Separation of Acetonitrile from Its Azeotropic Aqueous Solution with the Aid of Good's Buffer Ionic Liquid [TMA][EPPS]

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Abstract

In the present study, we have found that the biocompatible and self-buffering Good's buffer ionic liquid (GBIL), [TMA][EPPS], could induce liquid-liquid phase splitting in an aqueous solution of acetonitrile at ambient conditions. The investigated GBIL is composed of *tetra*-methylammonium (TMA) as a cation and a biological buffer, 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS), as an anion. The separation efficiency of this buffer-based GBIL for acetonitrile from its aqueous solution has been analysed by measuring solid-liquid-liquid equilibrium (SLLE) and liquid-liquid equilibrium (LLE) data for the ternary system of acetonitrile + water + [TMA][EPPS] at 298.2 K and under atmospheric pressure. The consistency of the LLE tie-line data was confirmed by using the Othmer-Tobias model. The binary interaction parameters were obtained by correlating experimental tie-line data with the non-random two-liquid (NRTL) activity coefficient model. By using the [TMA][EPPS] as an auxiliary agent, the maximum concentrations of acetonitrile (92.8 wt%) in the organic-rich phase found is greater than the azeotropic compositions of the corresponding aqueous system (83.7 wt%). These results clearly indicate that the investigated [TMA][EPPS] can serve as a high efficiency, non-corrosive, and biocompatible green agent for the separation of acetonitrile from its aqueous solutions. Based on the phase diagram obtained from the present study, a conceptual flowsheet is proposed, for separating acetonitrile from its aqueous solution with the aid of the GBIL, [TMA][EPPS].

Keywords: Separation, acetonitrile, aqueous, azeotrope, ionic liquid, [TMA][EPPS]

1. Introduction

Acetonitrile has a wide variety of applications in industrial sectors such as pharmaceuticals and photographic film. It is also a popular fluid served as a mobile phase in the operation of HPLC and LC–MS because of its highly soluble nature, ultraviolet transparency, low viscosity, and low reactivity. Moreover, it is commonly used in battery applications due to its relatively high dielectric constant and ability to dissolve electrolytes. Acetonitrile can be totally miscible with water under ambient conditions. Unfortunately, it forms an azeotropic mixture with water. Due to the formation of azeotrope, the separation of acetonitrile from its aqueous solution became difficult via simple distillation. Liquid-liquid extraction may be an economical alternative method for recovery of acetonitrile from its azeotropic mixture. Many inorganic salts were suggested as an auxiliary compound to induce liquid-liquid phase splitting for the aqueous solution of acetonitrile and thus to assist the recovery

of this solvent from its aqueous solution by extraction technique. However several disadvantages have been found using the inorganic salts in the separation processes because those compounds are corrosive in nature, and the pH value of the medium may change under high salt concentrations and resulting in the denaturation of biomolecules (Taha *et al*., 2012). To solve the above mentioned problems, we synthesized a Good's buffer ionic liquid (GBIL), [TMA][EPPS], and evaluated its suitability for recovery of acetonitrile from its aqueous solution. The new ionic liquid, [TMA][EPPS], has the cation part derived from *tetra*-methylammonium (TMA) and the anion part from the commonly used Good's buffer, 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS). [TMA][EPPS] has been confirmed to be self-buffering and biocompatible. In comparing with the use of inorganic salts, using [TMA][EPPS] as an auxiliary agent for the separation process may be more advantageous.

The liquid-liquid equilibrium (LLE) and solid-liquid-liquid equilibrium (SLLE) tie-line data were measured, in the present study, for the ternary system of acetonitrile (1) + water (2) + [TMA][EPPS] (3) at 298.15 K and 101.3 kPa. The consistency of the LLE tie-line data was tested with the Othmer-Tobias equation (Othmer and Tobias, 1942). Additionally, the model parameters of the NRTL (Renon and Prausnitz, 1968) for this studied system were also determined from the LLE tie-line data correlation.

2. Experimental Section

2.1. Materials

Acetonitrile (mass fraction purity > 0.99) was purchased from Arcos (USA). The buffer EPPS (mass fraction purity 0.998) and *tetra*-methylammonium hydroxide (25 *wt*% in water) were supplied by Sigma Chemical Co. (USA). The ionic liquid [TMA][EPPS] was synthesized in our lab by using the similar procedure as explained elsewhere (Taha *et al*., 2014). The purity and water content of the synthesized ionic liquid were analysed with H^1 NMR and Karl-Fischer titration, respectively. The double de-ionized highly pure water was used in the sample preparation which was treated by a Nano-pure-Ultra pure water purifying system with resistivity of 18.3 MΩ·cm. The experimental samples were prepared gravimetrically by using an electronic balance (Model GR-200, R&D, Japan) with an uncertainty of 0.1 mg.

2.2. Experimental Procedure

The experimental tie-line data of the investigated system were measured at 298.15 K under atmospheric pressure by using a jacketed equilibrium cell made up of Pyrex glass. The details of the experimental apparatus and the operation procedure have been presented in our previous paper (Taha *et al*., 2012). The total volume of the equilibrium cell is about 50 cm³. During the course of the experiment, the temperature of equilibrium cell was regulated at 298.15 K by circulating thermostatic water (Model-B402L, Firstec Scientific Co. Ltd., Taiwan) through the jacket of the equilibrium cell. The temperature in the equilibrium cell was monitored by a precise digital thermometer (Model-1560, Hart Scientific Co., USA) to an uncertainty of 0.1 K. In each experimental run, a mixture of acetonitrile + water + [TMA][EPPS] with a pre-specified composition was loaded into the equilibrium cell. The mixture was agitated vigorously with a magnetic stirrer bar for 12 hours. After the mixing stage, the stirrer was turned off and the mixture was then separated into two liquid phases. The settle stage was remained at least 8 hours. The samples of upper phase and the

lower phase were taken, respectively, with a syringe to composition analysis. A series of liquid-liquid equilibrium (LLE) and solid-liquid-liquid equilibrium (SLLE) data for this ternary system were measured by changing the feed composition of the loaded mixture.

2.3. Sample Analysis

The compositions of acetonitrile and water in the collected samples from the upper phase and the lower phase were analysed with a gas chromatograph (GC, Model 9800, China Chromatography Co., Taiwan). This GC was equipped with a thermal conductivity detector. A stainless steel packed column (Porapak QS, 80/100, and 2 m of length) was applicable to the separation of these two compounds. To protect the detector and the column from blocking by the GBIL, a stainless steel tube packed with glass wool, as a trapper for GBIL, was installed in between the injector section and the column of the GC. The trapper was replaced when significant amount of GBIL was collected. Helium with mass fraction purity > 0.9995 was used as a carrier gas. The peak-ABC chromatograph data handling system was adopted to analyse the response of gas chromatography for the injected samples.

Prior to the analysis of the collected samples, the GC was calibrated by using a series of standard samples over the entire composition range. These standard samples were prepared gravimetrically by using an electronic balance (GR-200, R&D, Japan), with an uncertainty of 0.1 mg. The compositions of [TMA][EPPS] in the upper and the lower phases were determined by gravimetric method. The sample of about 2 g from each phase was transferred on a watch glass and placed in an oven at 120°C. Water and acetonitrile in the sample were evaporated and the drying process was continued until the mass of (watch glass + sample) remained constant. The equilibrium compositions of acetonitrile, water, and [TMA][EPPS] in each phase were determined from at least five replications. The relative uncertainty of composition determination was estimated to be about 1 %.

3. Results and Discussion

3.1. Phase Diagram

According to the experimental results of the present study, the phase diagram of this ternary system is plotted as shown in Figure 1. In this phase diagram, it contains five phase regions, including homogeneous liquid phase region (L), liquid-liquid phase region (2L), liquid-liquid-solid phase region (2L+S), and two solid-liquid phase regions (S+L). The 2L region represents the biphasic behaviour, with the upper organic-rich phase and the lower water-rich phase. The majority of [TMA][EPPS] dissolves in the aqueous phase. The parabolic boundary separates the homogeneous liquid phase and the liquid-liquid phase regions. In the region (S+2L), there are three phases coexistence (two liquid phases and one solid phase). Two (S+L) regions exist next to the (S+2L) region. The first (S+L) region, on the right-side of (S+2L), represents the saturated [TMA][EPPS] in water-rich solution coexistence with solid [TMA][EPPS]. The second (S+L) region, near the bottom of phase diagram, represents the saturated [TMA][EPPS] in organic-rich solution equilibrium with solid [TMA][EPPS].

3.2. Data Correlation

The well-known Othmer-Tobias equation (Othmer and Tobias, 1942) was used to test the consistency of the experimental tie-line data. This equation is widely used to
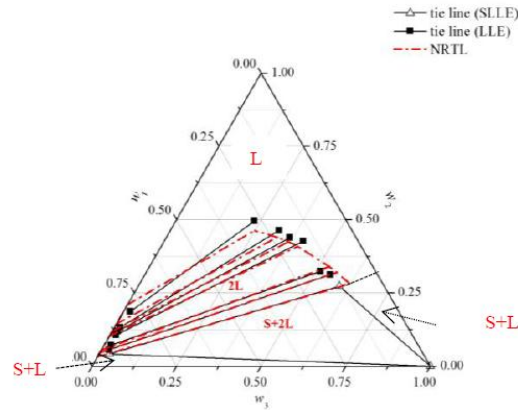
Fig. 1 Phase diagram of acetonitrile (1) + water (2) + [TMA][EPPS] (3)

validate the quality of the LLE tie-line data. The expression of the Othmer-Tobias model is given as the following equation:

$$ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) = m^* + n^* \ ln\left(\frac{1-w_1^{I}}{w_1^{I}}\right) \tag{1}$$

where w_1^{I} is the mass fraction of acetonitrile in the upper phase (organic-rich phase) and w_3^{II} is the mass fraction of [TMA][EPPS] in the lower phase (aqueous phase). The variables m^* and n^* are the coefficients of Othmer-Tobias model. The correlated results are shown in Figure 2. The correlation coefficient R^2 is as high as 0.9905 and the graphical comparison in Figure 2, revealing that the LLE tie-line data are consistently well.
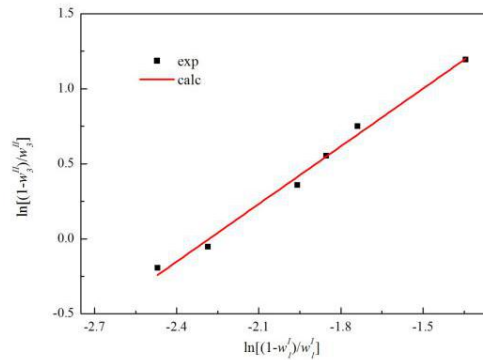

Fig. 2 Correlated results from the Othmer-Tobias equation.

The experimental LLE tie-line data of acetonitrile (1) + water (2) + [TMA][EPPS] (3) were also correlated with an activity coefficient model, the nonrandom two-liquid (NRTL) (Renon and Prausnitz, 1968). The expressions of this model is given below:

$$ln\gamma_i = \frac{\sum_{j=1}^{n_c} x_j \tau_{ij} G_{ji}}{\sum_{k=1}^{n_c} x_k G_{kj}} + \sum_{j=1}^{n_c} \frac{x_j G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{n_c} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{n_c} x_k G_{kj}}\right) \tag{2}$$

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{3}$$

$$\tau_{ij} = b_{ij}/T \tag{4}$$

where γ_i is the activity coefficient of the ith component in liquid mixture. The α_{ij} and b_{ij} are the non-randomness and the interaction parameters of the NRTL model. The value of α_{ij} was fixed to 0.2 for each (i-j) pair. The optimal values of interaction parameters (b_{ij} and b_{ji}) were obtained by fitting the experimental LLE and SLLE tie-line data to the NRTL model. In the regression process following objective function (F) was defined

$$F = \left(\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \left| \left(x_{ijk}^{calc} - x_{ijk}^{expt} \right) \right| \right) \Big/ 6n \qquad (5)$$

where n is the number of tie-lines and x_{ijk} is the mole fraction of component i in phase j on tie-line k. The superscripts *calc* and *expt* denote the calculated and the experimental values, respectively. The correlated results are graphically presented in Figure 1. Overall, the NRTL model correlated satisfactorily the LLE tie-line data, to a grand *AAD* as low as 0.004. These determined NRTL parameters are essentially needed for the separation process simulation and design.

3.3. Azeotropic Mixture Separation

The mixture of acetonitrile + water forms an azeotrope at 345.1 K with 0.837 mass fraction of acetonitrile under atmospheric pressure (Horsley, 1973). From the experimental SLLE tie-line data, we found that only trace amount of [TMA][EPPS] left in the organic-rich phase and, most interestingly, the mass fraction of acetonitrile in the organic-rich phase is as high as 0.928 which is significantly greater than the azeotropic composition (0.837 mass fraction of acetonitrile). It means that high purity of acetonitrile can be obtained from the organic-rich liquid phase via subsequent simple distillation. As a consequence, we attempt to taking this advantage to improve the separation process for recovering acetonitrile from its aqueous solutions, by using this new GBIL, [TMA][EPPS], as an auxiliary agent.

A conceptual flowsheet of the separation process is suggested as shown in Figure 3. It includes one extractor (E), two flash drums (F1 and F2), and two distillation columns (T1 and T2). High purity of acetonitrile can be obtained from the upper-phase stream of extractor (E) after processing with the flash drum (F1) and the distillation unit (T1), while [TMA][EPPS] can be almost totally re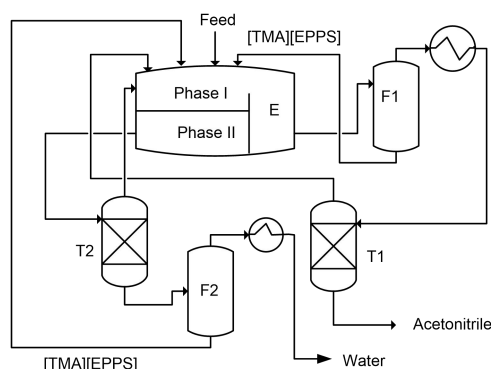cycled via the bottom streams of the flash drums F2 and F1. Since [TMA][EPPS] is non-corrosive, the application of this new GBIL in separation processes can be more advantageous over using conventional inorganic salts.

Fig. 3 Conceptual flowsheet for the separation of acetonitrile from its aqueous solution by using [TMA][EPPS].

4. Conclusions

In the present study, we found that a new synthesized GBIL, [TMA][EPPS], can induce liquid-liquid phase splitting for acetonitrile + water. To develop a new separation process, the LLE and the SLLE tie-line data of acetonitrile + water + [TMA][EPPS] were measured at 298.15 K and 101.3 kPa. The consistency of the experimental data has been confirmed by checking with the Othmer-Tobias model. The NRTL model was found to satisfactorily represent the LLE behaviour for acetonitrile + water + [TMA][EPPS] and the optimal values of the binary interaction parameters were determined by fitting the LLE and the SLLE tie-line data to the activity coefficient model. Moreover, the composition of acetonitrile in the organic-rich phase, near SLLE region, is substantially greater than the azeotropic composition. By taking this advantage, acetonitrile can be separated efficiently from its azeotropic aqueous mixture with the aid of a new GBIL, [TMA][EPPS]. A conceptual separation process has been proposed to recover the high purity of acetonitrile from its aqueous solution. Using this biocompatible, non-corrosive, and green compound as an auxiliary agent, the new separation process become much cleaner than conventional methods.

5. Acknowledgments

6. References

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