



Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Article

The phase behavior of *n*-ethylpyridinium tetrafluoroborate and sodium-based salts ATPS and its application in 2-chlorophenol extractionShuai Xu^{1,2}, Qi Zhu², Shaojie Xu^{1,3}, Manjing Yuan^{1,3}, Xuliang Lin^{1,3}, Wenjing Lin¹, Yanlin Qin^{1,3,*}, Yuliang Li^{2,*}¹ School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China² Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region, Ministry of Education, School of Water and Environment, Chang'an University, Xi'an 710064, China³ Guangzhou Key Laboratory of Clean Transportation Energy Chemistry, Guangdong University of Technology, Guangzhou 510006, China

ARTICLE INFO

Article history:

Received 12 March 2020

Received in revised form 1 July 2020

Accepted 19 July 2020

Available online 12 August 2020

Keywords:

Ionic liquid

Aqueous two-phase systems

2-chlorophenol

HPLC

Extraction

ABSTRACT

In this paper, the aqueous two-phase systems (ATPS) containing *n*-ethylpyridinium tetrafluoroborate ([EPy]BF₄), sodium-based salts, and water were studied and the extraction efficiency of 2-chlorophenol was measured to study the ATPS performance in extracting phenolic compounds. The binodal curves of [EPy]BF₄ + sodium carbonate (Na₂CO₃) ATPS and [EPy]BF₄ + sodium dihydrogen phosphate (NaH₂PO₄) ATPS have been determined at 308.15 K, 318.15 K, and 328.15 K and atmospheric pressure. After getting good correlation with Merchuk equation, the binodal curves together with gravimetric method were used to calculate the tie-lines data. Furthermore, the reliability of tie-lines data was verified using Othmer-Tobias and Bancroft equations. Then, the salt influence and temperature influence on the phase behavior were discussed and the results show the salt-outing ability of Na₂CO₃ is better than NaH₂PO₄. With the aim of studying the ATPS performance in extracting phenolic compounds, extraction efficiency for 2-chlorophenol at different temperatures were studied and the results show that [EPy]BF₄ + Na₂CO₃ ATPS is preferred than [EPy]BF₄ + NaH₂PO₄ ATPS in applications.

© 2020 The Chemical Industry and Engineering Society of China, and Chemical Industry Press Co., Ltd.

All rights reserved.

1. Introduction

Phenolic compounds, which is commonly from petrochemical and coking operations, pharmaceuticals industries, petroleum refinery, coloring textiles and paper-making processes [1]. Due to the weakly biodegradable, the degrade of phenolic compounds in the ecological system is limited and phenolic compounds in the natural environment tend to accumulate. The 2-chlorophenol is one of the toxic chlorinated phenols and it is water solubility and usually emit the unpleasant odor, which can cause serious threats to human health [1,2,52]. Therefore, 2-chlorophenol is considered as priority pollutant by many countries [3]. It is essential therefore, removal of 2-chlorophenol from wastewaters prior to discharge into the environment. The aqueous two-phase systems (ATPS) extraction technology has increasingly attracted people's attention and has been successfully applied in the extraction of antibiotics before the discharge of swine husbandry effluents [4], the detection of sulfonamides in meat products [5], and the extraction of herbicides in wastewaters [6].

ATPS are formed by mixing two mutual incompatible reagents contain polymer-salt or polymer-polymer at a certain critical concentration in aqueous solutions [7,8]. Compared with traditional organic solvent

extractions, ATPS present efficient, economical, and served as an environmentally friendly media. Consequently, ATPS extraction technology has been widely used for extraction of proteins [9,10], drug molecules [11], heavy metal ions [12], small organic molecules [13] and cell organelles [14]. In recent decades, ionic liquid (ILs) are under intense investigation and are considered a potential replacement for volatile organic solvents. ILs attracted much attention for greater application on account of that they not only present several beneficial properties such as low toxicity, negligible vapor pressure, and high ionic conductivity, but also possess unique features such as recyclability and high thermal chemical stability [15]. With high performance in reactions and separations, ILs have more used in separation processes [16], which is a breakthrough in the fields of solvents. Reported by Gutowski *et al.* [17] for the first time, the IL + salt ATPS have been increasingly investigated as novel ATPS. Compared with ionic liquid as adjuvants or organic solvent ATPS [18,19], the IL-based ATPS is considered to be more environmentally friendly.

To date, several IL-based ATPS have been developed including the [Bmim]BF₄ + salt (Na₂CO₃, NaCl, Na₂SO₃, Na₂SO₄, NaH₂PO₄, Na₃PO₄, NaC₂H₃O₂, Na₃C₆H₅O₇, Na₂C₄H₄O₆, (NH₄)₂SO₄, and (NH₄)₃C₆H₅O₇) ATPS [20–23]. Nevertheless, some researchers pointed out that the imidazolium-based ionic liquids possess certain toxicity [24]. Furthermore, as the study found that pyridine-based ionic liquids exhibit more merits than imidazolium-based ionic liquids, for instance, lower

* Corresponding authors.

E-mail addresses: ylqin@gdut.edu.cn (Y. Qin), yulianglee@hotmail.com (Y. Li).

vapor pressure, lower cost, less polluting and better stability [25]. More importantly, pyridine-based ionic liquids are more and more used in extraction and separation with their good two phase-forming properties [26,27]. Thus, determination of phase equilibrium data of pyridinium-based ILs and inorganic salts ATPS has theoretical and practical significance. Since the toxicity of IL is positively related to the length of alkyl chains in cations [28], the *n*-ethylpyridinium ([EPy]⁺), which possess shorter alkyl chain, was selected in this study. Notably, some researchers pointed out that the tetrafluoroborate (BF₄[−]) anion in imidazolium-based ILs could undergo hydrolysis and form hydrofluoric acid (HF) in the presence of water and the ILs with long alkyl chains are more easily to undergo hydrolysis [29]. However, for [EPy]BF₄ used in this work, the BF₄[−] was not found to undergo hydrolysis in our experiment process. First, as show in Fig. S1 (in the Supplementary Material), the glass centrifuge tubes (borosilicate glass) were found to no frost after one week [30]. As we know, HF is the most corrosive for glass, which minor (mg·L^{−1}) levels of HF could cause the frost in the glass and turn the glass to white [31]. Second, the samples were analyzed by ion chromatography and not found fluoride response. This may result from the cation-anion interaction strength in [EPy]BF₄ are strong enough to prevent the hydrolysis of BF₄[−].

Our group had studied the phase diagrams about [EPy]BF₄ + Na₂CO₃ and [EPy]BF₄ + NaH₂PO₄ ATPS at 298.15 K [32]. This work is the continued study of the [EPy]BF₄ + sodium salts ATPS, using both empirical equation and properties of ions to further studied the salt influence. The temperature influence on phase diagram is investigated to further study its effect on extraction performance. Meanwhile, 2-chlorophenol was used in this work to study the ATPS extraction performance in extracting phenolic compounds.

It is therefore in this study, binodal data and tie-lines data of the [EPy]BF₄ + Na₂CO₃ and [EPy]BF₄ + NaH₂PO₄ ATPS were determinate at 308.15 K, 318.15 K, and 328.15 K and atmospheric pressure. The appropriate methods, cloud point titration and gravimetric method, were used to obtain the binodal data and tie-lines data. The salts influence on the phase diagram was discussed using Setschenow-type equation and ions hydration Gibbs energy. The high-performance liquid chromatography (HPLC) method was used to analysis 2-chlorophenol content to study the extraction performance of [EPy]BF₄ + sodium-based salts ATPS.

2. Experimental

2.1. Materials

The sources of the reagents and their purity are listed in Table 1. The salts are of analytical grade and directly used without further purification. The [EPy]BF₄ was put in the vacuum oven at 333.15 K and moderate vacuum (0.01 MPa) for 24 h before using. Freshly prepared deionized water (HHitech, Master Evo-S45UVF) was used for the salt solution prepared.

2.2. Experimental procedure for ATPS characterization

The cloud point titration method is used to determine binodal data, and the method has been widely used in previous works [33]. Briefly, a great number of boundary data of immiscible regions can be obtained in

the method. Known mass fraction of [EPy]BF₄ were put in a pure and dry colorimetric tube. A syringe with a small needle was used to add the salt solution dropwise and slowly until the system cloudy. When the composition of the system is close to cloud point, only one drop (about 0.0050 g) of the salt solution can make the system cloudy, which hardly miss the cloud point. The mass of [EPy]BF₄, salt, and water can be easily measured and calculated. Then the water was added dropwise until the system turns to clear and the mass fraction of the components was calculated again. Repeat the procedure multiple times to obtain sufficient binodal data. The temperature was maintained by a water bath with an uncertainty of 0.05 K throughout the experiment. The analytical balance (model BS 124S, Beijing Sartorius Instrument Co., Ltd., China) with an uncertainty of 0.0001 g was used to measure the mass.

The tie lines were determined by the gravimetric method proposed by Merchuk *et al.* [34], and tie-lines data for a large amount of ATPS were successfully obtained using gravimetric method [35–37]. The total compositions were selected in the biphasic regions of the phase diagram to determine the tie lines data. Mixing [EPy]BF₄, salt, and water at the selected compositions and total mass of the systems are approximately 10 g, then vortex mixer was used to mix the system thoroughly and stand for 24 h to achieve complete phase separation. The syringe with a small needle was used to take the liquid of top and bottom phases, and then weight the top phase and bottom phase by analytical balance. The lever arm rule was used to calculate the compositions of the top and bottom phases using the following equations:

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3) \quad (1)$$

$$w_1^t = \frac{w_1^m}{a} - \frac{1-a}{a} \times w_1^b \quad (2)$$

$$w_2^t = \frac{w_2^m}{a} - \frac{1-a}{a} \times w_2^b \quad (3)$$

In the equations, w_1 and w_2 denote mass fraction of [EPy]BF₄ and salt, respectively; The superscript m, b, and t denote mixture, bottom phase, and top phase, respectively; a , b , and c are parameters from fitting to binodal curves; and α denotes the ratio between the top-phase mass and the total mass. Based on the tie-line data, the following Eqs. (4) and (5) were used to calculate the TLL and S:

$$\text{TLL} = \left[(w_2^t - w_2^b)^2 + (w_1^t - w_1^b)^2 \right]^{0.5} \quad (4)$$

$$S = (w_2^t - w_2^b) / (w_1^t - w_1^b) \quad (5)$$

where TLL and S are tie-line length and slope of tie line, respectively.

2.3. 2-chlorophenol extraction and quantification

The 2-chlorophenol extraction process is similar to above-mentioned tie-lines preparation. The salt, water, and [EPy]BF₄ were added in the centrifuge tubes according to the selected composition. The 2-chlorophenol was added to the tubes and the concentration was controlled at 0.200 g·L^{−1}. The vortex mixer was used to mix the system thoroughly and then stand for 24 h. The 2-chlorophenol concentrations in the top and bottom phase were determined using high-

Table 1

The sources and purities of chemicals used in the study

Chemical	CAS Number	Molar mass	Supplier	Final mass fraction purity	Water content/mg·kg ^{−1}
[EPy]BF ₄	350-48-1	194.97	Chengjie Chemical Reagent Co., Ltd. (Shanghai, China)	0.99	88 ± 17
Na ₂ CO ₃	497-19-8	105.99	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	0.99	73 ± 16
NaH ₂ PO ₄	7558-80-7	119.98	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	0.99	68 ± 21
2-chlorophenol	95-57-8	128.56	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	0.99	64 ± 14

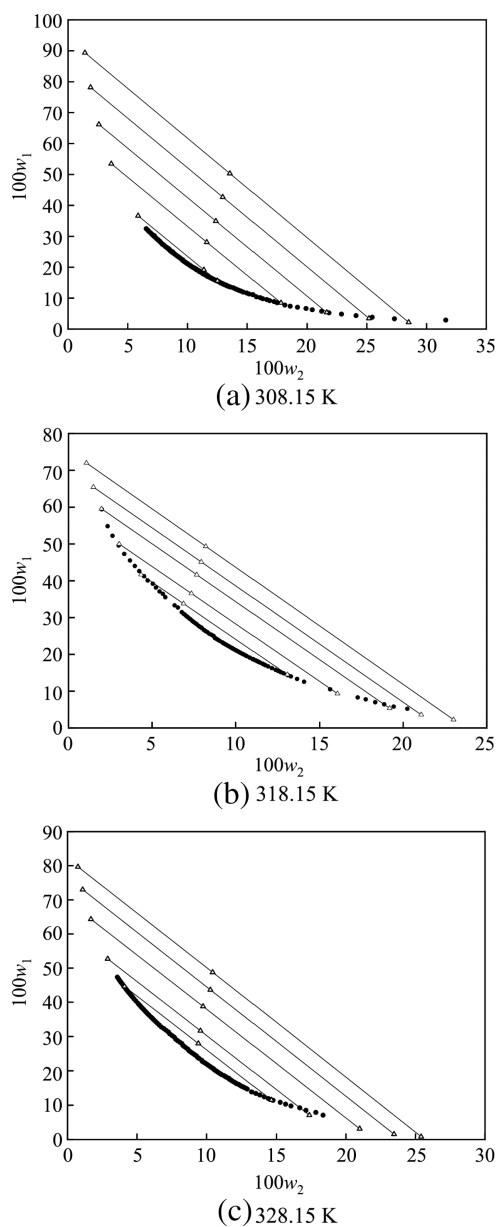


Fig. 1. Binodal curves and tie lines of [EPy]BF₄ (1) + Na₂CO₃ (2) + H₂O (3) ATPS at 308.15 K, 318.15 K and 328.15 K.

performance liquid chromatography (HPLC, Thermo Fisher Scientific U-3000, Germany) equipped with a Hypersil Gold C18 column (3.0 μ m particle size, 3 mm \times 150 mm, Thermo Fisher Scientific) and a UV detection. The mobile phase consisted of methanol (A) and water (B). A constant system with the condition of 0–15 min, 60% A and 40% B was used. The flow rate of the mobile phase was 1.0 ml \cdot min⁻¹. The injection volume was 5 μ l. The column temperature was set at 30 $^{\circ}$ C and the detection wavelength was set at 275 nm.

3. Results and Discussion

3.1. Binodal curves and correlation

The experimental binodal data of the [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ + H₂O ATPS at 308.15, 318.15 and 328.15 K and atmospheric pressure are given in Table S1 (in the Supplementary Material). Figs. 1 and 2 show the binodal curves of [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ + H₂O ATPS. For calculation convenience, the binodal curves can be transformed to

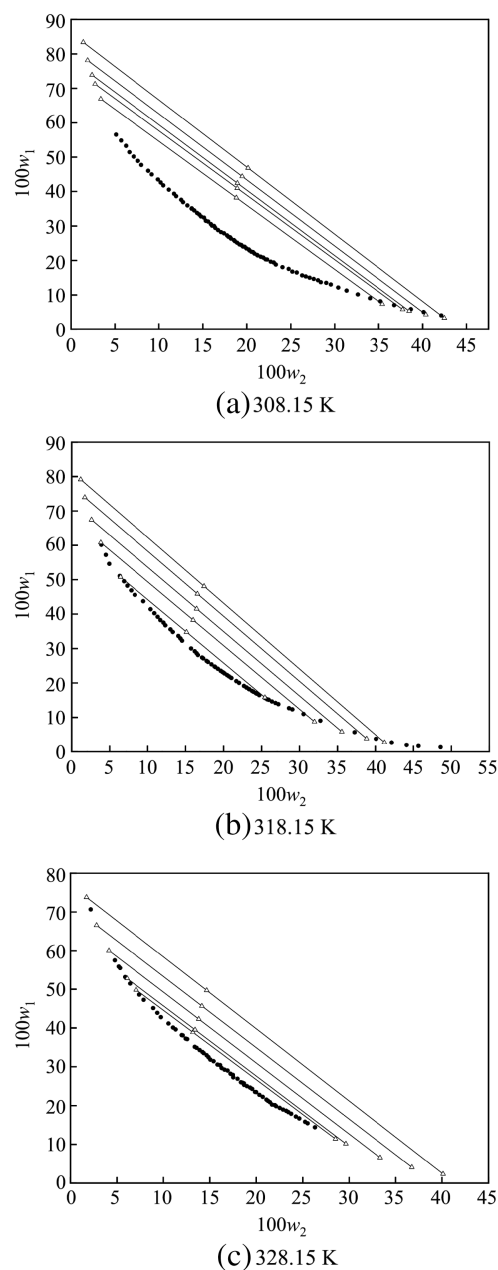


Fig. 2. Binodal curves and tie lines of [EPy]BF₄ (1) + NaH₂PO₄ (2) + H₂O (3) ATPS at 308.15 K, 318.15 K and 328.15 K.

mathematical formulas by fitting the binodal curves with the empirical equation in general. Besides the Merchuk equation [Eq. (1)], the following two equations were also used to fit the binodal curves:

$$w_1 = a_1 \exp\left(-\frac{w_2}{b_1}\right) + a_2 \left(-\frac{w_2}{b_2}\right) + c \quad (6)$$

Table 2
Values of the parameters of Eq. (1) for IL + Salt + Water ATPS at different temperatures

System	T/K	a	b	c	R ²	sd
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	2.09	-7.17	31.97	0.9988	2.4×10^{-3}
	318.15	1.22	-5.12	125.49	0.9986	3.9×10^{-3}
	328.15	1.22	-4.91	152.57	0.9988	3.9×10^{-3}
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	1.23	-3.32	19.05	0.9979	5.7×10^{-3}
	318.15	1.10	-3.01	25.37	0.9987	4.8×10^{-3}
	328.15	1.07	-2.84	31.16	0.9997	2.0×10^{-3}

Table 3

Values of the parameters of Eq. (6) for the IL + Salt + Water ATPS at different temperatures

	<i>T/K</i>	<i>a</i> ₁	<i>b</i> ₁	<i>a</i> ₂	<i>b</i> ₂	<i>c</i>	<i>R</i> ²	<i>sd</i>
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	0.31	0.08	0.44	0.08	0.01	0.9998	1.0 × 10 ^{−3}
	318.15	0.72	0.09	13.43	3.36 × 10 ^{−3}	−0.02	0.9999	1.2 × 10 ^{−3}
	328.15	0.75	0.10	−0.07	−3.60 × 10 ^{−24}	0.02	0.9995	2.5 × 10 ^{−3}
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	0.80	0.20	−4.94	9.71 × 10 ^{−4}	−0.05	0.9995	2.8 × 10 ^{−3}
	318.15	0.80	0.21	1.27 × 10 ⁵	2.43 × 10 ^{−3}	−0.07	0.9995	2.9 × 10 ^{−3}
	328.15	0.97	0.33	0.26	0.02	−0.29	0.9997	1.9 × 10 ^{−3}

Table 4

Values of the parameters of Eq. (7) for IL + Salt + Water ATPS at different temperatures

	<i>T/K</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>R</i> ²	<i>sd</i>
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	−1.12	6.98	−29.10	27.33	0.9999	8.0 × 10 ^{−4}
	318.15	0.02	−3.64	−1.78	−23.75	0.9995	2.2 × 10 ^{−3}
	328.15	−0.40	0.17	−10.28	−14.22	0.9997	2.1 × 10 ^{−3}
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	−0.28	−0.30	−4.27	−4.42	0.9995	2.8 × 10 ^{−3}
	318.15	9.61 × 10 ^{−3}	−2.91	1.65	−12.61	0.9995	3.0 × 10 ^{−3}
	328.15	0.21	−4.52	5.43	−18.24	0.9998	1.8 × 10 ^{−3}

$$w_1 = \exp(a + bw_2^{0.5} + cw_2 + dw_2) \quad (7)$$

where *a*₁, *a*₂, *b*₁, *b*₂, *a*, *b*, *c*, and *d* are fitting parameters. The following equation can be used to calculate the standard deviations (*sd*) values:

$$sd = \sqrt{\frac{\sum_{i=1}^N (w_1^{cal} - w_1^{exp})^2}{N}} \quad (8)$$

where the superscript cal and exp. denote calculated data and experimental data; *N* represents the number of data. It was found that binodal data for many IL-based ATPS could fit these equations very well [38,39]. Tables 2–4 give the fitting parameters, *sd* values, and correlation coefficient (*R*²). It is obvious that all the *sd* values are lower than 0.0057, which show the satisfactory fitting results of Eqs. (1), (6), and (7). Compared the *R*² values of the three equations, it can be found that the *R*² values of Eqs. (6) and (7) are larger than Eq. (1) and both are larger than 0.999. This is mainly because Eqs. (6) and (7) possess more fitting parameters than Eq. (1). However, for more convenient calculations, the

three-parameter equation, which the fitting results are good enough, was still used to calculate the tie-lines data.

3.2. Tie-line data and correlation

The tie lines, values of TLL, and *S* of ATPS composed of [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ + H₂O at 308.15 K, 318.15 K and 328.15 K and atmospheric pressure were provided in Table S2 (in the Supplementary Material) and shown in Figs. 1 and 2. We found that the values of *S* are almost equal to each other at the same temperature, which implies the tie lines are almost parallel to each other at the same temperature. This phenomenon can be observed in Figs. 1 and 2.

In this work, the Othmer–Tobias [40] and Bancroft [41] equations were used to ascertain the reliability of tie-lines data:

$$\left(\frac{1-w_1^t}{w_1^t}\right) = k_1 \left(\frac{1-w_2^b}{w_2^b}\right)^n \quad (9)$$

$$\left(\frac{w_3^b}{w_2^b}\right) = k_2 \left(\frac{w_3^t}{w_1^t}\right)^r \quad (10)$$

where *k*₁, *n*, *k*₂, and *r* denote the fitting parameters. Eqs. (9) and (10) have been widely used to correlate the tie lines for IL-based ATPS [42–44]. Tables 5 and 6 give the *k*₁, *n*, *k*₂, *r*, *sd*, and *R*² values. The lower *sd* values in the tables indicate the tie lines data fit the Eqs. (9) and (10) well, and ascertain the tie lines data are reliable.

3.3. Influence of temperature on binodal curves and tie lines

The influence of temperature on the [EPy]BF₄ + Na₂CO₃ ATPS and [EPy]BF₄ + NaH₂PO₄ ATPS at 308.15 K, 318.15 K and 328.15 K are

Table 5

Values of the parameters of Eq. (9) for IL + salt + water ATPS at different temperatures

System	<i>T/K</i>	<i>k</i> ₁	<i>n</i>	<i>R</i> ²	<i>sd</i> ^①
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	0.03823	1.967	0.9788	0.038
	318.15	0.05685	1.701	0.9852	0.011
	328.15	0.03503	2.037	0.9812	0.015
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	0.09104	2.861	0.9744	0.006
	318.15	0.1782	1.594	0.9725	0.016
	328.15	0.1746	1.904	0.9963	0.005

^① $sd = \left\{ \sum_{i=1}^N \sum_{j=1}^N [(100w_{i,j}^{top} - 100w_{i,j}^{top,exp})^2 + (100w_{i,j}^{bot} - 100w_{i,j}^{bot,exp})^2 / 6N] \right\}^{0.5}$, where *N* is the number of tie-lines and *j* is the number of components in each phase, and *sd* represent the mass percent standard deviations of IL and salt, respectively.

Table 6

Values of the parameters of Eq. (10) for IL + salt + water ATPS at different temperatures

System	<i>T/K</i>	<i>k</i> ₂	<i>r</i>	<i>R</i> ²	<i>sd</i> ^①
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	4.707	0.3563	0.9481	0.025
	318.15	4.864	0.4436	0.9874	0.007
	328.15	4.706	0.3696	0.9854	0.009
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	1.976	0.2628	0.9788	0.005
	318.15	2.441	0.4504	0.9731	0.010
	328.15	2.238	0.4126	0.9974	0.003

^① $sd = \left\{ \sum_{i=1}^N \sum_{j=1}^N [(100w_{i,j}^{top} - 100w_{i,j}^{top,exp})^2 + (100w_{i,j}^{bot} - 100w_{i,j}^{bot,exp})^2 / 6N] \right\}^{0.5}$, where *N* is the number of tie-lines and *j* is the number of components in each phase, and *sd* represent the mass percent standard deviations of IL and salt, respectively.

Table 7

Values of the Parameters of Eq. (11) for IL + Salt + Water ATPS at Different Temperatures

System	<i>T/K</i>	<i>k</i> _s	<i>β</i>	<i>R</i> ²	<i>sd</i> ^①
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	1477	−0.1080	0.9982	0.015
	318.15	1910	−0.6032	0.9885	0.029
	328.15	2384	−1.154	0.9838	0.050
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	1355	−1.427	0.9970	0.008
	318.15	1253	−0.9022	0.9848	0.035
	328.15	1378	−1.055	0.9896	0.026

^① $sd = \left\{ \sum_{i=1}^N \sum_{j=1}^N [(100w_{i,j}^{top} - 100w_{i,j}^{top,exp})^2 + (100w_{i,j}^{bot} - 100w_{i,j}^{bot,exp})^2 / 6N] \right\}^{0.5}$, where *N* is the number of tie-lines and *j* is the number of components in each phase.

illustrated in Fig. S2 (in the Supplementary Material). In order to compare the temperature dependence of the studied systems, the published binodal curve of the [EPy]BF₄ + Na₂CO₃ and [EPy]BF₄ + NaH₂PO₄ ATPS at 298.15 K [32] is also shown in Fig. S2. In the phase diagram, the immiscible regions are above the binodal curve, and the monophasic is below the curve. It is obvious from the figure that the temperature has no remarkable influence on the binodal curve with the studied temperature range. This phenomenon can also be found in some PEG + salt ATPS [45].

In order to investigate the influence of temperature on the tie lines, the tie lines of the studied ATPS at 308.15 K, 318.15 K, and 328.15 K were presented in Fig. S3 (in the Supplementary Material). For both [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ ATPS, the bottom phase is the salt-rich phase, and the top phase is the IL-rich phase. The two-side points of tie lines are the composition of the bottom phase and top phase, respectively. From Table S2 and Fig. S3, the slope of the tie lines almost no change with the variety of temperature, which indicates the [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ ATPS are insensitive to temperature.

3.4. Salting-out ability of salts

To study the salting-out ability of sodium salt, the Setschenow-type equation [46] was used to fit the tie-lines data for the [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ ATPS:

$$\ln \left(\frac{c_1^t}{c_1^b} \right) = \beta + k_s (c_2^b - c_2^t) \quad (11)$$

In this equation, parameters c_1 and c_2 denote the molality of the IL and salt; β is a fitting parameter; and k_s is a parameter related to the salting-out ability. Table 7 gives the k_s , β , and sd values of the studied ATPS. It is obvious that the k_s values of Na₂CO₃ systems were higher than the NaH₂PO₄ systems, which indicate the Na₂CO₃ have a better salt-outing ability than NaH₂PO₄.

The salting-out ability of salts can also be quantitatively described by checking the ions hydration Gibbs energy (ΔG_{hyd}), which have successfully used to describe the polymer + salt ATPS [47,48]. In our study, the common cation (Na⁺) was shared by the two inorganic salts, while the different anions involve different values of ΔG_{hyd} , and the absolute values are in the following order: $H_2PO_4^-$ ($\Delta G_{hyd} = -465 \text{ kJ} \cdot \text{mol}^{-1}$) < CO_3^{2-} ($\Delta G_{hyd} = -1315 \text{ kJ} \cdot \text{mol}^{-1}$). These values were taken from Marcus [49]. The higher absolute values of the ΔG_{hyd} represent hydration of anion happened easier and trend to hydrate more water molecules. Therefore, the water molecules available for IL to hydrate are reduced, and the system is easier to separate to IL-rich phase and salt-rich phase. For the salt, it is described as better salting-out ability. In other words, Na₂CO₃ is easier to obtain water from ionic liquid than NaH₂PO₄.

3.5. Application to 2-chlorophenol extraction

The concentration of 2-chlorophenol in both two phases were determined using HPLC method. As an example, a liquid chromatogram is

provided in Fig. S4 (in the Supplementary Material). Then, the partition coefficient (K) can be calculated using the following equation:

$$K = \frac{C^t}{C^b} \quad (12)$$

where C^t and C^b are concentration of 2-chlorophenol in top and bottom phase respectively. For the same ATPS at a constant temperature, the logarithm of K and TLL are in accordance with the following equation [38]:

$$\ln K = \lambda \times \text{TLL} \quad (13)$$

where λ is a constant value that related to ATPS composition. It is therefore in this study, the same total composition was prepared at each temperature to study the 2-chlorophenol extraction. The extraction efficiency (E) can also be calculated:

$$E = \left(\frac{1}{1 + \frac{1}{R_V K}} \right) \times 100\% \quad (14)$$

where R_V is the volume ratio of top phase and bottom phase. The selected total composition, TLL, K , and E are given in Table 8, from which we found the extraction efficiency for the [EPy]BF₄ + Na₂CO₃/NaH₂PO₄ ATPS are higher than 98%. From the table, extraction capacities are satisfactory for both studied systems, but [EPy]BF₄ + NaH₂PO₄ ATPS requires more ionic liquid to achieve the same extraction efficiency, i.e., the addition of NaCO₃ tend to reduce the use of ionic liquid, which reduced the cost of extraction process. Compared with the ATPS for extracting phenolic compounds in the literature, the extraction efficiency of [EPy]BF₄-based ATPS are very close to the [BPy]OTF-based ATPS [33], [Bmim]BF₄-based ATPS [50], [Pmim][NTf₂]-based ATPS, [Bmim][NTf₂]-based ATPS, and [Hmim][NTf₂]-based ATPS [51], while higher than PEG-based ATPS [19]. This phenomenon is mainly because of the ionic liquids have better solubility for phenolic compounds.

The flow chart of 2-chlorophenol wastewater treatment is presented in Fig. S5 (in the Supplementary Material). In summary, this work studied the salting-out ability of two sodium salts and the application of [EPy]BF₄-based ATPS in 2-chlorophenol extraction. Although the extraction condition in real phenolic compound wastewater is different (e.g. temperature, pH values, presence of undefined compounds, etc.), the data provided in this work are significant to further application.

4. Conclusions

This work provided a pyridine-based ionic liquid ATPS and its application in 2-chlorophenol extraction. Binodal data of and tie lines data for the [EPy]BF₄ + sodium salts ATPS were obtained at 308.15 K, 318.15 K, and 328.15 K and atmospheric pressure. The satisfactory fitting result of the empirical equations with binodal curve provides a mathematical formula for the tie lines determination using gravimetric method. The correlation of Bancroft and Othmer-Tobias equations present the good reliability of tie-lines data. The temperature has no apparent effect on

Table 8

Partition coefficient and extraction efficiency of 2-chlorophenol for IL (1) + salt (2) + water (3) ATPS at different temperatures and atmospheric pressure

System	T/K	Total composition			TLL	$K \pm \sigma$	$(E \pm \sigma)/\%$
		100w ₁	100w ₂	100w ₃			
[EPy]BF ₄ + Na ₂ CO ₃ ATPS	308.15	33.09	14.34	52.57	71.32	73.43 ± 0.42	98.43 ± 0.02
	318.15	33.09	14.34	52.57	77.66	97.66 ± 0.55	98.76 ± 0.03
	328.15	33.09	14.34	52.57	78.14	101.12 ± 0.48	98.87 ± 0.02
[EPy]BF ₄ + NaH ₂ PO ₄ ATPS	308.15	41.54	16.46	42.00	65.03	49.95 ± 0.32	98.12 ± 0.01
	318.15	41.54	16.46	42.00	69.90	66.47 ± 0.37	98.54 ± 0.02
	328.15	41.54	16.46	42.00	71.73	73.84 ± 0.49	98.66 ± 0.02

the $[\text{EPy}]\text{BF}_4 + \text{Na}_2\text{CO}_3/\text{NaH}_2\text{PO}_4$ ATPS. The Setschenow-type equation indicate the salting-out ability are in the order of the $\text{Na}_2\text{CO}_3 > \text{NaH}_2\text{PO}_4$, and this order is exactly consistent with the ΔG_{hyd} values of the anions. Both the $[\text{EPy}]\text{BF}_4 + \text{Na}_2\text{CO}_3/\text{NaH}_2\text{PO}_4$ ATPS perform well in 2-chlorophenol extraction, while NaCO_3 is more preferred because of the less use of ionic liquid.

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.

Acknowledgements

This work was sponsored by the Natural Science Foundation for Distinguished Young Scholars of Guangdong Province (2019B151502038), the National Natural Science Foundation of China (21706038, 21808042, 21808039), the Fundamental Research Funds for the Central Universities (300102299202), and the National Training Projects of the University Students' Innovation and Entrepreneurship program (201910710125), the Scientific Innovation Practice Project of Postgraduates of Chang'an University (300103703058, 300103703016).

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2020.07.024>.

References

- [1] W. Raza, J. Lee, N. Raza, Y. Luo, K. Kim, J. Yang, Removal of phenolic compounds from industrial waste water based on membrane-based technologies, *J. Ind. Eng. Chem.* 71 (2019) 1–18.
- [2] L. Yin, Z. Shen, J. Niu, J. Chen, Y. Duan, Degradation of pentachlorophenol and 2,4-Dichlorophenol by sequential visible-light driven photocatalysis and laccase catalysis, *Environ. Sci. Technol.* 44 (2010) 9117–9122.
- [3] L.G.C. Villegas, N. Mashhadi, M. Chen, D. Mukherjee, K.E. Taylor, N. Biswas, A short review of techniques for phenol removal from wastewater, *Curr. Pollut. Rep.* 2 (2016) 157–167.
- [4] M.S. Álvarez, L. Gómez, R.G. Ulloa, F.J. Deive, M.A. Sanromán, A. Rodríguez, Antibiotics in swine husbandry effluents: laying the foundations for their efficient removal with a biocompatible ionic liquid, *Chem. Eng. J.* 298 (2016) 10–16.
- [5] W. Nie, F. Wang, R. Hao, L. Zhang, Q. Chen, F. Wei, X. Li, R. Loffredo, Z. Liu, Y. Liu, New method of aqueous two phase with solid phase extraction (ATP-SPE) for detection of sulfonamides, *Microchem. J.* 150 (2019) 104076.
- [6] K.M. Sousa, L.H.Z. Merlo, M.N. Marques, E.B. Cavalcanti, R.L. Souza, C.M.F. Soares, A.S. Lima, Partitioning of diuron in a novel aqueous two-phase system based on polyols and tetrahydrofuran, *Fluid Phase Equilib.* 429 (2016) 325–330.
- [7] S.C. Silvério, O. Rodríguez, J.A. Teixeira, E.A. Macedo, The effect of salts on the liquid-liquid phase equilibria of PEG600 + salt aqueous two-phase systems, *J. Chem. Eng. Data* 58 (2013) 3528–3535.
- [8] C.E. de Araújo Padilha, S.D. de Oliveira Júnior, D.F. de Santana Souza, J.A. de Oliveira, G.R. de Macedo, E.S.D. Santos, Partition coefficient prediction of Baker's yeast invertase in aqueous two phase systems using hybrid group method data handling neural network, *Chin. J. Chem. Eng.* 25 (2017) 652–657.
- [9] Z. Tan, C. Wang, Y. Yi, H. Wang, M. Li, W. Zhou, S. Tan, F. Li, Extraction and purification of chlorogenic acid from ramie (*Boehmeria nivea* L. Gaud.) leaf using an ethanol/salt aqueous two-phase system, *Sep. Purif. Technol.* 132 (2014) 396–400.
- [10] C.C. Ibarra-Herrera, O. Aguilar, M. Rito-Palomares, Application of an aqueous two-phase systems strategy for the potential recovery of a recombinant protein from alfalfa (*Medicago sativa*), *Sep. Purif. Technol.* 77 (2011) 94–98.
- [11] B. Mokhtarani, R. Karimzadeh, M.H. Amini, S.D. Manesh, Partitioning of ciprofloxacin in aqueous two-phase system of poly(ethylene glycol) and sodium sulphate, *Biochem. Eng. J.* 38 (2008) 241–247.
- [12] L.R. de Lemos, R.A. Campos, G.D. Rodrigues, L.H.M. Da Silva, M.C.H. Da Silva, Green separation of copper and zinc using triblock copolymer aqueous two-phase systems, *Sep. Purif. Technol.* 115 (2013) 107–113.
- [13] J. Li, X. Li, Y. Liu, J. Zhang, Removal of mercaptans from light oils using ionic liquid–NaOH aqueous solution as extractants, *Chin. J. Chem. Eng.* 25 (2017) 171–174.
- [14] F. Luechau, T.C. Ling, A. Lyddiatt, Partition of plasmid DNA in polymer–salt aqueous two-phase systems, *Sep. Purif. Technol.* 66 (2009) 397–404.
- [15] R.D. Rogers, K.R. Seddon, Chemistry. Ionic liquids—solvents of the future? *Science*. 302 (2003) 792–793.
- [16] M.T. Zafarani-Moattar, H. Shekaari, P. Jafari, Design of novel biocompatible and green aqueous two-phase systems containing cholinium L-alaninate ionic liquid and polyethylene glycol di-methyl ether 250 or polypropylene glycol 400 for separation of bovine serum albumin (BSA), *J. Mol. Liq.* 254 (2018) 322–332.
- [17] K.E. Gutowski, G.A. Broker, H.D. Willauer, J.G. Huddleston, R.P. Swatloski, J.D.H. And, R.D. Rogers, Controlling the aqueous miscibility of ionic liquids: aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations, *J. Am. Chem. Soc.* 125 (2003) 6632.
- [18] R.L.S. de França Do, R.L. Rosário, F.O. Souza, M.R. Farias, C.M.F. Mafra, H. Soares, J.A.P. Passos, Á.S. Lima Coutinho, Acetonitrile as adjuvant to tune polyethylene glycol + K_3PO_4 aqueous two-phase systems and its effect on phenolic compounds partition, *Sep. Purif. Technol.* 223 (2019) 41–48.
- [19] R.L. Souza, S.P.M. Ventura, C.M.F. Soares, J.A.P. Coutinho, Á.S. Lima, Lipase purification using ionic liquids as adjuvants in aqueous two-phase systems, *Green Chem.* 17 (2015) 3026–3034.
- [20] C. Li, J. Han, Y. Wang, Y. Yan, J. Pan, X. Xu, Z. Zhang, Phase behavior for the aqueous two-phase systems containing the ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate and kosmotropic salts, *J. Chem. Eng. Data* 55 (2010) 1087–1092.
- [21] J. Han, R. Pan, X. Xie, Y. Wang, Y. Yan, G. Yin, W. Guan, Liquid-liquid equilibria of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate + sodium and ammonium citrate aqueous two-phase systems at (298.15, 308.15, and 323.15) K, *J. Chem. Eng. Data* 55 (2010) 3749–3754.
- [22] J. Han, C. Yu, Y. Wang, X. Xie, Y. Yan, G. Yin, W. Guan, Liquid-liquid equilibria of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate and sodium citrate/tartrate/acetate aqueous two-phase systems at 298.15 K: Experiment and correlation, *Fluid Phase Equilib.* 295 (2010) 98–103.
- [23] Y. Wang, X. Xu, Y. Yan, J. Han, Z. Zhang, Phase behavior for the $[\text{Bmim}]\text{BF}_4$ aqueous two-phase systems containing ammonium sulfate/sodium carbonate salts at different temperatures: experimental and correlation, *Thermochim. Acta* 501 (2010) 112–118.
- [24] M. Petkovic, K.R. Seddon, L.P.N. Rebelo, C. Silva Pereira, Ionic liquids: a pathway to environmental acceptability, *Chem. Soc. Rev.* 40 (2011) 1383–1403.
- [25] K.M. Docherty, J.K. Dixon, C.F. Kulpa Jr., Biodegradability of imidazolium and pyridinium ionic liquids by an activated sludge microbial community, *Biodegradation*. 18 (2007) 481–493.
- [26] X. Zhu, H. Zhang, Optimization of $[\text{C}_n\text{Py}]\text{Cl}$ ($n = 2,4,6$) ionic liquid aqueous two-phase system extraction of papain using response surface methodology with box-behnken design, *Process Biochem.* 77 (2019) 113–121.
- [27] Y. Li, R. Huang, Z. He, N. Li, X. Lu, Phase behavior of an aqueous two-phase ionic liquid containing (N-butylpyridinium)tetrafluoroborate + sulfate salts + water at different temperatures, *J. Mol. Liq.* 216 (2016) 174–184.
- [28] Y. Zhao, J. Zhao, Y. Huang, Q. Zhou, X. Zhang, S. Zhang, Toxicity of ionic liquids: database and prediction via quantitative structure-activity relationship method, *J. Hazard. Mater.* 278 (2014) 320–329.
- [29] M.G. Freire, C.M.S.S. Neves, I.M. Marrucho, J.A.P. Coutinho, A.M. Fernandes, Hydrolysis of tetrafluoroborate and hexafluorophosphate counter ions in Imidazolium-based ionic liquids†, *J. Phys. Chem. A* 114 (2010) 3744–3749.
- [30] T. Turnaoglu, S.G. Ritchie, M.B. Shiflett, Liquid-liquid equilibria in binary mixtures of dihydroxy alcohols and Imidazolium-based ionic liquids, *J. Chem. Eng. Data* 64 (2019) 3179–3186.
- [31] M. Pirrung, Handbook of Synthetic Organic Chemistry, second ed. Academic Press, New York, 2017.
- [32] Y. Li, X. Shu, X. Zhang, W. Guan, Liquid-liquid equilibria of the aqueous two-phase systems composed of the N-Ethylpyridinium tetrafluoroborate ionic liquid and ammonium sulfate/anhydrous sodium carbonate/sodium dihydrogen phosphate and water at 298.15 K, *J. Chem. Eng. Data* 59 (2014) 176–182.
- [33] J. Guo, S. Xu, Y. Qin, Y. Li, X. Lin, C. He, S. Dai, The temperature influence on the phase behavior of ionic liquid based aqueous two-phase systems and its extraction efficiency of 2-chlorophenol, *Fluid Phase Equilib.* 506 (2020) 112394.
- [34] J.C. Merchuk, B.A. Andrews, J.A. Asenjo, Aqueous two-phase systems for protein separation. Studies on phase inversion, *J. Chromatogr. B Biomed. Sci. Appl.* 711 (1998) 285–293.
- [35] W. Zhang, G. Zhang, J. Han, Y. Yan, B. Chen, C. Sheng, Y. Liu, Phase equilibrium and chloramphenicol partitioning in aqueous two-phase system composed of 1-hydroxyhexyl-3-methylimidazolium chloride-salt, *J. Mol. Liq.* 193 (2014) 226–231.
- [36] M.R. Almeida, H. Passos, M.M. Pereira, Á.S. Lima, J.A.P. Coutinho, M.G. Freire, Ionic liquids as additives to enhance the extraction of antioxidants in aqueous two-phase systems, *Sep. Purif. Technol.* 128 (2014) 1–10.
- [37] J. Han, Y. Wang, C. Chen, W. Kang, Y. Liu, K. Xu, L. Ni, (Liquid + liquid) equilibria and extraction capacity of (imidazolium ionic liquids + potassium tartrate) aqueous two-phase systems, *J. Mol. Liq.* 193 (2014) 23–28.
- [38] M.G. Freire, A.F. Claudio, J.M. Araujo, J.A. Coutinho, I.M. Marrucho, L.J. Canongia, L.P. Rebelo, Aqueous biphasic systems: a boost brought about by using ionic liquids, *Chem. Soc. Rev.* 41 (2012) 4966–4995.
- [39] Y. Wang, J. Han, J. Liu, Y. Hu, C. Sheng, Y. Wu, Liquid-liquid equilibrium phase behavior of imidazolium-based ionic liquid aqueous two-phase systems composed of 1-alkyl-3-methyl imidazolium tetrafluoroborate and different electrolytes ZnSO_4 , MgSO_4 and Li_2SO_4 at 298.15 K: Experimental and correlation, *Thermochim. Acta* 557 (2013) 68–76.
- [40] D. Othmer, P. Tobias, Liquid-liquid extraction data-the line correlation, *Ind. Eng. Chem.* 34 (1942) 690–692.
- [41] W.D. Bancroft, S.S. Hubbard, A new method for determining diner distribution, *J. Am. Chem. Soc.* 64 (1942) 347–353.
- [42] A. Hamta, M.R. Dehghani, M. Gholami, Novel experimental data on aqueous two-phase system containing PEG-6000 and Na_2CO_3 at $T = (293.15, 303.15 \text{ and } 313.15) \text{ K}$, *J. Mol. Liq.* 241 (2017) 144–149.

- [43] E. Gómez, P.F. Requejo, E. Tojo, E.A. Macedo, Recovery of flavonoids using novel biodegradable choline amino acids ionic liquids based ATPS, *Fluid Phase Equilib.* 493 (2019) 1–9.
- [44] L. Liu, Y. Liu, L. Du, Y. Zhao, H. Du, (Liquid + liquid) phase equilibrium of aqueous two-phase system containing (surfactant + sodium sulfate + water) at different temperatures, *Fluid Phase Equilib.* 415 (2016) 25–33.
- [45] E.C. de Souza, R.S. Diniz, J.S. Dos Reis Coimbra, M. de Oliveira Leite, G. Rocha Dos Santos, A.M. Da Cruz Rodrigues, L.H. Meller Da Silva, Measurements and modeling of liquid–liquid equilibrium of polyethylene glycol 400, sodium phosphate, or sodium citrate aqueous two-phase systems at (298.2, 308.2, and 318.2) K, *J. Chem. Eng. Data* 58 (2013) 2008–2017.
- [46] M.J. Hey, D.P. Jackson, H. Yan, The salting-out effect and phase separation in aqueous solutions of electrolytes and poly(ethylene glycol), *Polymer* 46 (2005) 2567–2572.
- [47] R.D. Rogers, A.H. Bond, C.B. Bauer, J. Zhang, S.T. Griffin, Metal ion separations in polyethylene glycol-based aqueous biphasic systems: Correlation of partitioning behavior with available thermodynamic hydration data, *J. Chromatogr. B Biomed. Sci. Appl.* 680 (1996) 221–229.
- [48] M.T. Zafarani-Moattar, S. Hamzehzadeh, Liquid-liquid equilibria of aqueous two-phase systems containing polyethylene glycol and sodium succinate or sodium formate, *Calphad* 29 (2005) 1–6.
- [49] Y. Marcus, Thermodynamics of solvation of ions part 5. Gibbs free energy of hydration at 298.15 K, *J. Chem. Soc. Faraday Trans.* 87 (1991) 2995–2999.
- [50] L. Wang, H. Zhu, Y. Sun, Y. Xu, Q. Wang, Y. Yan, Determination of trace chlorophenols endocrine disrupting chemicals in water sample using [Bmim]BF₄-NaH₂PO₄ aqueous two-phase extraction system coupled with high performance liquid chromatography, *Chin. J. Anal. Chem.* 39 (2011) 709–712.
- [51] O.G. Sas, I. Domínguez, Á. Domínguez, B. González, Using bis (trifluoromethylsulfonyl) imide based ionic liquids to extract phenolic compounds, *J. Chem. Thermodyn.* 131 (2019) 159–167.
- [52] Q. Zhu, Y. Sun, S. Xu, Y. Li, X. Lin, Y. Qin, Rational design of 3D/2D In₂O₃ nanocube/ZnIn₂S₄ nanosheet heterojunction photocatalyst with large-area “high-speed channels” for photocatalytic oxidation of 2,4-dichlorophenol under visible light, *J. Hazard. Mater.* 382 (2020) 121098.