569

35. Arcon, D.P., and Franco Jr, F.C. “All-fatty acid hydrophobic deep eutectic solvents towards a Simple and efficient microextraction method of toxic industrial dyes”, *J. Mol. Liq.*, **318**, 114220 (2020). https://doi.org/10.1016/j.molliq.2020.114220

36. Sas, O.G., Castro, M., Domínguez, Á., et al. “Removing phenolic pollutants using deep eutectic solvents”, *Sep. Purif. Technol.*, **227**, 115703 (2019). https://doi.org/10.1016/j.seppur.2019.115703

37. Van Osch, D.J., Dietz, C.H., Warrag, S.E., et al. “The curious case of hydrophobic deep eutectic solvents: a story on the discovery, design, and applications”, *ACS Sustain. Chem. Eng.*, **8**(29), pp. 10591–10612 (2020). https://doi.org/10.1021/acssuschemeng.0c00559

38. Aguirre, C.L., Cisternas, L.A., Valderrama, J.O. “Melting-point estimation of ionic liquids by a group contribution method”, *Int. J. Thermophys.*, **33**, pp. 34–46 (2012). https://doi.org/10.1007/s10765-011-1133-5

39. Van Osch, D.J., Dietz, C.H., Van Spronsen, J., et al. “A search for natural hydrophobic deep eutectic solvents based on natural components”, *ACS Sustain. Chem. Eng.*, **7**(3), pp. 2933–2942(2019). https://doi.org/10.1021/acssuschemeng.8b03520

40. Saien, J., and Daliri, S. “Modelling mass transfer coefficient for liquid–liquid extraction with the interface adsorption of hydroxyl ions”, *Korean J. Chem. Eng.*, **26**(4), pp. 963–968 (2009). https://doi.org/10.1007/s11814-009-0160-4

41. Saien, J., and Daneshamoz, S. “Experimental Studies on the effect of ultrasonic waves on single drop liquid–liquid extraction”, *Ultrason. Sonochem.*, **40**, pp. 11–16 (2018). https://doi.org/10.1016/j.ultsonch.2017.06.020

42. Grace, J.R. “Shapes and velocities of single drops and bubbles moving freely through immisicible liquids”, *Trans. Inst. Chem. Eng.*, **54**, pp. 167–173 (1976).

43. Klee, A.J., and Treybal, R.E. “Rate of rise or fall of liquid drops”, *AIChE J.*, **2**(4), pp. 444–447 (1956). https://doi.org/10.1002/aic.690020405

44. Vignes, A. Hydrodynamique des dispersions”, *Genie Chimi.*, **93**, pp. 129–142 (1965).

45. Bäumler, K., Wegener, M., Paschedag, A., et al. “Drop rise velocities and fluid dynamic behavior in standard test systems for liquid/liquid extraction: Experimental and numerical investigations”, *Chem. Eng. Sci.*, **66**(3), pp. 426–439 (2011). https://doi.org/10.1016/j.ces.2010.11.009

46. Godfrey, J.C., and Slater, M.J. (1994) “Liquid–Liquid Extraction Equipment”, Wiley New York. (1994).

47. Yung, K.K., Smith, C.D., Bowser, T., et al. “The use of an ionic liquid in a Karr reciprocating plate extraction column”, *Chem. Eng. Res. Des.*, **90**(11), pp. 2034–2040 (2012). https://doi.org/10.1016/j.cherd.2012.03.006

48. Yung, K.K., Smith, C.D., Bowser, T., et al. “The use of an ionic liquid in a Karr reciprocating plate extraction column: Drop size distribution”, *Sep. Sci. Technol.*, **47**(12), pp. 1733–1739 (2012). https://doi.org/10.1080/01496395.2012.681000

49. Saien, J., and Daliri, S. “Improving performance of liquid–liquid extraction with temperature for mass transfer resistance in both phases”, *J. Taiwan Inst. Chem. Eng.*, **45**(3), pp. 808–814 (2014). https://doi.org/10.1016/j.jtice.2013.09.027

50. Steiner, L. “Mass transfer rates from single drops and drop swarms”, *Chem. Eng. Sci.*, **41**(8), pp. 1979–1986 (1986). https://doi.org/10.1016/0009-2509(86)87114-7

51. Ghalehchian, J., Slater, M. “A possible approach to improving rotating disc contactor design accounting for drop breakage and mass transfer with contamination”, *Chem. Eng. J.*, **75**(2), pp.131–144 (1999). https://doi.org/10.1016/S1385-8947(99)00101-1

52. Boussinesq, J. “Calcul du pouvoir refroidissant des courants fluides”, *J. Math. Pures. Appl.*, **1**, pp. 285–332 (1905).

53. Sherwood, T., Evans, J., and Longcor, J. “Extraction in spray and packed columns”, *Ind. Eng. Chem.*, **31**(9), pp. 1144–1150 (1939). https://doi.org/10.1021/ie50357a021

54. Steiner, L., Oezdemir, G., and Hartland, S. “Single-drop mass transfer in the water-toluene-acetone system”, *Ind. Eng. Chem. Res.*, **29**(7), pp. 1313–1318 (1990). https://doi.org/10.1021/ie00103a034

55. Torab-Mostaedi, M., Safdari, J., Ghannadi-Maragheh, M., et al. “Prediction of overall mass transfer coefficients in a hanson mixer-settler using effective diffusivity”, *J. Chem. Eng. Jpn.*, **42**(2), pp. 78–85 (2009). https://doi.org/10.1252/jcej.08we089

56. Torab-Mostaedi, M., Ghaemi, A. and Asadollahzadeh, M. “Prediction of mass transfer coefficients in a pulsed disc and doughnut extraction column”, *Can. J. Chem. Eng.*, **90**(6), pp. 1570–1578 (2012). https://doi.org/10.1002/cjce.20649

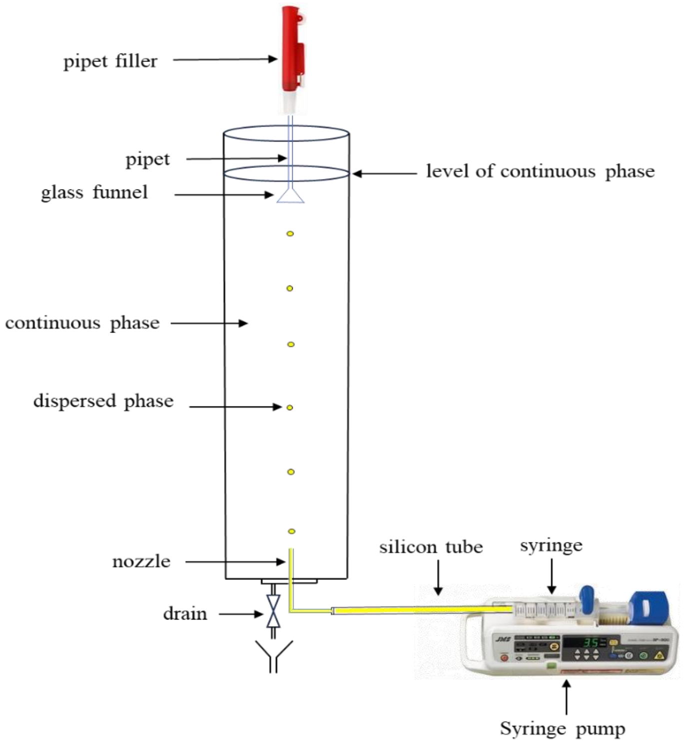
57. Rahbar Kelishami, A., Bahmanyar, H. Nazari, L., et al. “Development of an effective diffusivity model for regular packed liquid extraction columns”, *Aust. J. Basic Appl. Sci.*, **3**(2), pp. 407–417 (2009).

Figure captions

Figure 1. Schematic of the used setup for the single drop experiments.

Figure 2. Terminal velocity of drops as a function of drop size. Error bars represent the standard deviation of at least three replicates.

Figure 3. Extraction fraction (red circle) and the overall mass transfer coefficient (blue triangle) as functions of drop size. The error bars represent standard deviation from three replicates.



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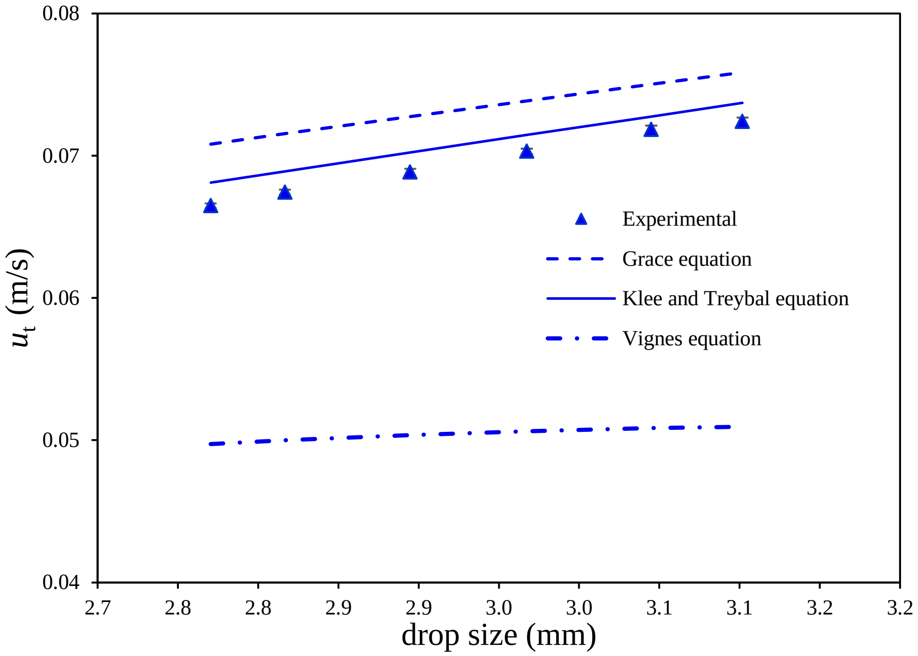

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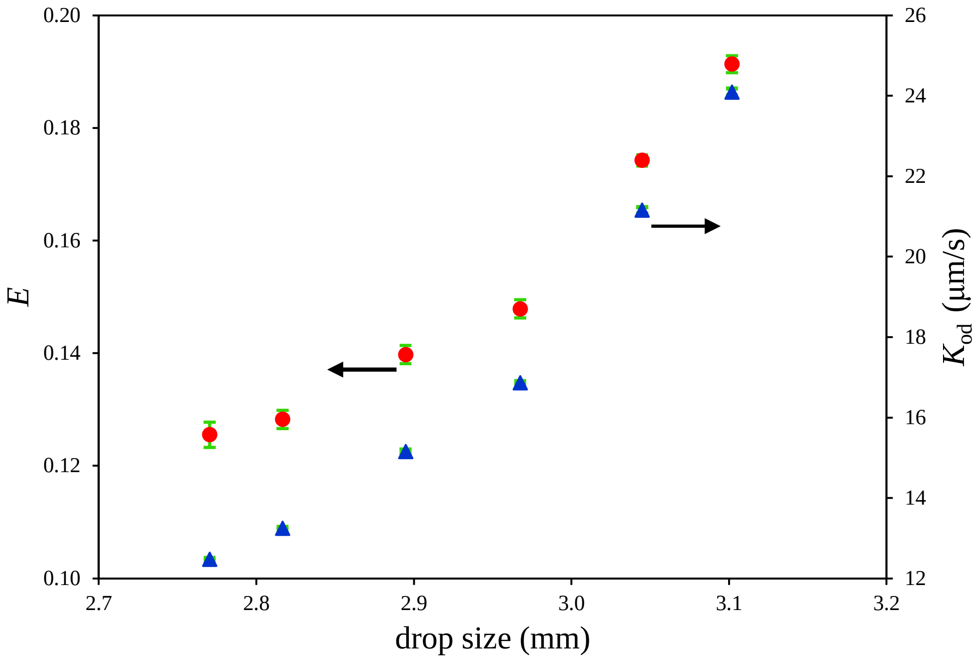

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Table captions

Table 1. Density (ρ) and viscosity (μ) of phases, molecular diffusivity of phenol (D) in the phases and the interfacial tension between phases (γ) at 25 ˚C.

Table 2. Nozzle tip diameter and generated drop size generated from each nozzle.

Table 3. The various criteria for circulating behavior of generated drops from different nozzles.

Table 4. Comparison of the hydrodynamic and mass transfer performance of drops in extracting phenol from aqueous phase using different solvents.

Table 5. Parameters of Equation (10).

Table 1. Density (ρ) and viscosity (μ) of phases, molecular diffusivity of phenol (D) in the phases and the interfacial tension between phases (γ) at 25 ˚C.

Phase	**ρ (kg/m^3)**	**μ (kg/m·s)**	**D (m^2/s)**	**γ (mN/m)**
dispersed (HDES)	900.64	9.210×10^{-3}	0.124×10^{-9}	4.90
continuous (aqueous)	998.81	0.908×10^{-3}	0.998×10^{-9} [a]	

[a] Ref [34]

Table 2. Nozzle tip diameter and generated drop size generated from different nozzles.

Nozzle number	1	2	3	4	5	6
Nozzle tip diameter (mm)	0.87	0.91	0.94	0.98	1.02	1.04
Drop size (mm)	2.77	2.82	2.89	2.97	3.04	3.10

Table 3. The various criteria for circulating behavior of generated drops from various nozzles.

$2 < H < 59.3$	$Re_c / N_{PG}^{-0.15} < 20$	$We < 3.58$	$200 < Re_c < 500$	$d < d_{cr}$ (mm)
34.01−42.64	11.71−14.28	2.50−3.32	202.62−247.11	2.77−3.10 < 3.2

Table 4. Comparison of the hydrodynamic and mass transfer performance of drops in extracting phenol from aqueous phase using different solvents.

Solvent	Method	$\Delta\rho$ (kg/m^3)	γ (mN/m)	Drop size (mm)	Continuous phase phenol conc. (wt%)	K_{od} (µm/s)	Ref.
[Bmim][PF$_6$][a]	swarm of drops	–	–	0.1−0.3	$(2.67-4.08)\times10^{-3}$	35−39[b]	[47,48]
[Hmim][NTf$_2$][c]	single drop	289.66	12.86	2.28−3.01	2	7.4−16.2	[27]
cumene	single drop	138.36	30.71	2.85−4.32	2	56.3−164.4	[27]
methyl isobutyl ketone	single drop	200.7	8	2.49−3.28	0.1−0.8	30.53−95.33	[28]
HDES	single drop	98.16	4.90	2.77−3.10	2	12.48−24.09	present work

[a] 1-butyl-3-methylimidazolium hexafluorophosphate (ionic liquid)

[b] based on mean drop size

[c] 1-hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide (ionic liquid)

Table 5. Parameters of Equation (10).

Parameter	a_0	a_1	a_2	a_3	R^2
Value	−9.03	0.008	1.24	1.94	0.951

Biographies

Javad Saien was born in 1958 in Hamedan, Iran. He received his PhD degree in Chemical Engineering, from University of Bradfored, UK, in 1995. From 1986, he has been the member of academic staff at Bu-Ali Sian University, Hamedan, where he was promoted to a full professor position about 16 years ago. His research, during these years, has been concerned mainly on liquid−liquid extraction. Single drop experiments, impinging streams, liquid−liquid equilibria and interfacial tension alteration. The influence of media and operating conditions like mass transfer intensification with external fields, use of ionic liquids and deep eutectic solvents as well as nanoparticles have been interested. Degradation of pollutants in wastewaters using homogenous/heterogeneous processes in different photo and solar reactors has been his other interest.

Mansoureh Bahiraei was born in 1989 in Nahavand, Iran. She received her B.Sc. in Chemistry from Razi University, Kermanshah in 2011, also her M.Sc. in Applied Chemistry from Bu-Ali Sina University, Hamedan in 2013. Currently, she is a PhD student in the Department of Applied Chemistry, Bu-Ali Sina University, Hamedan. During these years, she could successfully publish 2 scientific papers through international journals. Her research interests are liquid–liquid equilibrium and extraction process. Her recent research works are salt effect on mass transfer coefficient of phenol from water to a hydrophobic deep eutectic solvent.