Effects of temperature and pH on phase behavior for the ternary systems of water + inorganic salt + alkoxyethanols at atmospheric pressure

Xue Wang, Shuang Yu, Pei-Song Fu, Xin Li, Tao-Hua Zhu, Xin-Xue Li*

Department of Chemistry and Chemical Engineering, University of Science and Technology
Beijing, Beijing 100083, China

* Corresponding author. Tel.: +86-10-62333871; fax: +86-10-62332126.

E-mail address: xinxueli@ustb.edu.cn (X.-X. Li).

Abstract:

The effects of temperature, pH , inorganic salts, as well as molecular structure on the phase behavior of water + salt + alkoxyethanol(C_nE_m , $n = 2-4$, $m = 1-3$) ternary systems were investigated. Binodal data for water + NaCl + C_2E_1 , C_3E_1 , C_4E_1 , C_4E_2 , C_4E_3 were obtained and correlated to investigate how the system's phase-split ability is influenced by the type of alkoxyethanol. In addition, the binodal data for aqueous solution of C_4E_1 with NaCl, KCl, CsCl, NaF, NaBr were investigated to understand the effects of the salts. Furthermore, the complete two-liquid-phase coexistence regions for water + NaCl + C_4E_1 at $T = (283.15, 293.15, 303.15, 313.15)$ K were acquired to investigate the effects of temperature. The liquid-liquid equilibria (LLE) were also studied based on tie-line data, in which three correlation equations, the Othmer-Tobias equation, the Bancroft equation and the Setschenow equation were used. Finally, the binodal data of water + NaCl + C_4E_1 was measured at $pH = (3, 5, 7, 9, 11)$ to investigate the impact of pH .

Keywords:

Alkoxyethanol; Aqueous two-phase system; Temperature; Inorganic salt

1. Introduction

An aqueous two-phase system (ATPS) consists of two separated aqueous phases, which may be naturally generated from the spontaneous split of a mixture of some water soluble chemicals under the appropriate concentrations and the proper temperature. ATPS has rapidly developed after this term was firstly mentioned by Beijerinck in 1896 [1]. To date, the many examples of ATPS can be classified into following categories based on the ingredients: the traditional types, i.e., polymer-based [2-7] and surfactant-based ATPS [8, 9], and novel types like ionic liquid-based [10-15] and organic solvent-based ATPS [16-18].

On the other hand, ATPS's application in the separation engineering filed, which is named aqueous two-phase extraction (ATPE), has also gained prominence. Because of the distinct advantages over the conventional organic solvent liquid-liquid extraction, such as lower cost, lower toxicity and proper interfacial tension [19], ATPE based on various ATPSs is extensively applied in chemical and biological purification and extraction, e.g., separating metal ions [20-23], purifying proteins [24-26], viruses [27, 28] and other biological molecules [29, 30]. At the same time, the boom of the discoveries of new ATPSs is responsible for the wider application of ATPE. Before the practical use of a new ATPS, a transparent investigation on its phase behavior is required because it can contribute to the design and optimization process of ATPE.

The system of water + inorganic salt + alkoxyethanol is a class of novel ATPS that belongs to organic solvent-based ATPS, which has plenty of excellent properties like low viscosity and relatively easy recycling when applied into extraction. Unlike the familiar organic solvent-based ATPS composed of aliphatic alcohol, salt and water [16, 17], this new type of ternary system has rarely been covered before. Hence, it is essential to study the phase behavior of the water + inorganic salt + alkoxyethanol

system before using it for extraction. In our earlier papers, we proposed the water + inorganic salt + alkoxyethanol ATPS and acquired the phase diagram of water + NaCl + diethylene glycol monobutyl ether (DEGMBE, C₄E₂) ternary systems at 303.15 K, which can be generalized to the water +NaCl + alkoxyethanol ATPS [31]. Subsequently, the effect of temperature on the phase behavior of water +NaCl + ethylene glycol monopropyl ether (EGMPE, C₃E₁) was also reported [32].

In this work, additional factors that can affect the phase behavior of water + salt + alkoxyethanol ternary system were investigated. The effects of different components and *pH* on the phase behavior were analyzed based on experimental binodal data. Moreover, the temperature's influence was also studied based on the portrayed complete two-liquid-phase coexistence regions not just the binodal data, which makes the comparison results more comprehensive. The obtained results not merely supply adequate information to get insight into the phase behavior of water + salt + alkoxyethanol, but also conduct the design and optimization of aqueous two-phase extraction (ATPE) by using of this system.

2. Experimental

2.1. Materials

The chemicals used in this work are listed in Table 1. All of the alkoxyethanols and metal halides were used without further purification. The hydrochloric acid and sodium hydroxide were fed into doubly distilled deionized water to form a solution with a concentration of 0.1 mol·cm⁻³. Doubly distilled water was used in all of the procedures.

Table 1 about here

2.2. Apparatus and procedure

The binodal data of ternary systems were obtained via the cloud point method, which has been

widely reported in the previous literatures [33]. A glass of ether solution with known mass fraction was placed in a water thermostat (EYEL4 NCB-1200, TOKYO RIKAKIKAI CO. LTD. Japan) with an accuracy of ± 0.1 K. The salt solution of a known concentration at the same temperature was titrated into the glass vessel drop by drop until the solution appeared turbid. The mass of the compound was acquired using an electronic analytical balance (HANGPING FA2104, Shanghai, China) with a precision of ± 0.0001 g. Next, water was added into the mixture to make it limpid again, and the mass of the mixture was also noted. The procedure was repeated until no turbidity appeared.

Tie-line data were obtained through the following process. A series of ternary mixtures with known concentrations were placed in a water thermostat overnight to reach thermostatic equilibrium completely after vibration for 2 h. Next, samples of the conjugate phase were drawn out using a syringe needle. The salt concentrations in both phases were determined by evaporating these samples, which have a precision of ± 0.0008 . The ether concentrations were obtained using the refractive index method described before [34], in which the relationship between refractive indices measured at 293.15 K and the mass fraction of components within the low concentration range can be expressed as Eq. (1).

$$n_D = n_0 + k_2 w_2 + k_3 w_3 \quad (1)$$

where n_D and n_0 are the refractive indices of the ternary solution and pure water at 293.15 K; w_2 and w_3 are the mass fractions of salt and ether, respectively; and k_2 and k_3 are two constants corresponding to salt and ether, respectively. Once Eq. (1) was determined, the ether mass fractions could be calculated using the known refractive indices and salt concentrations of the samples. To acquire two parameters, the refractive indices of known mass fractions of several groups of dilute ternary solutions, which include salt and ether in proper concentration, were measured using a refractometer (WAY-2S, Shanghai, China) at 293.15 K. There should be noted that Eq. (1) is only valid for dilute solutions. Thus,

it is necessary to dilute the samples within a certain concentration range prior to the refractive index measurement.

3. Results and Discussion

3.1. Effects of alkoxyethanol

To evaluate the effects of different ethers, two groups of alkoxyethanols were opted to form ATPS along with NaCl at $T = 298.15$ K. The first group contains C₂E₁, C₃E₁ and C₄E₁, which share the same ethylene glycol group, but have different alkyl groups. While another group's members include C₄E₁, C₄E₂, C₄E₃, which share the butyl group, but vary in ether moiety. Binodal curves, which can appropriately describe the phase behavior of ATPSs, were obtained via the cloud point method. The experimental binodal data for different water + NaCl + alkoxyethanol ATPSs are listed in Table 2 except the C₂E₁ system because of the absence of the two-liquid-phase coexistence region. Also, the corresponding plots are shown in Fig. 1.

Table 2 Fig. 1

To correlate the binodal data, several empirical equations that have been used successfully in previous literatures [35-37] are used:

$$w_3 = k_1 \exp(k_2 w_2^{0.5} - k_3 w_2^3) \quad (2)$$

$$w_3 = k_1 + k_2 \ln w_2 + k_3 w_2 \quad (3)$$

$$w_3 = k_1 + k_2 w_2 + k_3 w_2^2 + k_4 w_2^3 \quad (4)$$

$$w_3 = \exp(k_1 + k_2 w_2^{0.5} + k_3 w_2 + k_4 w_2^2) \quad (5)$$

where w_2 and w_3 are the mass fractions of NaCl and alkoxyethanols, respectively. The fitting parameters k_1 , k_2 , k_3 , and k_4 along with the adjusted coefficients of determination ($Adj.R^2$) and the

corresponding standard deviations (*SD*) of Eqs. (2) - (5) are given in Table 3. From this table, all of the experimental binodal data are observed to correlate satisfactorily with Eqs. (2) - (5).

Table 3

Fig. 1 clearly shows the biphasic formation ability of the alkoxyethanols in the first group is in the following order: $C_2E_1 < C_3E_1 < C_4E_1$. This order occurs because the extension of hydrocarbon chain boosts the hydrophobicity of organic molecules, which is the main imputes of the solution's separation. In addition, Fig. 1 indicates that the biphasic formation ability of the ethers in the second group obeys the following sequence: $C_4E_1 > C_4E_2 > C_4E_3$. In this group, the hydrophilia of ethers is strengthening along with the increase in the number of hydrophilic groups, such as alcohol and ether moiety. Ultimately, the enhancement of the hydrophilia of ethers is beneficial to the dissolution of organics in water, in other words, it is detrimental to the splitting of the phase.

3.2 Effects of inorganic salts

The influence of different salts, i.e., the distinct anions and cations, on the ternary system was also investigated based on the comparison of the binodal curves. To obtain the binodal data, a series of saturated salt aqueous solutions, for which the dominant component of each member of the series is NaCl, KCl, CsCl, NaF and NaBr, were added into the C_4E_1 aqueous solution according to the cloud point method at $T = 298.15$ K. The acquired experimental data are listed in table 4. The obtained experimental binodal data were also correlated with Eqs. (2) - (5), and the results presented in Table 5. In addition, the binodal curves of water + salt + C_4E_1 are displayed in Fig. 2.

Table 4 Table 5 Fig. 2

The effects of different anions and cations on the phase split of a ternary system are clearly shown in Fig. 2. Anions have significantly distinct effects on the phase behavior, and the phase-separation ability

ranked from high to low is F^- , Cl^- and Br^- . The phenomenon is self-explanatory: the decrease in the radius of the anions strengthens the ability to combine with water. The more anions combined with water, the more competitors, i.e., C_4E_1 are forcedly released from hydrogen bonds, which urges the phase split. In contrast, the distinction between the salting-out abilities of different cations appears to be smaller. Among the cations applied in this experiment, Na^+ has a negligible advantage over K^+ in the aspect of phase-split ability, which is the same as the conclusion found in the literatures [38, 39]. Moreover, Cs^+ represents a less efficient salting-out ability compared to the other elements in the same category, e.g., Na^+ and K^+ .

A thermodynamic quantity, the molar Gibbs free energy of hydration ($\Delta_{hyd}G^*$), is used to compare the hydratability of the ions. Yizhak Marcus [40] measured the molar Gibbs free energy of hydration ($\Delta_{hyd}G^*$) of a large number of ions at 298.15 K and correlated the data with the ions' salting-out ability, in which the anion or cation embraces a stronger salting-out ability when it has a larger negative value. In this experiment, the molar Gibbs free energies of hydration ($\Delta_{hyd}G^*$) of the anions are F^- (-465 kJ/mol), Cl^- (-340 kJ/mol) and Br^- (-315 kJ/mol), the molar Gibbs free energies of hydration of the cations are Na^+ (-365 kJ/mol), K^+ (-295 kJ/mol) and Cs^+ (-250 kJ/mol), which coincides with the trend of experimental result satisfactorily.

3.3 Effect of temperature

The area enclosed by the binodal curve and the longest tie-line (the borderline of liquid–liquid equilibrium region and liquid–liquid–solid equilibrium region) is called as the complete two-liquid-phase coexistence region. Both the binodal data from the cloud point method and the tie-line data from the refractive method were required to determine this region. In order to investigate the effect of temperature, the bimodal curve and tie-line for the ternary system of water +NaCl + C_4E_1 were

determined at $T = (283.15, 293.15, 303.15, 313.15)$ K.

3.3.1. Binodal data

The binodal data for the studied ATPS from 283.15K to 313.15K (obtained using the cloud point method) are listed in Table 6. The experimental data were fitted with Eqs. (2) - (5); the relevant coefficients are listed in Table 7. Also, the binodal curves of water + salt + C₄E₁ with varied temperature are displayed in Fig. 3, which indicate that the higher temperature promotes the phase split. The possible reason for this phenomenon is that the increasing temperature benefits the breaking of hydrogen bonds between water and C₄E₁, which can further lead to the separation of water and ether.

Table 6 Table 7 Fig. 3

3.3.2. Tie-line data

The tie-line data, which were acquired through the refractive method, not merely make the two-liquid-phase coexistence area complete, but can also provide information regarding the liquid-liquid equilibria. To obtain the tie-line data, the parameters in Eq. (1) were determined according to the method mentioned in the experimental section; the relevant parameters are listed in Table 8. In addition, the obtained tie-line data under different temperatures are presented in Table 9.

Table 8 Table 9

To correlate the tie-line data, several equations have been mentioned previously. The three best known of these equations, called the Othmer-Tobias equation (Eq. 6) [41], the Bancroft equation (Eq. 7) [42] and the Seteschenow equation (Eq. 8) [43], are used in this work.

$$\left(\frac{1-w_3^f}{w_3^f}\right) = k_1 \left(\frac{1-w_2^b}{w_2^b}\right)^{k_2} \quad (6)$$

$$\left(\frac{w_1^b}{w_2^b}\right) = k_1 \left(\frac{w_1^f}{w_3^f}\right)^{k_2} \quad (7)$$

$$\left(\frac{w_2^t}{w_2^b}\right) = \exp \{k_1(w_3^b - w_3^t) + k_2\} \quad (8)$$

where “*t*” and “*b*” denote the top and bottom phases, respectively, and w_1 , w_2 , and w_3 represent the mass fractions of water, NaCl and C₄E₁, respectively. k_1 and k_2 listed in Table 10 are coefficients; the adjusted coefficients of determination ($Adj.R^2$) and the corresponding standard deviations (SD) of Eqs. (6) - (8) are also presented in this table.

Table 10

Moreover, the tie-line length (TLL) and the slope (STL) which can visually describe the variation of tie-lines were calculated based on Eqs. (9) - (10) [32].

$$TLL = \sqrt{\left(\frac{\sqrt{3}}{2}w_2^b - \frac{\sqrt{3}}{2}w_2^t\right)^2 + \left[\left(w_1^b + \frac{w_2^b}{2}\right) - \left(w_1^t + \frac{w_2^t}{2}\right)\right]^2} \quad (9)$$

$$STL = \left(\frac{\sqrt{3}}{2}w_2^b - \frac{\sqrt{3}}{2}w_2^t\right) / \left[\left(w_1^b + \frac{w_2^b}{2}\right) - \left(w_1^t + \frac{w_2^t}{2}\right)\right] \quad (10)$$

The results are also listed in Table 9, followed by the corresponding tie-line composition. The rise of the NaCl content is found to result in the increase of TLL and STL at the same time under a certain temperature.

Eventually, the complete two-liquid-phase coexistence regions at $T = (283.15, 293.15, 303.15, 313.15)$ K were obtained by assembling the binodal data and the tie-line data. The phase diagrams are shown in Fig. 4, which obviously exhibited the impact of temperature on water + NaCl + C₄E₁ ternary system. The whole biphasic zones of two coexisting liquid phases are expanding gradually with increasing temperature, which means that a higher temperature cannot only aid the phase-separation, but can also ensure the ATPS remains in a larger range of components' concentration.

Fig. 4

3.4 Effect of pH

To study the effect of pH , the binodal data of the water + NaCl + C₄E₁ ternary system with different pH at $T = 298.15$ K were obtained. In this part, hydrochloric acid or sodium hydroxide solution was added into the pure deionized water, saturated NaCl solution, and C₄E₁ aqueous solution respectively until the prospective pH (3, 5, 7, 9, 11) appeared. The acquired binodal data are listed in Table 11, and the correlation results using Eqs. (2) - (5) are presented in Table 12. Moreover, the relevant binodal curves are displayed in Fig 5.

Table 11 Table 12 Fig. 5

The above graph reveals that the pH has almost no influence on the binodal curve of water + NaCl + C₄E₁ ATPS. As mentioned above, the phase-split ability of the system is mainly dominated by hydration of ions. The concentration of hydrogen ion and hydroxide ion is fairly low compared with the concentration of NaCl. Thus the effect of pH on the phase behavior of water + NaCl + C₄E₁ is negligible. The insensitivity to pH is a remarkable advantage for ATPS when applied into the extraction field because the yield of proteins or metal ions can be boosted through adjustment of the pH of ATPS without any variation of the system, which can simplify the design and operation of ATPE.

4. Conclusions

The phase behavior of water + inorganic salt + alkoxyethanol ternary system was affected by molecular structure of alkoxyethanol, the type of salt, and temperature. Through the investigation of phase-split ability of C₂E₁, C₃E₁, C₄E₁, C₄E₂ and C₄E₃ aqueous solution with NaCl, it was found that the elongation of alkyl promotes the phase-split while the increase of alcohol and ether moiety hinders it. According to the observation of phase behavior of C₄E₁ aqueous solution with alkali halides (NaCl, KCl, CsCl, NaF and NaBr), it is shown that phase-separation ability is consistent with salting-out capacity of ion. The anions have a remarkable effect on ATPS in the order $F^- > Cl^- > Br^-$, while cations

have less effect in the sequence $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$. In particular, Na^+ and K^+ are similar regarding their phase-separation ability. The temperature also plays an important role in the phase-split process. The region of two-liquid-phase coexistence expands with the rise of temperature. The effect of pH on the ATPS formation of water + NaCl + C₄E₁ system was found to be negligible. The binodal data at various temperatures were obtained and satisfactorily correlated with four empirical equations. The experimental tie-line data at different temperatures were also fitted by the Othmer-Tobias equation, the Bancroft equation and the Seteschenow equation fairly well.

Based on the experimental results, the construction of ATPS using water + inorganic salt + alkoxyethanol system can be controlled by choosing suitable molecular structure of alkoxyethanol and suitable inorganic salt. In addition, the occurrence and disappearance of ATPS can also be tuned merely by raising or lowering the temperature. Moreover, the pH of the system can be adjusted to enhance the separation efficiency with ATPS nearly unaffected.

Acknowledgments

The authors are grateful for the financial support provided by the National Science Foundation of China (No. 51274019).

References

- [1] M.T. Zafarani-Moattar, V. Hosseinpour-Hashemi, (Liquid+liquid) equilibrium of the ternary aqueous system containing poly ethylene glycol dimethyl ether 2000 and tri-potassium citrate at different temperatures, *J. Chem. Thermodyn.*, 48 (2012) 75-83.
- [2] Y. Liu, Z.Y. Wu, Y.J. Zhao, Liquid–liquid equilibrium correlation of aqueous two-phase systems composed of polyethylene glycol and nonionic surfactant, *Thermochimi. Acta*, 602 (2015) 78-86.
- [3] Y. Lu, J. Han, C.Z. Sheng, P. Yu, Z.J. Tan, Y.S. Yan, Measurement and correlation of phase diagram data for polyoxyethylene (10) lauryl ether and potassium hydroxide/potassium carbonate/potassium phosphate aqueous two-phase systems at 298.15 K, *Thermochimi. Acta*, 543 (2012) 1-8.
- [4] W.L. Zhang, Y.T. Hu, Y. Wang, J. Han, L. Ni, Y.C. Wu, Liquid–liquid equilibrium of aqueous two-phase systems containing poly(ethylene glycol) of different molecular weights and several ammonium salts at 298.15K, *Thermochimi. Acta*, 560 (2013) 47-54.
- [5] Y. Lu, T.F. Hao, Y. Zhou, J. Han, Z.F. Tan, Y.S. Yan, Aqueous two-phase systems of polyoxyethylene lauryl ether and potassium gluconate/potassium oxalate/potassium citrate at different temperature-experimental results and modeling of (liquid+liquid) equilibrium data, *J. Chem. Thermodyn.*, 71 (2014) 137-147.
- [6] M. Milosevic, K.J.J. Staal, B. Schuur, A.B. de Haan, Liquid–liquid phase equilibria for ternary systems of several polyethers with NaCl and H₂O, *Fluid Phase Equilibria*, 376 (2014) 76-84.
- [7] M. Milosevic, K.J.J. Staal, B. Schuur, A.B. de Haan, Experimental data and thermodynamic modeling of ternary aqueous biphasic systems of EO/PO polymers–Na₂SO₄–H₂O, *Fluid Phase Equilibria*, 366 (2014) 45-56.
- [8] J.L. He, S.S. Zhang, Q. Zheng, Q.F. Lei, W.J. Fang, Phase property, composition and temperature-induced phase inversion of ATPS-C formed by aqueous cationic–anionic surfactant mixtures, *Colloids Surface A*, 436 (2013) 193-200.
- [9] A. Salabat, M. Alinoori, Salt effect on aqueous two-phase system composed of nonylphenyl ethoxylate non-ionic surfactant, *Calphad*, 32 (2008) 611-614.
- [10] Y.L. Li, Q. Liu, M.S. Zhang, H. Su, Liquid–liquid equilibrium of the [4-MBP][BF₄]-NaCl-H₂O systems at T=293.15, 303.15, 313.15, and 323.15K: Experimentation and correlation, *Thermochimi. Acta*, 565 (2013) 234-240.
- [11] Y. Wang, J. Han, J. Liu, Y. Hu, C.Z. Sheng, Y.C. Wu, Liquid–liquid equilibrium phase behavior of iminazolium-based ionic liquid aqueous two-phase systems composed of 1-alkyl-3-methyl imidazolium tetrafluoroborate and different electrolytes ZnSO₄, MgSO₄ and Li₂SO₄ at 298.15K: Experimental and correlation, *Thermochimi. Acta*, 557 (2013) 68-76.
- [12] G.W. Yin, S.N. Li, Q.G. Zhai, Y.C. Jiang, M.C. Hu, Phase behavior of aqueous two-phase systems composed of 1-alkyl-3-methylimidazolium bromide+Rb₂CO₃/Cs₂CO₃+water, *Thermochimi. Acta*, 566 (2013) 149-154.
- [13] E. Alvarez-Guerra, S.P.M. Ventura, J.A.P. Coutinho, A. Irabien, Ionic liquid-based three phase partitioning (ILTPP) systems: Ionic liquid recovery and recycling, *Fluid Phase Equilibria*, 371 (2014) 67-74.
- [14] A.Q. Gong, X.S. Zhu, Surfactant/ionic liquid aqueous two-phase system extraction coupled with spectrofluorimetry for the determination of dutasteride in pharmaceutical formulation and biological samples, *Fluid Phase Equilibria*, 374 (2014) 70-78.
- [15] C.Z. Sheng, J. Han, Y. Wang, B. Chen, Y. Liu, G.C. Zhang, Y.S. Yan, X.H. Zhao, Liquid–liquid equilibria of ionic liquid 1-(2-methoxyethyl)-3-methylimidazolium bromide+potassium carbonate, potassium phosphate, dipotassium phosphate+water aqueous two-phase systems, *Fluid Phase Equilibria*, 364 (2014) 55-61.
- [16] W.L. Guo, J.J. Ma, Y. Wang, J. Han, Y.F. Li, S. Song, Liquid–liquid equilibrium of aqueous two-phase systems composed of hydrophilic alcohols (ethanol/2-propanol/1-propanol) and MgSO₄/ZnSO₄ at (303.15 and 313.15)K and correlation, *Thermochimi. Acta*, 546 (2012) 8-15.
- [17] J. Han, Y.C. Wu, Y.Y. Xiang, Y. Wang, J.J. Ma, Y.T. Hu, Liquid–liquid equilibria of hydrophilic alcohol+sodium hydroxide+water systems: Experimental and correlation, *Thermochimi. Acta*, 566 (2013) 261-267.
- [18] Y. Lu, T.F. Hao, S.P. Hu, J. Han, Z.J. Tan, Y.S. Yan, Measurement and correlation of phase diagram data for acetone and

sulfate aqueous two-phase systems at different temperatures, *Thermochimi. Acta*, 568 (2013) 209-217.

- [19] A. Blanco, A. Gayol, D. Gómez-Díaz, J.M. Navaza, Physicochemical characterization of aqueous two phase systems containing Triton X-102 and sodium salts in the range of temperature from 288.15K to 318.15K, *J. Mol. Liq.*, 195 (2014) 1-8.
- [20] L. Bulgariu, D. Bulgariu, Selective extraction of Hg(II), Cd(II) and Zn(II) ions from aqueous media by a green chemistry procedure using aqueous two-phase systems, *Sep. Purif. Technol.*, 118 (2013) 209-216.
- [21] 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.
- [22] L.R. de Lemos, I.J. Santos, G.D. Rodrigues, L.H. da Silva, M.C. da Silva, Copper recovery from ore by liquid-liquid extraction using aqueous two-phase system, *J. Hazard. Mater.*, 237-238 (2012) 209-214.
- [23] R. Patricio Pda, M.C. Mesquita, L.H. da Silva, M.C. da Silva, Application of aqueous two-phase systems for the development of a new method of cobalt(II), iron(III) and nickel(II) extraction: a green chemistry approach, *J. Hazard. Mater.*, 193 (2011) 311-318.
- [24] Y.M. Lu, Y.Z. Yang, X.D. Zhao, C.B. Xia, Bovine serum albumin partitioning in polyethylene glycol (PEG)/potassium citrate aqueous two-phase systems, *Food Bioprod. Process.*, 88 (2010) 40-46.
- [25] C.W. Ooi, S.L. Hii, S.M.M. Kamal, A. Ariff, T.C. Ling, Extractive fermentation using aqueous two-phase systems for integrated production and purification of extracellular lipase derived from *Burkholderia pseudomallei*, *Process Biochem.*, 46 (2011) 68-73.
- [26] İ. Yücekan, S. Önal, Partitioning of invertase from tomato in poly(ethylene glycol)/sodium sulfate aqueous two-phase systems, *Process Biochem.*, 46 (2011) 226-232.
- [27] F. Luechau, T.C. Ling, A. Lyddiatt, Recovery of B19 virus-like particles by aqueous two-phase systems, *Food Bioprod. Process.*, 89 (2011) 322-327.
- [28] K.S. Vijayaragavan, A. Zahid, J.W. Young, C.L. Heldt, Separation of porcine parvovirus from bovine serum albumin using PEG-salt aqueous two-phase system, *J. Chromatogr. B*, 967 (2014) 118-126.
- [29] M.F.F. Silva, A. Fernandes-Platzgummer, M.R. Aires-Barros, A.M. Azevedo, Integrated purification of monoclonal antibodies directly from cell culture medium with aqueous two-phase systems, *Sep. Purif. Technol.*, 132 (2014) 330-335.
- [30] X.J. Zuo, Y.Q. Cao, A.J. Gong, K.X. Wang, Comparison of Two Aqueous Two-Phase Systems for Extracting Microcystin-LR from Algae Pulp, *Solvent Extr. Res. Dev.*, 22 (2015) 147-157.
- [31] X.X. Li, F. Wang, X.X. Ma, Z.L. Zhang, G.C. Fan, J.Y. Qu, Phase Behavior and Spectroscopic Properties for Ternary Systems Water + Sodium Chloride + Diethylene Glycol Monobutyl Ether at 303.15 K and Atmospheric Pressure, *J. Chem. Eng. Data*, 57 (2012) 384-388.
- [32] X. Wang, X.X. Li, Q. Liu, D. Li, Temperature dependence of ternary phase diagrams for water+sodium chloride+ethylene glycol monopropyl ether at atmospheric pressure, *Fluid Phase Equilibria*, 398 (2015) 26-35.
- [33] E. Nemati-Knade, H. Shekaari, S.A. Jafari, Thermodynamic study of aqueous two phase systems for some aliphatic alcohols+sodium thiosulfate+water, *Fluid Phase Equilibria*, 321 (2012) 64-72.
- [34] E. L. Cheluget, S. Gelinas, J. H. Vera, M. E. Weber, Liquid-liquid equilibrium of aqueous mixtures of poly(propyleneglycol) with NaCl, *J. Chem. Eng. Data*, 39(1994) 127-130.
- [35] J.C. Merchuk, B.A. Andrews, J.A. Asenjo, Aqueous two-phase systems for protein separation: Studies on phase inversion, *J. Chromatogr. B*, 711 (1998) 285 –293.
- [36] E. Nemati-Kande, H. Shekaari, Thermodynamic investigation of the ATPSs composed of some (aliphatic alcohol + sodium carbonate + water) ternary systems, *J. Chem. Thermodyn.*, 57 (2013) 541-549.
- [37] M. Hu, Q. Zhai, Z. Liu, S. Xia, Liquid-liquid and solid-liquid equilibrium of the ternary system ethanol + cesium sulfate + water at (10, 30, and 50) °C, *J. Chem. Eng. Data*, 48(2003) 1561-1564.
- [38] E. Nemati-Kande, H. Shekaari, Salting-out effect of sodium, potassium, carbonate, sulfite, tartrate and thiosulfate ions on aqueous mixtures of acetonitrile or 1-methyl-2-pyrrolidone: A liquid-liquid equilibrium study, *Fluid Phase Equilibria*, 360 (2013)

357-366.

[39] Y. Wang, Y. Mao, J. Han, Y. Liu, Phase Diagram Data for Ethanol/Propan-1-ol/Propan-2-ol-2,3-Dihydroxybutanedioate Aqueous Two-Phase Systems at 298.15 K and Data Correlation, *J. Chem. Eng. Data*, 56 (2011) 622-626.

[40] Y. Marcus, Thermodynamics of solvation of ions. Part 5.—Gibbs free energy of hydration at 298.15 K, *J. Chem. Soc. Faraday*, 87 (1991) 2995-2999.

[41] D.F. Othmer, P.E. Tobias, Liquid-Liquid extraction data toluene and acetaldehyde systems, *Ind. Eng. Chem*, 34 (1942) 690-692.

[42] W.D. Bancroft, S. S. Hubbard, A new method for determining Dimeric Distribution, *J. Am. Chem. Soc*, 64 (1942) 347-353.

[43] J. Setschenow, Concerning the constitution of salt solutions on the basis of their behavior to carbonic acid, *Z. Phys. Chem*, 4 (1889) 117-125.

Table captions

Table 1. Sample provenance table

Table 2. Binodal data for the water (1) + NaCl (2) + alkoxyethanol (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of alkoxyethanol (EGMPE, EGMBE, DEGMBE, TEGMBE).

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 3. Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) + NaCl (2) + alkoxyethanol (3) system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of

parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and experimental values, respectively.

Table 4. Binodal data for the water (1) + salt (2) + EGMBE (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

w_1 , mass fraction of water. w_2 , mass fraction of salt (KCl, CsCl, NaF, NaBr). w_3 , mass fraction of EGMBE.

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 5. Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) + salt (2) + EGMBE (3) system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and experimental values, respectively.

Table 6. Binodal data for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.^a

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of EGMBE.

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 7. Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) + NaCl (2) + EGMBE (3) system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.^a

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and experimental values, respectively.

Table 8. Values of the parameters of Eq. (1) for the water (1) + NaCl (2) + EGMBE (3) system at $T = 293.15$ K and pressure $p = 0.1$ MPa.^a

w_2 , mass fraction of NaCl. n_0 , refractive index of pure water at $T = 293.15$ K.

^a Standard uncertainties u are $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 9. Tie-line data for the water (1) + NaCl (2) + EGMBE (3) system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.^a

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of EGMBE. TLL and STL stand for the length and slope of tie-line respectively.

^a Standard uncertainties u are $u(w_2) = 0.002$, $u(w_3) = 0.0008$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b Data for SLLE, the composition of solid phase is anhydrous NaCl (cr), which was determined by comparing its thermogravimetric analysis curve with that of pure sodium chloride.

Table 10. Values of the parameters of Eqs. (6) - (8) used for the correlation of experimental tie-line data for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.^a

^a Standard uncertainties u are $u(w_2) = 0.002$, $u(w_3) = 0.0008$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

$$^b SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (Y^{cal} - Y^{exp})^2} .$$

Table 11. Binodal data for the water (1) + NaCl (2) + EGMBE (3) ternary system with different pH at T

= 298.15 K and pressure $p = 0.1$ MPa.^a

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of EGMBE.

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 12. Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the

water (1) + NaCl (2) + EGMBE (3) system with different pH at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of

parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and experimental values, respectively.

Figure Captions

Fig. 1. Binodal curves for the water (1) + NaCl (2) + alkoxyethanol (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.

Fig. 2. Binodal curves for the water (1) + salt (2) + EGMBE (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.

Fig. 3. Binodal curves for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.

Fig. 4. Complete two-liquid-phase coexistence areas for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa. The cross (×) represents binodal data from cloud point method, and the circle (●) represents tie-line data; the solid line (—) and dash-dot line (-.-.-.-) represents Binodal curves and tie-lines respectively.

Fig. 5. Binodal curves for the water (1) + NaCl (2) + EGMBE (3) ternary system with different pH at $T = 298.15$ K and pressure $p = 0.1$ MPa.

Table 1

Sample provenance table

Chemical name	CAS#	Source	Mass fraction purity	Purification method
Ethylene glycol monoethyl ether (EGMEE, C ₂ E ₁)	110-80-5	Alfa-Aesar	> 99.0%	None
Ethylene glycol monopropyl ether (EGMPE, C ₃ E ₁)	2807-30-9	Sigma-Aldrich	> 99.0%	None
Ethylene glycol monobutyl ether (EGMBE, C ₄ E ₁)	111-76-2	Alfa-Aesar	> 99.0%	None
Diethylene glycol monobutyl ether (DEGMBE, C ₄ E ₂)	112-34-5	Alfa-Aesar	> 99.0%	None
Triethylene glycol monobutyl ether (TEGMBE, C ₄ E ₃)	143-22-6	Alfa-Aesar	> 98.0%	None
Sodium chloride (NaCl)	7647-14-5	Sinopharm Chemical Reagent Corp. Ltd.	>99.5%	None
Potassium chloride (KCl)	7447-40-7	Sinopharm Chemical Reagent Corp. Ltd.	>99.5%	None
Cesium chloride (CsCl)	7647-17-8	Alfa-Aesar	>99.0%	None
Sodium bromide (NaBr)	7647-15-6	Sinopharm Chemical Reagent Corp. Ltd.	>99.5%	None
Sodium fluoride (NaF)	7681-49-4	Sinopharm Chemical Reagent Corp. Ltd.	>98.0%	None
Hydrochloric acid (HCl)	7647-01-0	Sinopharm Chemical Reagent Corp. Ltd.	36.0%-38.0%	None
Sodium hydroxide (NaOH)	1310-73-2	Sinopharm Chemical Reagent Corp. Ltd.	>96.0%	None

Table 2

Binodal data for the water (1) + NaCl (2) + alkoxyethanol (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

water + NaCl + EGMPE			water + NaCl + EGMBE			water + NaCl + DEGMBE			water + NaCl + TEGMBE		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
39.13	8.24	52.63	27.54	1.85	70.61	26.05	4.06	69.89	44.68	9.95	45.38
41.12	8.89	49.99	30.26	1.93	67.81	30.47	4.78	64.75	49.24	11.32	39.44
44.95	9.93	45.12	34.56	1.99	63.45	33.60	5.16	61.24	51.30	11.89	36.81
48.24	11.35	40.41	38.87	2.05	59.08	36.81	5.57	57.62	54.15	12.91	32.94
51.91	12.69	35.40	41.70	2.10	56.20	39.81	5.99	54.19	57.38	13.97	28.65
54.26	13.66	32.08	44.77	2.19	53.04	42.51	6.42	51.07	60.63	14.80	24.57
56.06	14.16	29.77	46.98	2.21	50.81	45.42	7.04	47.54	63.53	15.94	20.53
58.61	14.94	26.45	50.47	2.35	47.18	48.00	7.70	44.30	65.53	16.68	17.79
60.84	15.62	23.54	53.59	2.44	43.96	51.20	8.26	40.54	68.04	17.59	14.37
62.33	16.05	21.62	56.88	2.52	40.59	54.41	9.06	36.52	69.71	18.26	12.03
64.38	17.07	18.55	59.41	2.66	37.93	56.71	9.62	33.67	70.71	18.55	10.73
65.76	17.62	16.62	62.46	2.78	34.76	58.93	9.88	31.19	71.66	18.93	9.40
67.38	18.55	14.07	65.04	2.92	32.05	60.82	10.27	28.91	72.42	19.22	8.37
			67.52	3.03	29.46	62.56	10.78	26.66	73.17	19.66	7.17
			71.14	3.23	25.63	65.41	11.43	23.15	73.79	19.98	6.24
			73.76	3.45	22.79	67.84	12.00	20.16	74.16	20.24	5.60
			76.62	3.73	19.65	70.26	12.63	17.11			
			79.18	4.08	16.74	72.81	13.15	14.04			
			81.66	4.39	13.95	74.49	13.58	11.92			
			83.73	5.29	10.98	75.51	14.20	10.29			
			84.73	6.34	8.93						

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of alkoxyethanol (EGMPE, EGMBE, DEGMBE, TEGMBE).

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 3

Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) +

NaCl (2) + alkoxyethanol (3) system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

<i>ATPS</i>	k_1	k_2	k_3	k_4	<i>Adj.R</i> ²	100 <i>SD</i> ^b
Eq.2						
water + NaCl + EGMPE	0.9490	-1.7199	184.8846		0.9987	1.4659
water + NaCl + EGMBE	20.2251	-24.7939	-2943.4370		0.9988	2.9541
water + NaCl + DEGMBE	1.5327	-3.7958	421.8936		0.9982	3.2863
water + NaCl + TEGMBE	0.4898	0.5843	278.8053		0.9982	1.9849
Eq.3						
water + NaCl + EGMPE	0.6099	-0.0729	-3.2299		0.9983	1.6446
water + NaCl + EGMBE	-4.4142	-1.1875	18.8478		0.9871	9.7417
water + NaCl + DEGMBE	0.0766	-0.2333	-3.0719		0.9991	2.3030
water + NaCl + TEGMBE	0.0915	-0.2525	-2.1921		0.9999	1.0412
Eq.4						
water + NaCl + EGMPE	0.7166	-0.6268	-26.9095	72.5160	0.9985	1.4847
water + NaCl + EGMBE	1.8717	-89.0364	1459.6776	-7740.3930	0.9901	8.3187
water + NaCl + DEGMBE	1.1176	-12.4796	59.5124	-157.9520	0.9989	2.4364
water + NaCl + TEGMBE	0.8128	-2.5410	-15.5234	47.2127	0.9999	0.7576
Eq.5						
water + NaCl + EGMPE	5.0882	-44.0063	99.5502	-191.6781	0.9990	1.2092
water + NaCl + EGMBE	2.8894	-20.6992	-31.1376	464.6070	0.9989	2.8266
water + NaCl + DEGMBE	3.3829	-35.1465	94.2251	-287.0075	0.9989	2.4439
water + NaCl + TEGMBE	17.6151	-137.5004	295.7834	-450.5733	0.9999	1.0848

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of

parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and

experimental values, respectively.

Table 4

Binodal data for the water (1) + salt (2) + EGMBE (3) ternary system at $T = 298.15$ K and pressure $p =$

0.1 MPa.^a

water + KCl + EGMBE			water + CsCl + EGMBE			water + NaF + EGMBE			water + NaBr + EGMBE		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
28.97	1.97	69.06	34.17	4.10	61.73	26.72	0.23	73.05	34.67	11.21	54.12
32.00	2.02	65.98	37.71	4.53	57.76	30.00	0.27	69.73	38.19	11.48	50.33
35.17	2.06	62.77	41.73	4.83	53.44	34.19	0.32	65.49	40.48	11.72	47.80
39.20	2.13	58.66	45.15	5.04	49.81	37.25	0.35	62.40	43.94	11.92	44.14
42.22	2.16	55.62	46.73	5.41	47.86	40.37	0.39	59.24	46.41	12.39	41.20
44.85	2.25	52.89	49.78	5.58	44.64	43.44	0.42	56.13	49.03	12.59	38.38
47.58	2.33	50.08	51.60	5.89	42.51	46.59	0.44	52.97	51.24	12.96	35.81
50.01	2.42	47.57	54.02	6.00	39.99	49.91	0.47	49.62	53.48	13.53	32.99
53.82	2.62	43.56	57.07	6.60	36.33	53.32	0.50	46.18	55.91	13.90	30.19
56.44	2.70	40.86	58.93	7.02	34.05	55.73	0.52	43.75	57.63	14.49	27.88
59.19	2.90	37.91	62.32	7.91	29.77	59.14	0.55	40.31	60.24	15.08	24.68
62.36	3.05	34.59	65.56	8.36	26.08	61.00	0.57	38.43	63.11	15.69	21.20
64.96	3.22	31.82	67.30	8.81	23.89	63.43	0.58	35.99	64.78	16.40	18.82
67.58	3.42	29.00	69.33	9.47	21.20	66.75	0.61	32.64	66.90	17.14	15.96
70.16	3.59	26.25	71.20	10.30	18.50	69.69	0.64	29.68	68.58	18.49	12.93
72.66	3.76	23.58	73.05	10.98	15.97	72.85	0.68	26.47	70.23	19.83	9.93
75.07	4.03	20.90	75.17	11.87	12.96	75.83	0.71	23.46	70.99	22.03	6.98
77.82	4.31	17.87	75.38	14.59	10.04	78.73	0.74	20.53	70.97	23.05	5.98
80.12	4.77	15.11	75.05	16.36	8.59	81.51	0.76	17.73	70.07	25.10	4.83
82.37	5.54	12.10	73.59	19.87	6.54	84.24	0.80	14.97	68.75	27.32	3.93
84.14	7.47	8.39	69.15	26.00	4.86	87.01	0.86	12.13	68.24	28.30	3.46

w_1 , mass fraction of water. w_2 , mass fraction of salt (KCl, CsCl, NaF, NaBr). w_3 , mass fraction of EGMBE.

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 5

Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) + salt (2) + EGMBE (3) system at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

<i>ATPS</i>	k_1	k_2	k_3	k_4	<i>Adj.R</i> ²	100 <i>SD</i> ^b
Eq.2						
water + KCl + EGMBE	12.1278	-20.7865	-1715.9133		0.9951	1.2944
water + CsCl + EGMBE	5.3160	-10.5032	-29.1420		0.9969	0.9864
water + NaF + EGMBE	1.1063	-7.8476	2.5357E+06		0.9984	0.7514
water + NaBr + EGMBE	89.7921	-15.3550	-9.6752		0.9986	0.6346
Eq.3						
water + KCl + EGMBE	-4.0169	-1.1043	16.7330		0.9911	1.7417
water + CsCl + EGMBE	-1.7133	-0.6870	3.2843		0.9961	1.1069
water + NaF + EGMBE	0.8047	-0.0281	-98.9684		0.9942	1.4189
water + NaBr + EGMBE	-4.3253	-1.8392	7.2608		0.9944	1.2475
Eq.4						
water + KCl + EGMBE	1.8244	-84.4864	1423.2671	-8096.0573	0.9903	1.8253
water + CsCl + EGMBE	1.1803	-17.6341	93.3313	-162.7628	0.9955	1.2001
water + NaF + EGMBE	0.7498	56.5862	-3.3584E+04	2.1502E+06	0.9989	0.6063
water + NaBr + EGMBE	2.7419	-32.2171	130.7220	-179.3281	0.9968	0.9483
Eq.5						
water + KCl + EGMBE	3.9937	-41.4021	74.9800	-153.7195	0.9953	1.2731
water + CsCl + EGMBE	0.2615	2.6462	-33.5184	61.1075	0.9979	0.8091
water + NaF + EGMBE	0.0204	-14.2090	241.1784	-3.9798E+04	0.9989	0.6112
water + NaBr + EGMBE	4.3163	-13.8741	-3.5382	7.6040	0.9985	0.6541

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of

parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and experimental values, respectively.

Table 6

Binodal data for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15,$

313.15) K and pressure $p = 0.1$ MPa.^a

$T = 283.15$ K			$T = 293.15$ K			$T = 303.15$ K			$T = 313.15$ K		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
24.10	3.79	72.12	21.97	2.51	75.52	22.91	1.36	75.73	19.86	0.65	79.49
33.40	4.01	62.60	28.32	2.56	69.11	30.40	1.42	68.18	28.99	0.68	70.33
39.22	4.10	56.67	37.47	2.70	59.83	37.29	1.45	61.26	33.91	0.70	65.39
44.71	4.26	51.03	43.14	2.81	54.05	43.15	1.49	55.36	39.17	0.73	60.11
47.74	4.35	47.91	49.96	2.96	47.08	50.21	1.60	48.19	45.16	0.74	54.10
50.80	4.48	44.72	52.94	3.08	43.98	54.22	1.68	44.10	50.95	0.77	48.28
53.67	4.66	41.67	56.91	3.25	39.85	58.72	1.74	39.54	55.14	0.80	44.06
56.01	4.85	39.15	60.23	3.43	36.34	62.51	1.87	35.62	60.29	0.83	38.88
58.84	4.98	36.18	63.52	3.62	32.86	65.49	1.98	32.53	65.30	0.88	33.82
61.82	5.17	33.00	66.85	3.76	29.39	68.64	2.09	29.27	69.13	0.93	29.95
64.26	5.37	30.37	68.51	3.96	27.54	71.64	2.27	26.10	72.26	0.96	26.78
66.65	5.64	27.71	71.01	4.20	24.79	74.32	2.40	23.28	75.78	0.98	23.24
68.15	5.94	25.91	73.95	4.46	21.59	76.71	2.61	20.68	79.58	1.09	19.33
70.24	6.09	23.67	75.19	4.74	20.07	77.73	2.75	19.52	81.64	1.21	17.16
72.25	6.41	21.34	77.42	4.97	17.62	79.62	2.95	17.44	83.89	1.34	14.77
74.36	6.69	18.95	79.22	5.49	15.29	80.86	3.15	15.99	85.82	1.56	12.61
76.82	7.09	16.09	81.02	6.10	12.87	82.11	3.44	14.46	87.37	1.68	10.95
78.72	7.57	13.71	81.89	6.65	11.46	83.46	3.96	12.58	88.49	2.55	8.96
80.43	7.94	11.63	82.62	7.14	10.24	83.75	4.19	12.06	88.99	3.72	7.29
82.35	8.58	9.07	83.72	8.33	7.95	84.88	5.07	10.05	88.72	5.11	6.17

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of EGMBE.

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 7

Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) +

NaCl (2) + EGMBE (3) system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.^a

T	k_1	k_2	k_3	k_4	$Adj.R^2$	$100SD^b$
Eq.2						
$T = 283.15$ K	104.2997	-26.0494	-1.2237E+04		0.9907	7.0356
$T = 293.15$ K	51.2090	-27.3025	-2882.2562		0.9901	8.2158
$T = 303.15$ K	36.5313	-34.2501	-1.5887E+04		0.9813	11.2116
$T = 313.15$ K	89.9679	-59.2696	-4.6671E+04		0.9718	15.8430
Eq.3						
$T = 283.15$ K	-7.6913	-2.2443	26.7922		0.9801	10.2811
$T = 293.15$ K	-5.8598	-1.6099	23.8609		0.9690	14.5465
$T = 303.15$ K	-5.8866	-1.4084	36.3489		0.9547	17.4557
$T = 313.15$ K	-4.5300	-0.9800	34.7161		0.8460	37.0176
Eq.4						
$T = 283.15$ K	4.3362	-168.5932	2330.0592	-1.1003E+04	0.9888	7.4699
$T = 293.15$ K	2.6393	-118.4403	1864.0427	-9766.1574	0.9783	11.8068
$T = 303.15$ K	2.3431	-181.4873	4926.0498	-4.3905E+04	0.9657	14.7343
$T = 313.15$ K	1.4873	-167.7744	5792.5213	-5.9953E+04	0.8380	36.8293
Eq.5						
$T = 283.15$ K	19.3789	-193.1378	524.4836	-1380.3575	0.9967	4.1110
$T = 293.15$ K	13.2356	-147.2531	420.1637	-1207.6630	0.9971	4.3128
$T = 303.15$ K	13.1146	-195.2873	734.4986	-3415.1657	0.9961	5.0000
$T = 313.15$ K	11.5973	-223.3840	989.7839	-5598.4479	0.9963	5.5408

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of

parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and

experimental values, respectively.

Table 8

Values of the parameters of Eq. (1) for the water (1) + NaCl (2) + EGMBE (3) system at $T = 293.15$ K and

pressure $p = 0.1$ MPa.^a

w_2	$w_2 = 0.00$	$w_2 = 0.02$	$w_2 = 0.04$	$w_2 = 0.06$	average
k_2	/	0.1750	0.1825	0.1867	0.1814
k_3	0.1196	0.1206	0.1187	0.1193	0.1196
n_0	1.3329	1.3329	1.3329	1.3329	1.3329

w_2 , mass fraction of NaCl. n_0 , refractive index of pure water at $T = 293.15$ K.

^a Standard uncertainties u are $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 9

Tie-line data for the water (1) + NaCl (2) + EGMBE (3) system at $T = (283.15, 293.15, 303.15, 313.15)$

K and pressure $p = 0.1$ MPa.^a

total			top phase			bottom phase			TLL	STL
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$		
$T = 283.15$ K										
62.62	6.51	30.87	39.61	4.09	56.31	82.79	8.55	8.66	0.4558	0.0852
60.99	9.00	30.01	30.70	3.82	65.48	82.11	12.61	5.28	0.5632	0.1364
59.14	11.61	29.25	25.90	3.81	70.30	80.55	17.05	3.19	0.6235	0.1872
57.79	13.59	28.62	23.31	3.78	72.91	78.43	19.48	2.09	0.6442	0.2159
55.64	16.82	27.54	20.88	3.76	75.36	74.83	23.81	1.35	0.6630	0.2715 ^b
$T = 293.15$ K										
62.64	4.62	32.74	52.22	3.03	44.75	82.83	6.90	10.27	0.3272	0.1032
61.05	7.08	31.87	37.64	2.72	59.64	84.29	11.15	4.56	0.5139	0.1434
58.37	11.22	30.41	22.69	2.53	74.78	81.28	16.45	2.27	0.6665	0.1839
56.17	14.42	29.41	19.02	2.45	78.53	77.15	21.01	1.84	0.6930	0.2384
54.32	17.32	28.36	17.19	2.37	80.44	74.07	25.02	0.92	0.7096	0.2876 ^b
$T = 303.15$ K										
63.45	4.79	31.76	36.27	1.45	62.28	86.75	7.29	5.96	0.5364	0.0948
61.26	7.79	30.95	25.04	1.38	73.58	84.53	11.60	3.87	0.6520	0.1369
58.60	11.93	29.47	17.73	1.19	81.07	80.52	17.35	2.13	0.7223	0.1975
56.41	15.28	28.31	15.05	1.15	83.80	77.23	22.06	0.72	0.7486	0.2492
54.58	17.97	27.45	13.38	1.03	85.59	73.74	25.56	0.70	0.7567	0.2925 ^b
$T = 313.15$ K										
65.16	2.55	32.29	35.81	0.72	63.47	89.50	3.74	6.76	0.5526	0.0473
62.04	7.40	30.56	22.03	0.67	77.30	85.38	10.99	3.62	0.6910	0.1305
59.04	11.72	29.24	17.47	0.60	81.93	81.09	17.22	1.68	0.7336	0.2001
56.43	15.75	27.82	13.82	0.58	85.59	76.56	22.75	0.68	0.7628	0.2601
54.55	18.48	26.97	10.84	0.55	88.61	73.83	25.88	0.29	0.7877	0.2900 ^b

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of EGMBE. TLL and STL

stand for the length and slope of tie-line respectively.

^a Standard uncertainties u are $u(w_2) = 0.002$, $u(w_3) = 0.0008$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b Data for SLLE, the composition of solid phase is anhydrous NaCl (cr), which was determined by

comparing its thermogravimetric analysis curve with that of pure sodium chloride.

Table 10

Values of the parameters of Eqs. (6) - (8) used for the correlation of experimental tie-line data for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.^a

T	k_1	k_2	$Adj.R^2$	100SD ^b
Eq.6				
$T = 283.15$ K	0.1287	0.752	0.9887	3.2863
$T = 293.15$ K	0.0558	1.1907	0.9923	6.3797
$T = 303.15$ K	0.0579	0.9185	0.9935	2.5117
$T = 313.15$ K	0.0795	0.6111	0.9919	2.7671
Eq.7				
$T = 283.15$ K	2.27	0.6931	0.953	97.0860
$T = 293.15$ K	10.7136	0.7434	0.9881	69.2611
$T = 303.15$ K	20.7376	1.0102	0.9938	50.1926
$T = 313.15$ K	59.5831	1.5981	0.9966	89.3370
Eq.8				
$T = 283.15$ K	3.9642	1.1572	0.9947	1.6042
$T = 293.15$ K	3.0381	0.2301	0.9893	2.5148
$T = 303.15$ K	4.8260	1.1197	0.9747	1.7861
$T = 313.15$ K	7.0252	2.3411	0.9993	0.3313

^a Standard uncertainties u are $u(w_2) = 0.002$, $u(w_3) = 0.0008$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

$$^b SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (Y^{cal} - Y^{exp})^2} .$$

Table 11

Binodal data for the water (1) + NaCl (2) + EGMBE (3) ternary system with different pH at $T = 298.15$

K and pressure $p = 0.1$ MPa.^a

$pH = 3$			$pH = 5$			$pH = 9$			$pH = 11$		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
28.81	1.52	69.67	28.47	1.35	70.18	27.71	1.79	70.50	29.01	1.75	69.24
32.77	1.58	65.65	31.49	1.43	67.08	30.83	1.81	67.37	33.64	1.78	64.58
37.84	1.62	60.54	35.19	1.46	63.35	34.22	1.83	63.95	37.67	1.84	60.49
41.48	1.67	56.85	38.01	1.50	60.49	38.65	1.90	59.46	42.50	1.90	55.60
45.05	1.72	53.23	40.73	1.56	57.71	43.87	1.99	54.15	45.91	1.94	52.15
47.91	1.79	50.30	43.22	1.62	55.16	47.77	2.04	50.19	49.64	2.07	48.29
50.09	1.89	48.02	45.65	1.73	52.62	50.87	2.11	47.03	53.49	2.12	44.39
52.34	1.94	45.72	48.16	1.74	50.10	53.36	2.17	44.47	57.87	2.24	39.89
55.13	2.05	42.82	50.90	1.76	47.33	55.67	2.26	42.07	61.39	2.37	36.25
57.49	2.12	40.39	54.00	1.79	44.21	57.70	2.31	39.99	63.00	2.42	34.58
60.59	2.23	37.18	57.19	1.82	41.00	60.81	2.42	36.77	65.97	2.51	31.52
63.26	2.38	34.35	61.76	2.03	36.21	63.53	2.50	33.97	69.12	2.67	28.21
66.63	2.54	30.83	65.41	2.15	32.44	66.37	2.64	30.98	72.29	2.91	24.80
69.35	2.69	27.96	69.35	2.28	28.37	71.12	2.97	25.91	74.54	3.00	22.46
72.50	2.82	24.69	72.12	2.48	25.40	74.14	3.21	22.65	76.48	3.27	20.25
75.31	3.02	21.67	75.76	2.71	21.54	76.41	3.45	20.14	77.60	3.38	19.02
78.44	3.31	18.25	78.48	3.04	18.48	78.92	3.72	17.35	79.38	3.56	17.07
81.28	3.52	15.20	80.96	3.31	15.74	81.30	4.18	14.52	81.40	3.84	14.76
83.76	4.00	12.23	83.47	3.75	12.78	84.06	4.60	11.33	84.39	4.52	11.09
84.43	4.16	11.40	85.97	4.59	9.44	84.94	5.45	9.61	85.73	6.02	8.25
85.94	5.72	8.35	86.61	6.87	6.52	85.75	6.46	7.79			

w_1 , mass fraction of water. w_2 , mass fraction of NaCl. w_3 , mass fraction of EGMBE.

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

Table 12

Coefficients of Eqs. (2) - (5) used for the correlation of the experimental binodal data of the water (1) +

NaCl (2) + EGMBE (3) system with different pH at $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

	pH	k_1	k_2	k_3	k_4	$Adj.R^2$	$100SD^b$
Eq.2							
	$pH = 3$	13.1103	-24.1920	-3548.0723		0.9943	1.4082
	$pH = 5$	15.0521	-26.2917	-4712.1494		0.9930	1.6755
	$pH = 9$	31.1281	-28.9601	-5801.2310		0.9930	1.6501
	$pH = 11$	33.3243	-29.8973	-6680.3567		0.9955	1.2416
Eq.3							
	$pH = 3$	-4.4344	-1.1340	22.4704		0.9911	1.7559
	$pH = 5$	-4.1552	-1.0589	20.5870		0.9805	2.8085
	$pH = 9$	-5.3162	-1.3635	26.2760		0.9753	3.0929
	$pH = 11$	-5.5951	-1.4158	28.6947		0.9808	2.5668
Eq.4							
	$pH = 3$	1.8238	-108.4184	2326.8750	-1.6861E+04	0.9893	1.9283
	$pH = 5$	1.8164	-113.7938	2471.0203	-1.7271E+04	0.9863	2.3518
	$pH = 9$	2.2683	-134.3358	2798.5979	-1.9314E+04	0.9808	2.7254
	$pH = 11$	2.4010	-151.7045	3377.8468	-2.4906E+04	0.9879	2.0355
Eq.5							
	$pH = 3$	3.3606	-36.0951	45.9261	1.7591	0.9940	1.4412
	$pH = 5$	2.6705	-23.6282	-26.3456	562.2873	0.9929	1.6952
	$pH = 9$	9.5895	-121.5485	375.8430	-1350.9949	0.9979	0.9024
	$pH = 11$	8.0372	-98.0248	273.8202	-831.9443	0.9980	0.8193

^a Standard uncertainties u are $u(w) = 0.002$, $u(T) = 0.1$ K and $u(p) = 10$ kPa.

^b $SD = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (w_3^{cal} - w_3^{exp})^2}$, where n is the number of binodal data pairs, p represents the number of

parameters of the equation, and the superscripts “*cal*” and “*exp*” represent the calculated and

experimental values, respectively.

Fig. 1. Binodal curves for the water (1) + NaCl (2) + alkoxyethanol (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.

Fig. 2. Binodal curves for the water (1) + salt (2) + EGMBE (3) ternary system at $T = 298.15$ K and pressure $p = 0.1$ MPa.

Fig. 3. Binodal curves for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa.

(a)

(b)

(c)

(d)

Fig. 4. Complete two-liquid-phase coexistence areas for the water (1) + NaCl (2) + EGMBE (3) ternary system at $T = (283.15, 293.15, 303.15, 313.15)$ K and pressure $p = 0.1$ MPa. The cross ($\times$) represents binodal data from cloud point method, and the circle ($\bullet$) represents tie-line data; the solid line (—) and dash-dot line (- · - · -) represents Binodal curves and tie-lines respectively.

Fig. 5. Binodal curves for the water (1) + NaCl (2) + EGMBE (3) ternary system with different pH s at T

$= 298.15$ K and pressure $p = 0.1$ MPa.