Chinese Journal of Chemical Engineering 24 (2016) 365–372

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Chemical Engineering Thermodynamics

Effect of methylimidazolium-based ionic liquids on vapor–liquid equilibrium behavior of *tert*-butyl alcohol + water azeotropic mixture at 101.3 kPa☆

Zhigang Zhang, Qiang Zhang, Tao Zhang, Qinqin Zhang, Wenxiu Li *

Liaoning Provincial Key Laboratory of Chemical Separation Technology, Shenyang University of Chemical Technology, Shenyang 110142, China

A R T I C L E I N F O

Article history:
Received 31 December 2014
Received in revised form 13 August 2015
Accepted 31 August 2015
Available online 30 October 2015

Keywords:
Azeotrope
Ionic liquids
Vapor–liquid equilibrium
Relative volatility
NRTL model

A B S T R A C T

Three ionic liquids (ILs), 1-ethyl-3-methylimidazolium bromine ([EMIM]Br), 1-butyl-3-methylimidazolium bromine ([BMIM]Br), and 1-hexyl-3-methylimidazolium bromine ([HMIM]Br), were used as the solvent for separation of {*tert*-butyl alcohol (TBA) + water} azeotrope. Vapor–liquid equilibrium (VLE) data for {TBA + water + IL} ternary systems were measured at 101.3 kPa. The results indicate that all the three ILs produce an obvious effect on the VLE behavior of {TBA + water} system and eliminate the azeotropy in the whole concentration range. [EMIM]Br is the best solvent for the separation of {TBA + water} system by extractive distillation among the three ILs. The experimental VLE data for the ternary systems are correlated with the NRTL model equation with good correlations. Explanations are given with activity coefficients of water and TBA, and the experimental VLE-temperature data for {TBA or water + IL} binary systems.

1. Introduction

Water is the main by-product in the production of tert-butyl alcohol (TBA) in chemical and pharmacy industries, and it is difficult to separate {TBA + water} azeotrope by conventional distillation techniques. Extractive distillation is a well-known technology to reduce operational and capital expenditures for separation of close boiling point mixtures such as {alcohol + water} system [1–3], with solvent added to the mixtures to promote the effect of the separation. Traditional solvents such as organic substance and metal salt have the disadvantage of high cost, lower efficiency, and pollution. A suitable solvent is very demanding for this purpose [4,5].

Ionic liquids (ILs), also known as liquid salts or ionic fluids, are a new chemical substances consisting of an organic cation and an inorganic or organic anion [6]. With the outstanding physicochemical properties of low vapor pressure and melting point, high stability, full of design ability, and environment-friendly, ILs are under intensive investigation to determine their potential as replacement solvents for extractive distillation [7,8]. ILs are used in the separation of many azeotropic mixtures, such as {alcohol + water}, {alcohol + ketone}, and {alcohol + ester} [9–15]. The search for task-specific ionic liquids has generated a substantial amount of research in recent years [16–18]. The ILs composed of 1-alkyl-3-methylimidazolium and halogen can well dissolve in {alcohol + water} mixtures and receive wide attentions [17–20]. Zhang *et al.* [21] have studied the relative volatility of TBA to water with ILs composed of an anion from $[OAc]^-$ or $[Cl]^-$ and a cation from 1-ethyl-3-methylimidazolium ($[EMIM]^+$), 1-butyl-3-methylimidazolium ($[BMIM]^+$), or 1-hexyl-3-methylimidazolium ($[HMIM]^+$) at a fixed TBA mole fraction of 0.95. The effect on enhancement of relative volatilities of TBA to water is [EMIM]Cl > [EMIM]OAc > [BMIM]Cl > [BMIM]OAc > [HMIM]OAc > [HMIM]Cl. The interactions of ILs with TBA and water are discussed by activity coefficients calculated using the NRTL model equation from the vapor–liquid equilibrium (VLE) data for {TBA + water + IL} ternary systems.

Usually, with the addition of ILs, azeotropic components may change their non-ideality to a different extent. It is desirable that these changes remove the azeotropy [22]. Therefore, it is necessary to understand the effects of ILs on the VLE behavior of azeotropic mixtures and this can be reflected by VLE data. Information from the phase equilibrium study is the fundamental for ILs to be effectively used as replacement solvents in extractive distillation [23–25].

The objective of this work is to explore the suitability of three ILs, [EMIM]Br, [BMIM]Br and [HMIM]Br, for use as the solvent for separation of {TBA + water} system. The three ILs and their molar mass, *M*, are listed in Table 1, and their structures are shown in Fig. 1. In this work, new experimental VLE data for {TBA + water + IL} ternary systems are reported. The water mole fraction on an IL-free basis varies from 0.0 to 1.0, and the IL mole fraction is fixed at 0.05, 0.10

☆ Supported by the National Natural Science Foundation of China (21076126), the Program for Liaoning Excellent Talents in University (2012013) and the Liaoning Province Science Foundation of China (2014020140).

* Corresponding author.
E-mail address: wenxli@126.com (W. Li).

http://dx.doi.org/10.1016/j.cjche.2015.10.012
1004-9541/

Table 1
Three ILs and their molar mass

Name	$M/\mathrm{g\cdot mol^{-1}}$
1-Ethyl-3-methylimidazolium bromine	190
1-Butyl-3-methylimidazolium bromine	218
1-Hexyl-3-methylimidazolium bromine	246

or 0.20. The effect of ILs on the VLE behavior of {TBA + water} system is evaluated. The experimental VLE data, T, x, y, are correlated with the NRTL model equation, and the interactions of ILs with TBA and water are discussed.

2. Materials and Methods

2.1. Chemicals

The CAS No., supplier, and purity in mass fraction of the chemicals are as follows: bromoethane (74-96-4, Sinopharm, >99%); bromobutane (109-65-9, Sinopharm, >99%); bromohexane (111-25-1, Sinopharm, >99%); *n*-alkylimidazole (616-47-7, Kaile, >99%); tert-butyl alcohol (75-65-0, Sinopharm, >99%); and distilled water (Sinopharm).

The ILs used in this work were synthesized by the method described in the literature [26]. The synthesized ILs were purified by subjecting the liquid to a very low pressure of about 8×10^{-3} MPa at a temperature about 353 K for approximately 3 h, and were analyzed by Agilent 1260 Infinity liquid chromatography. The purity of [EMIM]Br, [BMIM]Br, and [HMIM]Br is 99.1%, 99.1%, and 99.0%, respectively.

2.2. Apparatus

The apparatus used were all-glass dynamic recirculating still (NGW, Wertheim, Germany) described by Hunsmann [27]; Agilent 7890A gas chromatography (GC), and HS-9 headspace sampler.

2.3. Procedure

The temperature was measured using a Beckmann thermometer. After the VLE temperature was maintained at a constant value for 1 h, the amounts of TBA and water in the liquid and vapor phases were determined by the GC with a headspace sampler. The uncertainty of the temperature is ± 0.15 K, including the visual detection and the purity of ILs. The precision of the electronic balance is $\pm 1 \times 10^{-4}$ g.

2.4. Analysis

A thermal conductivity detector was used with a Agilent 19091J-413 capillary column (30 m × 0.32 mm × 0.25 μm) in the GC. The GC response peaks were integrated using an Agilent Chemstation. The temperatures of column, injector, and detector were 373 K, 473 K, and 473 K, respectively. Every example was analyzed at least three times, and the standard deviation in the mole fraction was less than 0.002.

3. Results and Discussion

To test the performance of the equilibrium apparatus, VLE data for {TBA (1) + water (2)} binary system were measured at 101.3 kPa and compared with those in literature [28], as shown in Fig. 2. The experimental data are in good agreement with the data in literature, so the equilibrium apparatus is qualified. The experimental VLE data for {TBA (1) or water (2) + IL (3)} binary systems are listed in Table 2.

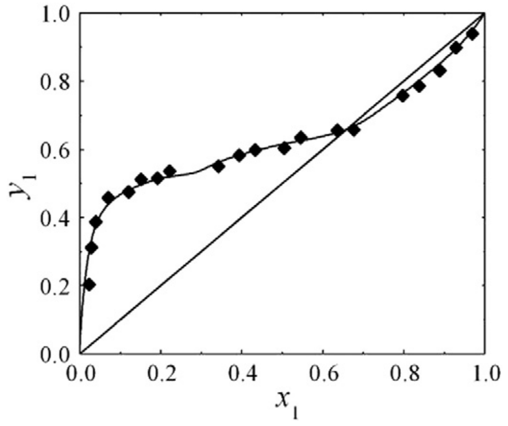

Fig. 2. The comparison between the experimental VLE data for {TBA (1) + water (2)} binary system and the data in literature. ■ experimental data; solid line — data in literature [28].

Table 2
Experimental VLE data for {TBA (1) or water (2) + IL (3)} binary systems at 101.3 kPa

x_1	y_1	T/K	γ_1	x_2	y_2	T/K	γ_2
TBA + [EMIM]Br				Water + [EMIM]Br			
1.000	1.000	355.55	1.000	1.000	1.000	373.15	1.000
0.990	1.000	355.82	1.000	0.991	1.000	373.42	0.999
0.971	1.000	356.22	1.004	0.978	1.000	373.83	0.998
0.939	1.000	356.93	1.010	0.963	1.000	374.37	0.994
0.893	1.000	357.91	1.022	0.917	1.000	375.88	0.989
0.852	1.000	358.58	1.044	0.842	1.000	378.52	0.982
0.838	1.000	358.75	1.054	0.861	1.000	378.27	0.970
0.802	1.000	359.30	1.079	0.767	1.000	383.12	0.922
0.780	1.000	359.51	1.100	0.674	1.000	389.68	0.844
0.747	1.000	360.06	1.125	0.628	1.000	393.67	0.797
TBA + [BMIM]Br				Water + [BMIM]Br			
1.000	1.000	355.55	1.000	1.000	1.000	373.15	1.000
0.992	1.000	355.76	1.000	0.993	1.000	373.34	1.000
0.982	1.000	356.01	1.001	0.971	1.000	374.01	0.999
0.947	1.000	356.89	1.003	0.920	1.000	375.73	0.991
0.904	1.000	357.80	1.014	0.885	1.000	376.89	0.990
0.885	1.000	358.25	1.018	0.836	1.000	378.81	0.979
0.853	1.000	359.08	1.023	0.804	1.000	380.32	0.966
0.821	1.000	359.75	1.036	0.767	1.000	382.15	0.952
0.796	1.000	360.41	1.042	0.735	1.000	383.93	0.936
0.754	1.000	361.41	1.059	0.693	1.000	386.48	0.911
TBA + [HMIM]Br				Water + [HMIM]Br			
1.000	1.000	355.55	1.000	1.000	1.000	373.15	1.000
0.996	1.000	355.66	1.000	0.992	1.000	373.40	0.999
0.987	1.000	355.91	0.999	0.975	1.000	373.94	0.997
0.975	1.000	356.25	0.998	0.958	1.000	374.46	0.996
0.951	1.000	357.20	0.986	0.936	1.000	375.18	0.994
0.935	1.000	357.80	0.980	0.904	1.000	376.23	0.992
0.910	1.000	358.73	0.972	0.875	1.000	377.23	0.989
0.893	1.000	359.32	0.968	0.848	1.000	378.41	0.980
0.864	1.000	360.65	0.951	0.830	1.000	379.22	0.973
0.838	1.000	362.45	0.917	0.800	1.000	380.55	0.964

Note: Standard uncertainties u are: $u(T) = 0.15$ K, $u(x_1) = u(x_2) = 0.002$.

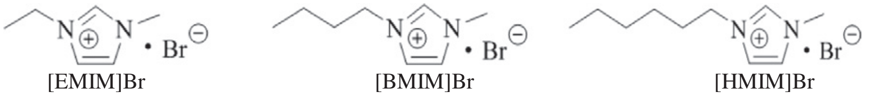

Fig. 1. Structures of the three ILs.