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Nitrogen-containing switchable solvents for separation of hydrocarbons and their derivatives

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Solvent extraction is commonly used to separate mixtures of hydrocarbons and their derivatives, and solvent choice is strongly influenced by the affinity to the target component, cost and safety. Nitrogen-containing switchable solvents can switch from water-immiscible form to water-miscible bicarbonate salts when CO₂ is injected and back to water-immiscible form when N₂ is injected. Switchable solvents, as a type of recyclable green solvent, can be used not only to separate such mixtures but also to reduce process costs. Herein, four switchable solvents, namely, dipropylamine, di-*sec*-butylamine, *N,N*-dimethylcyclohexylamine (CyNMe₂), and *N,N,N',N'*-tetraethyl-1,3-propanediamine (TEPDA), were employed to separate benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane mixtures, and the corresponding partition and selectivity coefficients were determined. In all cases, separation selectivity increased in the order of dipropylamine < di-*sec*-butylamine < CyNMe₂ < TEPDA, *i.e.*, TEPDA was best suited for the separation of hydrocarbons and their derivatives. In addition, cycling experiments revealed that the TEPDA can be re-used at least 15 times and was well suited for industrial applications. In the end, the mechanism of the separation was put forward.

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1. Introduction

The effective separation of mixtures of hydrocarbons and their derivatives, which are important petroleum components, can make petroleum resource utilisation more efficient. At present, the above separation is widely realised using solvent extraction, with much attention directed at the investigation of traditional solvents such as sulfolanes, esters, alcohols, and ionic liquids (ILs). However, as the toxicity, volatility, and flammability of organic solvents pose potential hazards during industrial-scale separation, new, highly efficient, and environmentally friendly solvents for hydrocarbon mixture separation are highly sought.^{1–4}

As a type of recyclable green solvents, switchable solvents are soluble in water under a CO₂ atmosphere and insoluble in the absence of CO₂.^{1–7} The polarity, hydrophobic–hydrophilic and other properties of switchable solvents can be reversibly changed in the presence of triggers. Taking advantage of this property, a switchable solvent can be used to extract the product first, and then, a trigger is added to separate the product from the solvent through a phase transition process, and the solvent can be recovered after removal of the trigger, all without any distillation step, which greatly simplifies the process of solvent recovery. However, most switchable solvents are amines, as

these compounds are protonated in aqueous media in an atmosphere of CO₂ and deprotonated under N₂,⁸ however, not all amines are switchable solvents.^{9,10} Nitrogen-containing switchable solvents have been widely used for extraction,^{11–15,17} *e.g.*, Holland *et al.* used *N,N*-dimethylcyclohexylamine (CyNMe₂) to extract bitumen, achieving bitumen recoveries of 94–97%.¹⁸ Besides, the above amine was also used to extract lipids from *Botryococcus braunii* microalgae with an extraction efficiency of 22%.¹¹ Wang *et al.* studied the physicochemical properties of switchable-hydrophilicity solvent systems,¹⁹ and Bediako *et al.* used CyNMe₂ as a switchable solvent in their novel method of producing fine silica aerogel powder from silica hydrogel.²⁰ In the past few years, switchable solvent microextraction has been extensively studied.^{16,21–26} These findings indicate that nitrogen-containing switchable solvents can be effectively applied in extraction-based separation.

Hydrocarbon mixtures are generally difficult to separate using conventional solvents, *e.g.*, benzene/cyclohexane mixtures can only be separated by extractive distillation in view of the similar volatilities of these hydrocarbons.^{27–30} Li *et al.* showed that ILs can be used as entrainers to facilitate the separation of benzene and cyclohexane by extractive distillation,²⁷ which is also the only method allowing the separation of ethyl acetate/acetonitrile and ethyl acetate/*n*-heptane mixtures^{31–33} and is characterised by high energy consumption and equipment cost.³³ Although many researchers have applied switchable solvents to the separation of mixtures of

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hydrocarbons and their derivatives, the corresponding studies involving nitrogen-containing switchable solvents are few.

Accordingly, we make use of the variable ability of nitrogen-containing switchable solvents to separate different hydrocarbons and their derivatives to design a novel procedure for the separation of hydrocarbons and their derivatives, employing benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane as model mixtures and dipropylamine, di-*sec*-butylamine, CyNMe₂, and *N,N,N',N'*-tetraethyl-1,3-propanediamine (TEPDA) as model solvents. In addition, process parameters are optimised, and the effects of switchable solvent and mixture component identities on separation selectivity and solvent recyclability are revealed.

2. Materials and methods

2.1. Materials

Chemicals, including dipropylamine, di-*sec*-butylamine, CyNMe₂, TEPDA, benzene, cyclohexane, ethyl acetate, acetonitrile, and *n*-heptane were of analytical grade and were purchased from Aladdin Reagent Company Co., Ltd., China. The chemical structures of nitrogen-containing switchable solvents are shown in Fig. 1. CO₂ and N₂ were used at a purity of 99.9%. Milli-Q water (18.2 MΩ cm at 25 °C) was used throughout.

2.2. Separation of benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane

Details of the separation procedure are provided in Fig. 2. Typically, a benzene/cyclohexane mixture (2 mL of each component) was treated with dipropylamine (16 mL), and the resulting homogenous solution was transferred into a 100 mL beaker held at a constant temperature of 45 °C in a water bath. Then, CO₂ (300 mL) was injected into the mixture over 30 min, which was followed by the injection of deionised water (16 mL) to induce separation into upper (cyclohexane) phase and lower (benzene + dipropylamine) phases. The concentrations of cyclohexane and benzene were determined by gas chromatography (GC) and used to calculate the cyclohexane partition coefficient, the benzene partition coefficient, and the benzene selectivity coefficient, with the benzene selectivity coefficient employed to assess separation

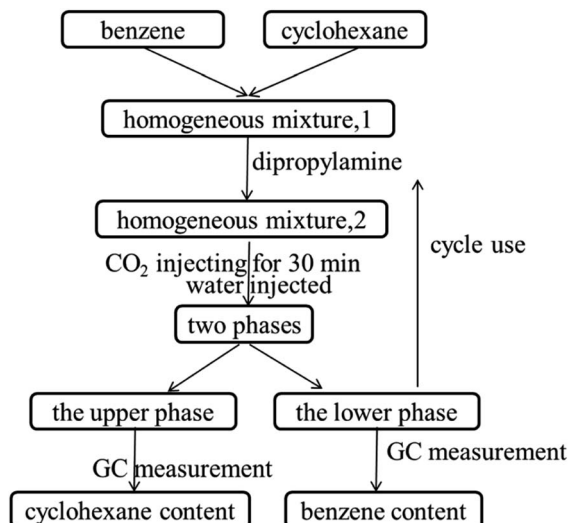


Fig. 2 Separation of benzene/cyclohexane based on the use of dipropylamine.

efficiency. Subsequently, N₂ was injected into the lower phase to induce separation into the upper dipropylamine phase and the lower benzene phase, and then the upper phase and the lower phase was phase separation, and then the amine could be recycling use. In the next experiment, the amine was used for the separation again, and then the separation effect was calculated. In addition, using different switchable solvents (CyNMe₂, di-*sec*-butylamine and TEPDA) to separate ethyl acetate/acetonitrile and ethyl acetate/*n*-heptane mixtures according to the method described above under the same operating conditions. The detailed device diagram of separating benzene and cyclohexane was shown in Fig. 3, and other hydrocarbons and their derivatives separation was similar. The selectivity coefficient was determined according to eqn (1). D_{benzene} and $D_{\text{cyclohexane}}$ were the partition coefficient of benzene and cyclohexane, which were calculated by the eqn (2). In the eqn (2), y_m and y_n represent the mole fractions of components in the m and n phases, respectively, V_m and V_n represent the volumes of the m and n phases, respectively.

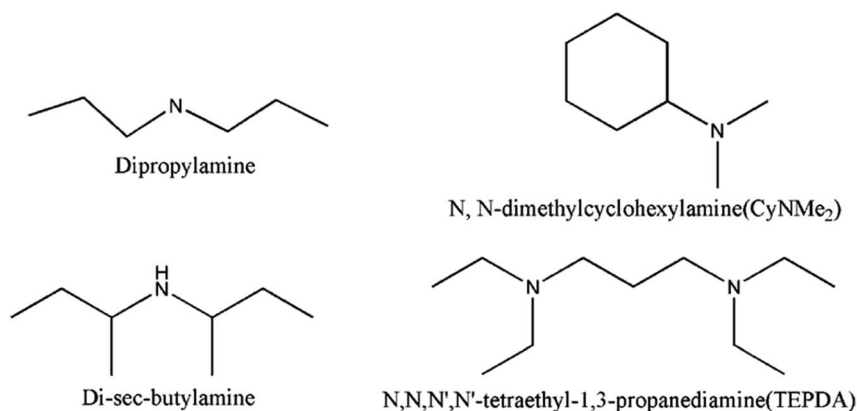


Fig. 1 Chemical structures of nitrogen-containing switchable solvents.



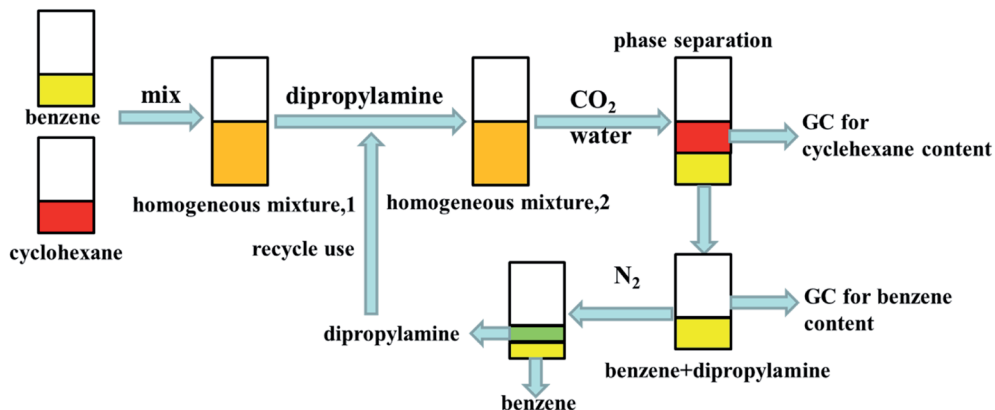


Fig. 3 Experimental steps followed in this work to separate hydrocarbons and their derivatives.

$$\text{Benzene selectivity coefficient} = \frac{D_{\text{benzene}}}{D_{\text{cyclohexane}}} \quad (1)$$

$$D_{\text{cyclohexane}} = \frac{y_m}{V_m} / \frac{y_n}{V_n} \quad (3)$$

$$D_{\text{benzene}} = \frac{y_m}{V_m} / \frac{y_n}{V_n} \quad (2)$$

All the experimental data were repeated at least three times to obtain a reliable result. The error bars value of experimental

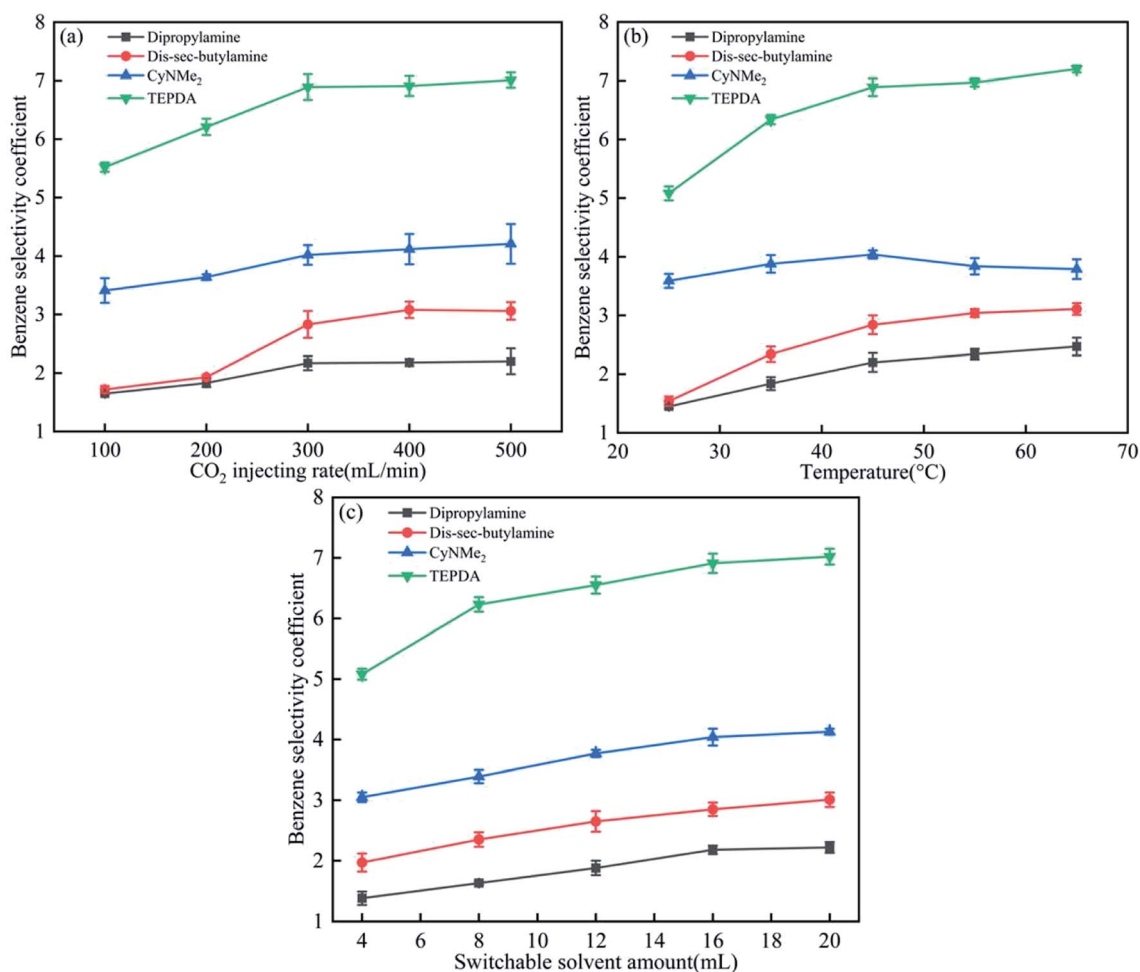


Fig. 4 Effects of (a) CO₂ injection rate, (b) temperature, and (c) switchable solvent amount on the benzene selectivity coefficient.



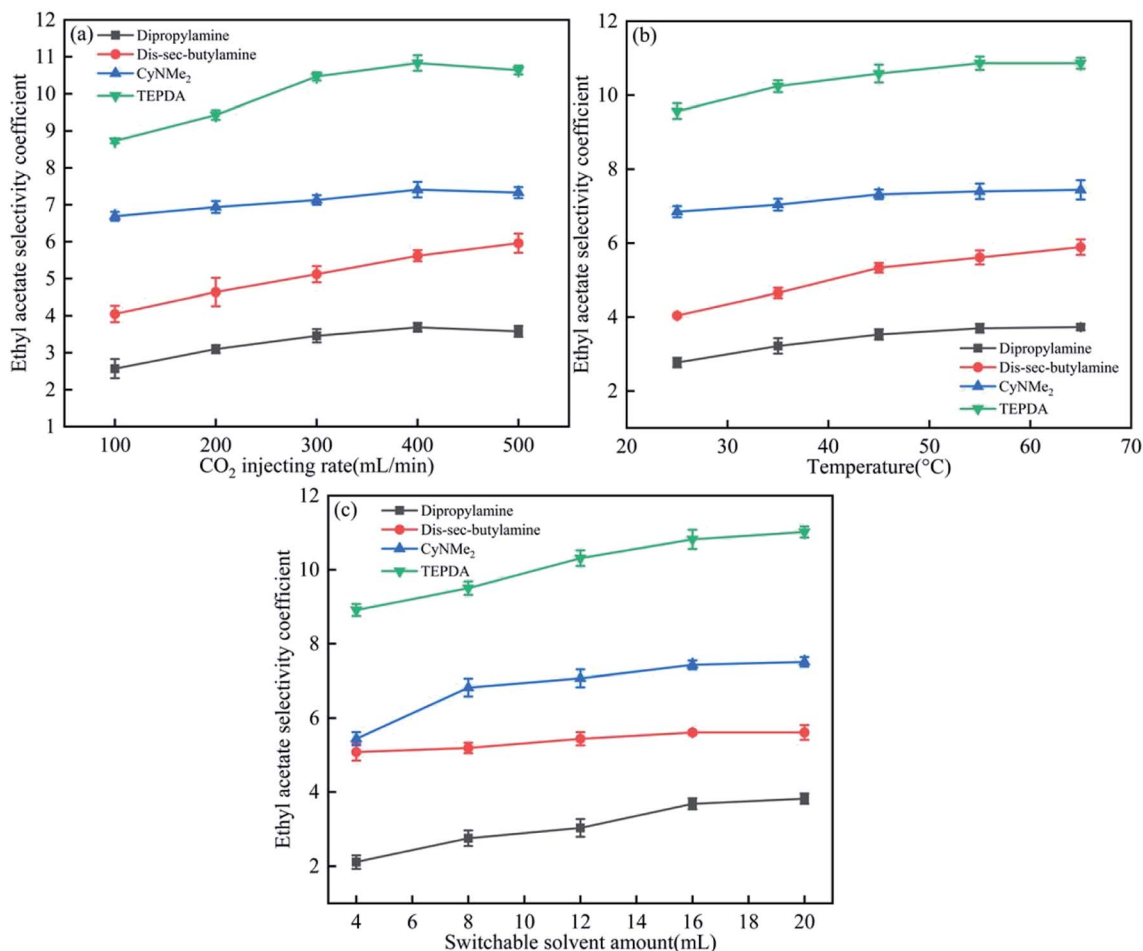


Fig. 5 Effects of (a) CO₂ injection rate, (b) temperature, and (c) switchable solvent amount on the ethyl acetate selectivity coefficient.

data was calculated according to the following eqn (4). The error bars were the standard deviation. In eqn (4), the N represents the total measurement times, and the x_i represents every measurement value, and the \bar{x} represents the average value of every measurement.

$$s = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} \quad (4)$$

2.3. Optimisation of the separation process and cycling experiments

The performances of the four switchable solvents for the separation of benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane mixtures were optimised using the setup in Fig. 2 by varying (1) the CO₂ injection rate (100, 200, 300, 400, and 500 mL min⁻¹), (2) temperature (25, 35, 45, 55, and 65 °C), and (3) solvent amount (4, 8, 12, 16, and 20 mL).

Cycling experiments were performed to evaluate the suitability of the developed method for industrial applications. After N₂ injection into the lower phase, the solvents were recovered and re-used, and selectivity coefficients were calculated after each cycle.

3. Results and discussion

3.1. Benzene/cyclohexane separation

For all solvents and mixtures, a homogeneous phase was formed after CO₂ injection into amine–water mixtures because of amine protonation (amine + H₂O + CO₂ → amineH⁺ + HCO₃⁻), whereas subsequent N₂ injection resulted in separation into two phases due to the reverse process (*i.e.*, decomposition into the amine and CO₂).

Fig. 4 presents the effects of the three parameters on the benzene selectivity coefficient, revealing that TEPDA showed the best performance among the four solvents. The benzene selectivity coefficient increased with CO₂ injection rate (Fig. 3(a)), as high injection rates favoured switchable intermediate formation, reaching saturation at 300 mL min⁻¹, which indicated the establishment of equilibrium. Due to the CO₂ injecting rate influence the formation of switchable hydrophilic solvent salts,⁸ and when the switchable hydrophilic salts formed, then the phase separation between benzene and cyclohexane was clear. With the higher CO₂ injecting rate, the switchable hydrophilic solvent salts would form faster, and then the benzene selectivity coefficient would increase. A similar trend was observed for temperature, with saturation observed at 45 °C in cases of dipropylamine, di-*sec*-butylamine, and TEPDA (Fig. 3(b)). In the



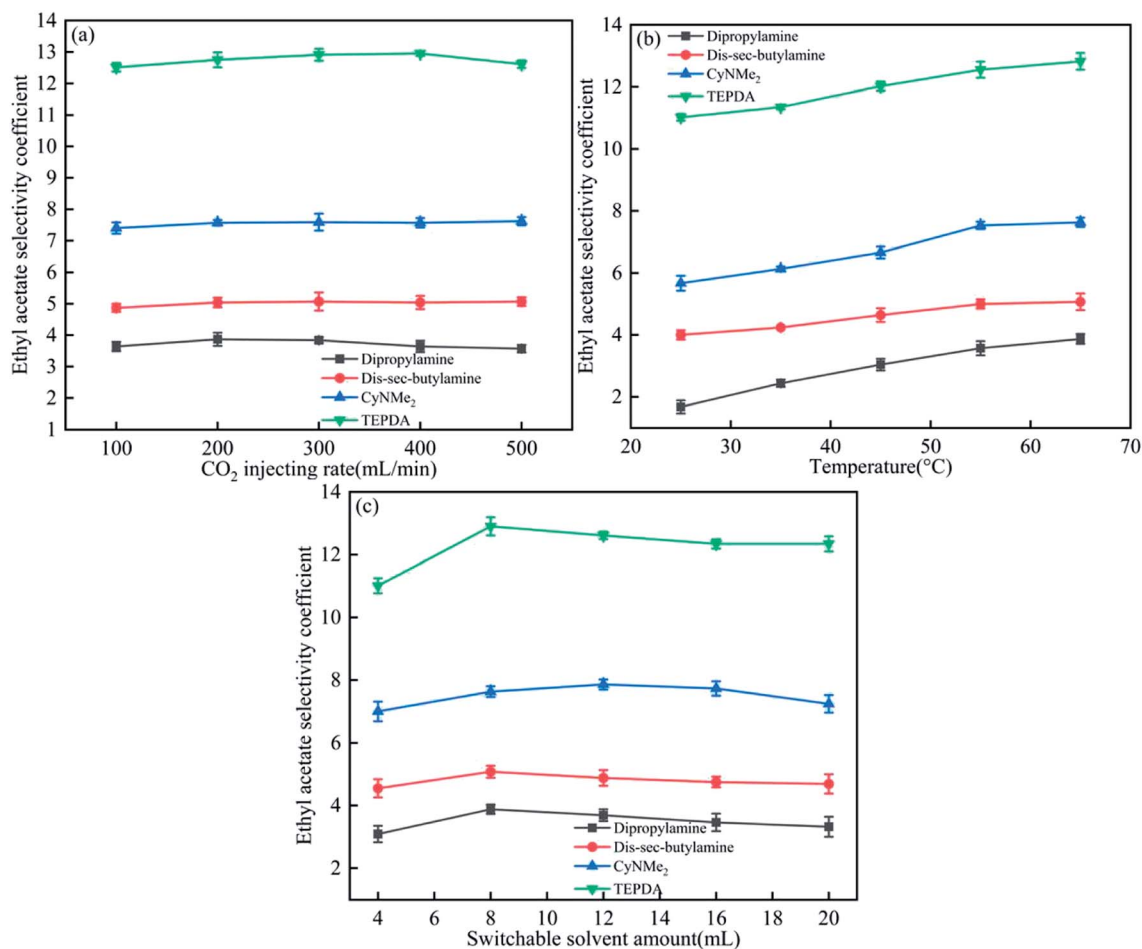


Fig. 6 Effects of (a) CO₂ injection rate, (b) temperature, and (c) switchable solvent amount on the ethyl acetate selectivity coefficient.

case of CyNMe₂, the benzene selectivity coefficient decreased at temperatures above 45 °C because of the concomitant decrease of CyNMe₂ switchability. Therefore, the optimal temperature was identified as 45 °C. Finally, the benzene selectivity coefficient increased with solvent amount (Fig. 3(c)), saturating at 16 mL, which was therefore selected as the optimal solvent volume. Among the four solvents, TEPDA was most influenced by the three to-be-optimised parameters, and this high sensitivity was ascribed to the relatively slow protonation attributable to the presence of two amine groups.

3.2. Ethyl acetate/acetonitrile separation

As shown in Fig. 5(a), the ethyl acetate selectivity coefficient increased with increasing CO₂ injection rate, saturating above 400 mL min⁻¹, which was therefore chosen as the optimal injection rate. Temperature and solvent amount had similar effects (Fig. 5(b) and (c)), with optimal values determined as 45 °C and 16 mL, respectively.

3.3. Ethyl acetate/*n*-heptane separation

As shown in Fig. 6(a), the ethyl acetate selectivity coefficient remained almost unchanged with increasing CO₂ injection rate, and the smallest rate of 100 mL min⁻¹ was therefore chosen as

optimal. The above coefficient increased with increasing temperature and solvent amount (Fig. 6(b) and (c)), with saturation-marking values of 55 °C and 8 mL chosen as optimal.

3.4. Partition and selectivity coefficients

As shown in Fig. 7, the benzene partition coefficient increased in the order of dipropylamine (0.85) < di-sec-butylamine (0.97) < CyNMe₂ (1.13) < TEPDA (1.45), and the cyclohexane partition coefficient decreased in the order of dipropylamine (0.39) > di-sec-butylamine (0.34) > CyNMe₂ (0.28) > TEPDA (0.21), *i.e.*, separation efficiency increased in the order of dipropylamine < di-sec-butylamine < CyNMe₂ < TEPDA. The same behaviour was observed for the ethyl acetate partition coefficient in cases of ethyl acetate/acetonitrile and ethyl acetate/*n*-heptane separation, which was ascribed to the increase of amine steric hindrance (and, hence, of separation efficiency) in the order of dipropylamine < di-sec-butylamine < CyNMe₂ < TEPDA. The enhanced performance of TEPDA was ascribed to its diamine nature. Fig. 8 indicates that all selectivity coefficients increased in the order of dipropylamine < di-sec-butylamine < CyNMe₂ < TEPDA, in agreement with the results presented in Fig. 6. For the same switchable solvent, the selectivity coefficient increased in the order of benzene < ethyl acetate (in acetonitrile mixture) < ethyl acetate (in *n*-heptane mixture), which was ascribed to the concomitant decrease of



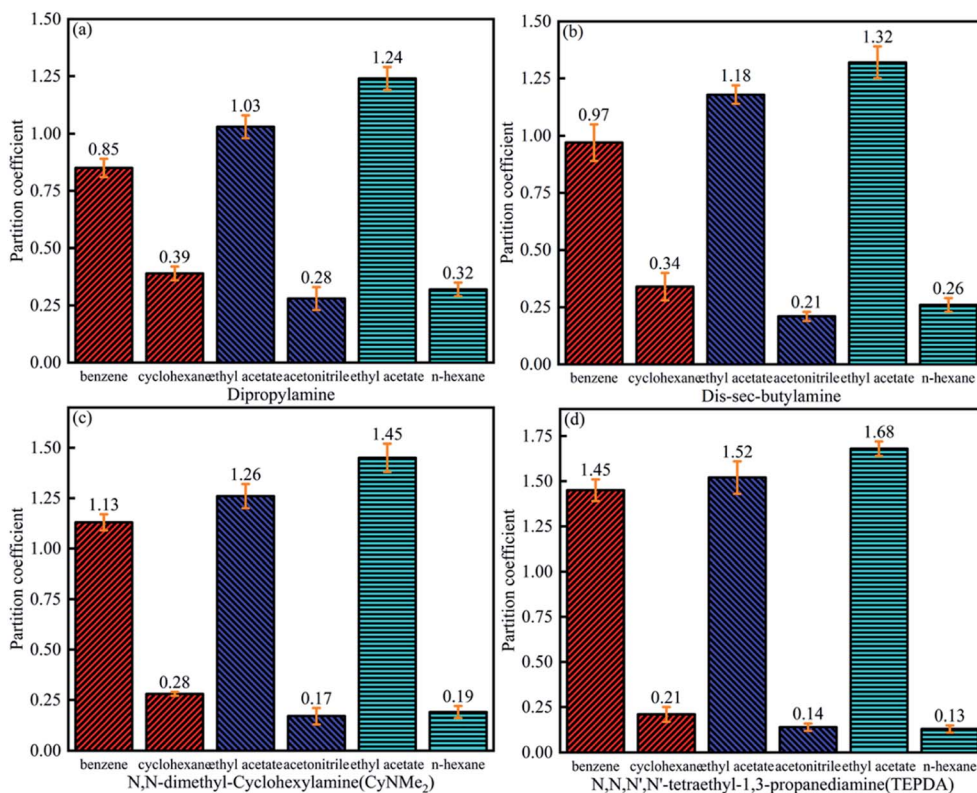


Fig. 7 Partition coefficients obtained for benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane separations using (a) dipropylamine, (b) di-sec-butylamine, (c) CyNMe₂, and (d) TEPDA.

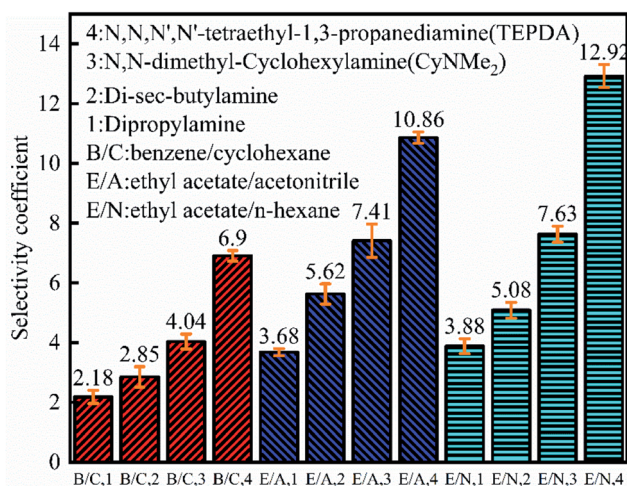


Fig. 8 Selectivity coefficients obtained for benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane separations.

structural similarity between mixture components. The chosen switchable solvents were an organic solvent which could be used to dissolve the hydrocarbons and their derivatives for separation. Take the TEPDA for example, after the separation of hydrocarbons and their derivatives, the switchable solvents could be separated from the mixed hydrocarbons by the addition of water and CO₂ injection. This protonated TEPDA would be switched back to TEPDA by heating or N₂ bubbling to remove the CO₂. However,

when the water was added to the TEPDA in the separation system, things become more complex. The TEPDA would play several different roles in this aqueous/non-aqueous hybrid process. Most of the TEPDA still acted as a solvent in its non-ionic state to soften and dissolve the mixed hydrocarbons and their derivatives. The dissolution of mixture in the TEPDA allowed the solubility between the mixed hydrocarbons. At the same time, a small amount of TEPDA was ionized in water. The TEPDA ions (*i.e.*, (C₂H₅)₂N-(CH₂)₃-NH⁺(C₂H₅)₂) in the water solution acts like a surfactant in enhancing the mixed hydrocarbons and their derivatives separation. The accumulation of TEPDA ions at the interface reduces the mixed hydrocarbons and their derivatives-water interfacial tension, resulting in the separation.

3.5. Recyclability of nitrogen-containing switchable solvents

Fig. 9 summarises the effects of solvent recycling on separation performance. For dipropylamine and di-sec-butylamine, selectivity coefficients decreased from the first cycle to the tenth cycle, subsequently stabilising. For CyNMe₂ and TEPDA, stabilisation was observed after the seventh and fifth cycles, respectively. In general, the employed solvents could be recycled for at least 15 times, and the corresponding decrease of separation efficiency was acceptable for industrial applications. In addition, the switchable solvent (TEPDA) was applied to oil-solid separation. Xingang Li *et al.* used TEPDA to separate heavy oil from a carbonate solid surface, resulting in over 10% additional oil recovery.³⁴



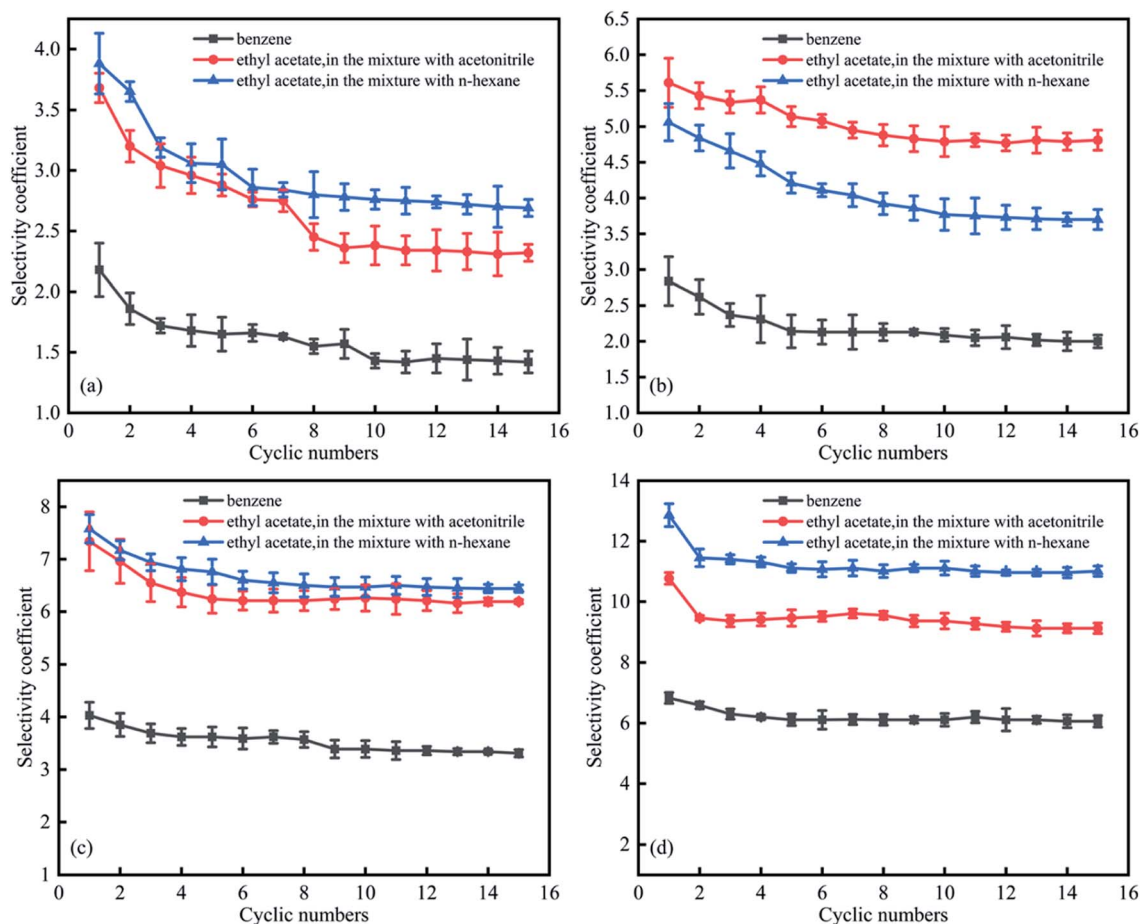


Fig. 9 Effect of cycle number on selectivity coefficients for (a) dipropylamine, (b) di-*sec*-butylamine, (c) CyNMe₂, and (d) TEPDA.

Table 1 The four switchable solvents (dipropylamine, di-*sec*-butylamine, CyNMe₂, TEPDA) in the solubility in the products and recovery

Switchable solvent	Separation products	Solubility (g g ⁻¹)	Recovery (%)
Dipropylamine	Benzene/cyclohexane	0.002	99.63
	Ethyl acetate/acetonitrile	0.021	99.83
	Ethyl acetate/ <i>n</i> -heptane	0.006	98.97
Di- <i>sec</i> -butylamine	Benzene/cyclohexane	0.012	98.67
	Ethyl acetate/acetonitrile	0.015	99.32
	Ethyl acetate/ <i>n</i> -heptane	0.023	99.58
CyNMe ₂	Benzene/cyclohexane	0.008	99.67
	Ethyl acetate/acetonitrile	0.041	99.63
	Ethyl acetate/ <i>n</i> -heptane	0.032	99.32
TEPDA	Benzene/cyclohexane	0.009	99.21
	Ethyl acetate/acetonitrile	0.013	99.72
	Ethyl acetate/ <i>n</i> -heptane	0.021	98.67

3.6. The mutual solubility of switchable solvents in the products

The four different switchable solvents (dipropylamine, di-*sec*-butylamine, CyNMe₂ and TEPDA) solubility and recovery were shown in Table 1. The mutual solubility of switchable solvents in the products were low, and the switchable solvents recovery were high.

4. Conclusions

Four nitrogen-containing switchable solvents (dipropylamine, di-*sec*-butylamine, CyNMe₂, and TEPDA) were used to separate benzene/cyclohexane, ethyl acetate/acetonitrile, and ethyl acetate/*n*-heptane mixtures, and the following conclusions were drawn.

(1) Optimal separation conditions depended on the chosen mixture.

(2) All selectivity coefficients increased in the order of dipropylamine < di-*sec*-butylamine < CyNMe₂ < TEPDA. For the same solvent and operating conditions, the selectivity coefficient increased in the order of benzene < ethyl acetate (in acetonitrile mixture) < ethyl acetate (in *n*-heptane mixture).

(3) The tested solvents could be recycled for at least 15 times, thus being well suited for industrial-scale separation of hydrocarbons and their derivatives.

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Conflicts of interest

The authors declare no conflict of interests.

References

- P. G. Jessop, S. M. Mercer and D. J. Heldebrant, CO₂-Triggered Switchable Solvents, Surfactants, and Other Materials, *Energy Environ. Sci.*, 2012, 5, 7240–7253.
- G. J. Philip, L. Phan, A. Carrier, S. Robinson, J. D. Christoph and R. H. Jitendra, A solvent having switchable hydrophilicity, *Green Chem.*, 2010, 12, 809–814.
- P. G. Jessop, C. A. Eckert, C. L. Liotta and D. J. Heldebrant, Switchable solvents and methods of use thereof, *US Pat.*, 2008/005849A1, United States Patent Application Publication, 2008.
- J. Durelle, J. R. Vanderveen, Yi Quan, C. B. Chalifoux, J. Kostin and P. G. Jessop, Extending the range of switchable-hydrophilicity solvents, *Phys. Chem. Chem. Phys.*, 2015, 17, 5308–5313.
- C. Samori, L. Pezzolesi, D. López Barreiro, A. Quintavalla, A. Pasteris and E. Tagliavini, Synthesis of new polyethoxylated tertiary amines and their use as Switchable Hydrophilicity Solvents, *RSC Adv.*, 2014, 4, 5999–6008.
- P. Pollet, C. A. Eckert and C. L. Liotta, Switchable solvents, *Chem. Sci.*, 2011, 2, 609–614.
- A. D. Wilson and F. F. Stewart, Structure–function study of tertiary amines as switchable polarity solvents, *RSC Adv.*, 2014, 4, 11039–11049.
- Y. Kazemzadeh, I. Ismail, H. Rezvani, M. Sharifi and M. Riazi, Experimental investigation of stability of water in oil emulsions at reservoir conditions: Effect of ion type, ion concentration, and system pressure, *Fuel*, 2019, 243, 15–27.
- P. G. Jessop, J. R. Vanderveen and J. Durelle, Design and evaluation of switchable-hydrophilicity solvents, *Green Chem.*, 2014, 16, 1187–1197.
- J. Durelle, J. R. Vanderveen and G. Philip, Jessop, Modelling the behaviour of switchable-hydrophilicity solvents, *Phys. Chem. Chem. Phys.*, 2014, 16, 5270–5275.
- A. R. Boyd, P. Champagne, P. J. McGinn, K. M. MacDougall, J. E. Melanson and P. G. Jessop, Switchable hydrophilicity solvents for lipid extraction from microalgae for biofuel production, *Bioresour. Technol.*, 2012, 118, 628–632.
- P. Lam, H. Brown, J. F. White, A. Hodgson and P. G. Jessop, Soybean oil extraction and separation using switchable or expanded solvents, *Green Chem.*, 2009, 11, 53–59.
- C. Samori, D. López Barreiro, R. Vet, L. Pezzolesi, W. Brilman, P. Galletti and E. Tagliavini, Effective lipid extraction from algae cultures using switchable solvents, *Green Chem.*, 2013, 15, 353–356.
- Y. Du, B. Schuur, R. Sascha, A. Kersten and D. W. F. Brilman, Opportunities for switchable solvents for lipid extraction from wet algal biomass: An energy evaluation, *Algal Res.*, 2015, 11, 271–283.
- N. R. Carty, J. A. Kornfield and J. Lal, Using the “Switchable” Quality of Liquid Crystal Solvents To Mediate Segregation between Coil and Liquid Crystalline Polymers, *Macromolecules*, 2006, 39, 3921–3926.
- M. Khan and S. Mustafa, Switchable solvent based liquid phase microextraction of mercury from environmental samples: a green aspect, *RSC Adv.*, 2016, 6, 10–1039.
- E. Yilmaz and M. Soylak, Switchable solvent based liquid phase microextraction of copper(II): optimization and application to environmental samples, *J. Anal. At. Spectrom.*, 2015, 30, 1629–1635.
- A. Holland, D. Wechsler, A. Patel, B. M. Molloy, A. R. Boyd and P. G. Jessop, Separation of bitumen from oil sands using a switchable hydrophilicity solvent, *Can. J. Chem.*, 2012, 90, 805–810.
- J. Wang, Y. Du, C. Du, A. Xu, G. Yao, H. Zhao, X. Zhu and X. Guo, Physicochemical properties of switchable-hydrophilicity solvent systems: N,N-Dimethylcyclohexylamine, water and carbon dioxide, *J. Chem. Thermodyn.*, 2019, 133, 1–9.
- A. Bediako, B. Bernard, P. Zhou, R. Benoit, Q. Liu, Y. Su, H. Wang and J. Li, A switchable hydrophilicity solvent mediated process to prepare fine silica aerogel powder as an excellent flattening agent, *Adv. Powder Technol.*, 2019, 30, 565–571.
- Y. Xu, F. Wang, Q. Hou, Y. Zhao, G. Ding and X. Xu, Strategy for Synthesizing Novel Acetamidines as CO₂-Triggered Switchable Surfactants via Acetimidates, *Trans. Tianjin Univ.*, 2019, 25, 237–244.
- G. Lasarte-Aragonés, R. Lucena, S. Cárdenas and M. Valcárcel, Use of switchable solvents in the microextraction context, *Talanta*, 2015, 131, 645–649.
- G. Lasarte-Aragonés, R. Lucena, S. Cárdenas and M. Valcárcel, Use of switchable hydrophilicity solvents for the homogeneous liquid–liquid microextraction of triazine herbicides from environmental water samples, *J. Sep. Sci.*, 2015, 38, 990–995.
- R. Jamileh, K. S. Hasheminasab, A. Laleh and A. Hamid, Switchable-hydrophilicity solvent-based microextraction combined with gas chromatography for the determination of nitroaromatic compounds in water samples, *J. Sep. Sci.*, 2017, 40, 3114–3119.
- M. Recló, E. Yilmaz, Y. Bazel and M. Soylak, Switchable solvent based liquid phase microextraction of palladium coupled with determination by flame atomic absorption spectrometry, *Int. J. Environ. Anal. Chem.*, 2017, 97, 1315–1327.
- S. Mustafa, M. Khan and E. Yilmaz, Switchable solvent based liquid phase microextraction of uranium in environmental samples: A green approach, *Anal. Methods*, 2016, 8, 979–986.
- W. Li, B. Xu, Z. Lei and C. Dai, Separation of benzene and cyclohexane by extractive distillation intensified with ionic liquid, *Chem. Eng. Process.*, 2018, 126, 81–89.
- L. Li, Y. Tu, L. Guo, L. Sun and Y. Tian, Optimization and Control of Extractive Distillation with Heat Integration for Separating Benzene/Cyclohexane Mixtures, *China Pet. Process. Petrochem. Technol.*, 2016, 18, 117–127.



- 29 J. Qin, Q. Ye, X. Xiong and Li Ning, Control of Benzene-Cyclohexane Separation System *via* Extractive Distillation Using Sulfolane as Entrainer, *Ind. Eng. Chem. Res.*, 2013, **52**, 10754–10766.
- 30 Y. Liu, Z. Qiu, H. Zhong, Z. Nie, Li Jia, W. Huang and X. Zhao, Bitumen Recovery from Crude Bitumen Samples from Halfaya Oilfield by Single and Composite Solvents-Process, Parameters, and Mechanism, *Materials*, 2019, **12**, 2656.
- 31 W. Ma, J. Sun, W. Hongpu and R. Wang, Study on separation of acetonitrile and ethyl acetate mixture by extractive distillation, *Appl. Chem. Ind.*, 2010, **39**, 781–782.
- 32 W. Kang, M. Li, Y. Wu, J. Cheng and R. Gao, Separation of ethyl acetate and n-heptane by Extractive Distillation, *Mod. Chem. Ind.*, 2017, **37**, 167–170.
- 33 J. Gu, X. You, C. Tao, J. Li, W. Shen and J. Li, Improved design and optimization for separating tetrahydrofuran–water azeotrope through extractive distillation with and without heat integration by varying pressure, *Chem. Eng. Res. Des.*, 2018, **133**, 303–313.
- 34 X. Li, Z. Yang, H. Sui, A. Jain and L. He, A hybrid process for oil-solid separation by a novel multifunctional switchable solvent, *Fuel*, 2018, **221**, 303–310.

