

Isobaric Vapor–Liquid Equilibrium Experiments of Butyl Acetate + Butanol with Different Ionic Liquids at 101.3 kPa

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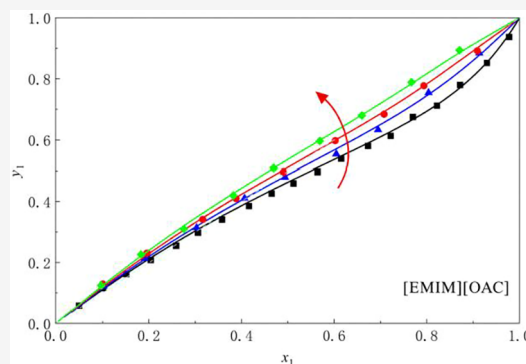


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ABSTRACT: This study examines the vapor–liquid equilibrium (VLE) of the butyl acetate + butanol binary system and the corresponding ternary mixtures containing [EMIM][OAC], [EMIM][Cl], or [BMIM][OAC]. The results show that [EMIM][OAC] and [BMIM][OAC] enhance the separation driving force and effectively eliminate azeotropic behavior. Among the tested ionic liquids, [EMIM][OAC] provides the strongest enhancement. The phase equilibrium data were correlated with the NRTL model, yielding average relative deviations (ARDs) of 4.80% for the binary system and 3.48, 3.65, and 3.57% for the ternary systems. Thermodynamic consistency tests further support the reliability of both the experimental data and the fitted model. Overall, these findings highlight the potential of ionic liquids (particularly [EMIM][OAC]) to improve separation efficiency in azeotropic systems.



1. INTRODUCTION

Separating azeotropes remains a persistent challenge in chemical manufacturing. Butyl acetate is widely used as a solvent in coatings, adhesives, and fragrances, yet it forms a binary azeotrope with butanol during production and downstream processing (azeotropic temperature ≈ 117.6 °C; butyl acetate mass fraction ≈ 0.60 at 101.3 kPa). Conventional azeotropic distillation often relies on volatile organic entrainers (e.g., benzene or cyclohexane); however, their volatility, environmental burden, and energy demand motivate the development of greener separation strategies.^{1,2} The separation of the butyl acetate–butanol azeotrope is of practical importance in product purification and solvent recovery. Butyl acetate is widely used as a solvent in coatings, adhesives, and fine chemicals, and its production is often accompanied by butanol-containing streams that require efficient separation. In addition, butanol is also involved in biomass conversion and fermentation-related processes. Therefore, developing effective methods for separating the butyl acetate–butanol azeotrope is of clear industrial significance. In recent years, emerging strategies such as the chemical-looping concept have also been proposed for azeotrope separation.³

Ionic liquids (ILs), salts that are liquid at or near room temperature, combine negligible vapor pressure, high thermal stability, and tunable ion structures, making them attractive green entrainers for azeotrope separation.^{1,4–7} By tailoring cation–anion combinations, specific interactions with mixture components (e.g., hydrogen bonding and hydrophobic effects) can be strengthened, thereby shifting activity coefficients and disrupting azeotropic behavior.^{7,8} Accordingly, systematic vapor–liquid equilibrium measurements for butyl acetate +

butanol in the presence of structurally diverse ILs are needed to clarify separation mechanisms and guide process design.

Over the past decade, ionic liquids have been increasingly explored for azeotrope separation, and substantial experimental and modeling data have been reported.^{3–31} Studies on alcohol–ester azeotropes consistently show that ILs alter liquid phase nonideality by reducing alcohol activity coefficients and increasing relative volatility, thereby weakening or breaking azeotropes.^{10–15} For the ethanol–ethyl acetate system, isobaric vapor–liquid equilibrium measurements with IL entrainers have demonstrated effective azeotrope disruption.³ Similarly, acetate-based ILs have been reported to improve the separability of propyl acetate–ethanol mixtures.^{10,19,29} ILs have also been applied to ethyl acetate–acetonitrile azeotropes, for which satisfactory correlations were obtained using the NRTL model.¹¹

However, systematic vapor–liquid equilibrium information for the butyl acetate–butanol azeotrope remains limited, and most studies assess only one ionic liquid or a narrow set of candidates.¹⁸ For example, ionic-liquid-assisted separation has been evaluated for *sec*-butanol/*sec*-butyl acetate mixtures, but the conclusions are not directly transferable to the *n*-butanol/*n*-butyl acetate system.³² Freire and co-workers investigated multiphase equilibria in *n*-butanol + *n*-butyl acetate mixtures

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Table 1. Material Specifications^a

material	source	mass fraction	CAS number	<i>M</i> (g/mol)	purification method	final water mass fraction	analysis method
butyl acetate	Macklin	≥0.997	123–86–4	116.16	none	none	GC KF
butanol	Macklin	≥0.999	71–36–3	74.12	none	none	GC KF
[EMIM][OAC]	Macklin	≥0.99	143314–17–4	170.21	vacuum desiccation	<0.0005	LC KF
[BMIM][OAC]	Aladdin	≥0.99	284049–75–8	198.26	vacuum desiccation	<0.0005	LC KF
[EMIM][Cl]	Aladdin	≥0.99	65039–09–0	146.62	vacuum desiccation	<0.0005	LC KF

^a[EMIM][OAC] = 1-ethyl-3-methylimidazolium acetate; [BMIM][OAC] = 1-butyl-3-methylimidazolium acetate; [EMIM][Cl] = 1-ethyl-3-methylimidazolium chloride. GC = gas chromatography; LC = liquid chromatography; KF = Karl Fischer titration.

with an imidazolium-based ionic liquid and provided detailed thermodynamic model analyses.¹ In addition, COSMO-RS screening and molecular simulations have been used to evaluate acetate-based ionic liquids as entrainers for *n*-butanol/*n*-butyl acetate, offering complementary mechanistic insight.

Nevertheless, comparative studies covering variations in ionic-liquid structure (e.g., cation alkyl-chain length and anion identity) are still scarce for this system. The three ionic liquids investigated in this work were selected to allow a systematic comparison of structural effects on the phase behavior of the butyl acetate–butanol system. [EMIM][OAC] and [BMIM][OAC] were chosen to examine the influence of cation alkyl-chain length while keeping the anion unchanged, whereas [EMIM][OAC] and [EMIM][Cl] were compared to evaluate the effect of anion identity under the same cation framework. This combination, therefore, provides a representative basis for assessing how ionic-liquid structure affects azeotrope breaking and separation performance in this system. The relationship between ionic-liquid concentration and separation efficiency has not been quantified systematically, limiting data support for ionic-liquid design and process optimization. Moreover, some published data sets have not been subjected to rigorous thermodynamic consistency tests, which constrains their use in model development and process simulation.^{33–36}

This study addresses these gaps by measuring isobaric vapor–liquid equilibrium data for the butyl acetate–butanol binary system and for ternary mixtures containing [EMIM][OAC], [EMIM][Cl], or [BMIM][OAC] at 101.3 kPa using a modified Othmer still. The effects of ionic-liquid type and mole fraction on activity coefficients, relative volatility, and the azeotropic temperature were quantified to elucidate separation enhancement. The experimental data were correlated with the NRTL model, and data quality was evaluated using deviation statistics and thermodynamic consistency tests.

These results provide a consistent vapor–liquid equilibrium data set and model parameters for selecting effective ionic-liquid entrainers and for designing extractive-distillation processes to separate butyl acetate–butanol azeotropes. The obtained VLE data and correlated thermodynamic parameters can also serve as a useful basis for the future design and optimization of extractive-distillation processes for separating the butyl acetate–butanol azeotrope.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials employed in this study included butyl acetate (BA), butanol (BuOH), and the ionic liquids (ILs) [EMIM][OAC], [BMIM][OAC], and [EMIM][Cl]. Before the experiments, the ILs were dried at 393 K under 0.2 kPa for 48 h to remove residual moisture, and the water content was subsequently quantified by Karl Fischer titration to confirm a moisture level below 0.0005 mass

percent. Before the experiments, the ionic liquids were dried at 393 K under 0.2 kPa for 48 h to remove residual moisture, and the water content was subsequently quantified by Karl Fischer titration to confirm a moisture level below 0.0005 mass %. After drying, the ionic liquids were stored in sealed glass bottles in a desiccator to minimize moisture uptake from the air. During sample preparation and VLE measurements, the exposure time to ambient conditions was kept as short as possible. After the experiments, no obvious color change, phase instability, or abnormal analytical response was observed, indicating that no significant degradation occurred under the present operating conditions.

Table 1 provides detailed information about the materials used, including their names, sources, purities, CAS numbers, molecular weights, purification methods, and analysis methods.

2.2. Apparatus and Procedure

The vapor–liquid equilibrium (VLE) experiments were conducted using a modified equilibrium still, as shown in Figure S1. The system was heated by using a copper heating rod with an integrated temperature sensor. Vapor was generated, condensed, and then returned to the system via a condenser. The cooling medium was water, maintained at temperatures lower than ambient, while the nitrogen pressure regulated the system at 101.3 kPa. A drying tube was installed to prevent moisture from nitrogen from affecting the equilibrium.

Each chemical was precisely weighed using an analytical balance with 0.001 g accuracy. The components were thoroughly mixed before being introduced into the 60 mL equilibrium still. The system was maintained at the steady state for at least 30 min, with heating power adjusted to achieve a drip rate of 2–3 drops per second. Temperature was monitored with a calibrated mercury thermometer, and the vapor and liquid phase compositions were analyzed by gas chromatography (GC).

In the binary mixture of butyl acetate and butanol, the mole fraction of butyl acetate ranged from 0.05 to 0.95 in increments of 0.05. In the ternary system of butyl acetate, butanol, and ionic liquid, the ionic liquid mole fraction was fixed at three levels: 0.02, 0.04, and 0.06. The ionic-liquid mole fractions were fixed at 0.02, 0.04, and 0.06 because these concentration levels were sufficient to reflect the main trend of ionic-liquid effects on the vapor–liquid equilibrium behavior and separation performance of the system. In addition, excessively high ionic-liquid concentrations are not always desirable in practical applications, since they may cause a stronger thermal effect and increase the energy demand of the separation process. Therefore, the ionic-liquid concentration was controlled within a relatively low range in the present study. For each composition group, the mole fraction of butyl acetate was varied from 0.1 to higher values, enabling phase equilibrium analysis under different conditions.

2.3. Sample Analysis

Vapor and liquid phase compositions were analyzed using gas chromatography (GC) equipped with a flame ionization detector (FID) and a KB-Wax column. The column oven, injector, and detector temperatures were maintained at 353.15, 403.15, and 423.15 K, respectively. Component quantification was performed using the area normalization method. The detailed operating conditions and analytical information for the GC measurements are provided in the Supporting Information (Table S1). Due to the negligible saturated vapor pressure of the ionic liquid under atmospheric conditions, only

butyl acetate and butanol were observed in the vapor phase. The ionic liquid content in the liquid phase was determined by the mass difference method. Approximately 2.5 g of the sample was weighed and dried under vacuum at 393 K until a constant weight was reached. The mole fraction of the ionic liquid was calculated based on the mass change before and after drying. The activity coefficients of the two components were calculated from the experimental temperature, pressure, and phase composition data. The relative volatility was then determined from the calculated activity coefficients, and the pure-component vapor pressures were evaluated using the Antoine equation. The corresponding equations used in this work are given in eqs 1–3.

$$\gamma_i = \frac{y_i p}{x_i p_i^{\text{sat}}} \quad (1)$$

$$\alpha_{12} = \frac{y_1 x_2}{y_2 x_1} \quad (2)$$

$$\ln(p_i^s/\text{mmHg}) = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i} \ln T + C_{6i}T^{C_{7i}} \quad (3)$$

The experimental VLE data were correlated using the NRTL model. The corresponding model equations, parameter definitions, and regression objective function used in this work are given in eqs 4–6.

$$\ln \gamma_i = \frac{\sum_j \tau_{ij} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{G_{ki} x_k} \left[\tau_{ij} - \frac{\sum_k \tau_{ik} G_{kj} x_k}{\sum_k G_{kj} x_k} \right] \quad (4)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (5)$$

$$\tau_{ij} = \frac{g_{ij} - g_{ji}}{RT} \quad (6)$$

Model parameters were estimated with the Levenberg–Marquardt algorithm by minimizing the objective function defined in eq 7. The optimized binary interaction parameters and corresponding non-randomness parameters are listed in Table 7.

$$F = \sum_n \left[\left(1 - \frac{\gamma_1^{\text{calcd}}}{\gamma_1^{\text{exptl}}} \right)^2 + \left(1 - \frac{\gamma_2^{\text{calcd}}}{\gamma_2^{\text{exptl}}} \right)^2 \right] \quad (7)$$

Agreement between the experimental and calculated results was quantified using the average relative deviation (ARD) (eq 8). In addition, the mean absolute deviations and standard deviations for the equilibrium temperature (δ_T , σ_T) and vapor phase (δ_y , σ_y) composition were calculated using eqs 9–12.

$$\text{ARD}/\% = \frac{1}{n} \sum_n \sum_i \left| \frac{y_i^{\text{exptl}} - y_i^{\text{calcd}}}{y_i^{\text{exptl}}} \right| \times 100 \quad (8)$$

$$\delta_y = (1/n) \sum |y_{\text{exptl}} - y_{\text{calcd}}| \quad (9)$$

$$\sigma_y = \left[\sum (y_{\text{exptl}}^2 - y_{\text{calcd}}^2) / (n - m) \right]^{1/2} \quad (10)$$

$$\delta_T = (1/n) \sum |T_{\text{exptl}} - T_{\text{calcd}}| \quad (11)$$

$$\sigma_T = \left[\sum (T_{\text{exptl}}^2 - T_{\text{calcd}}^2) / (n - m) \right]^{1/2} \quad (12)$$

The thermodynamic consistency of the binary and ternary data sets was further assessed using the Fredenslund criterion (eq 13).

$$\Delta y = (1/n) \sum |y_{\text{exptl}} - y_{\text{calcd}}| \quad (13)$$

3.. RESULTS AND DISCUSSION

3.1. Experimental Data

Table 2 summarizes the measured isobaric VLE data for the butyl acetate + butanol binary mixture at 101.3 kPa, where x_1

Table 2. VLE Data for the Butyl Acetate (1) + Butanol (2) System at Pressure $p = 101.3$ kPa, Showing Equilibrium Temperature T , Liquid Phase Mole Fraction x_1 , and Vapor Phase Mole Fraction y_1 ^a

T/K	x_1	y_1	γ_1	γ_2	α_{12}
390.55	0.049	0.058	1.522	0.997	1.201
390.35	0.101	0.116	1.477	0.998	1.167
390.2	0.151	0.162	1.391	1.006	1.090
390.10	0.204	0.208	1.324	1.020	1.023
390.15	0.259	0.255	1.281	1.033	0.979
390.20	0.306	0.298	1.268	1.041	0.961
390.30	0.358	0.341	1.242	1.053	0.930
390.50	0.416	0.385	1.202	1.077	0.881
390.75	0.465	0.426	1.185	1.094	0.854
391.05	0.512	0.459	1.154	1.125	0.809
391.40	0.564	0.496	1.124	1.162	0.761
391.85	0.615	0.539	1.110	1.191	0.732
392.40	0.673	0.580	1.076	1.259	0.671
393.00	0.722	0.613	1.047	1.340	0.611
393.70	0.770	0.675	1.062	1.336	0.620
394.50	0.822	0.712	1.026	1.483	0.538
395.45	0.872	0.780	1.027	1.526	0.520
396.55	0.930	0.852	1.003	1.779	0.433
397.75	0.978	0.937	0.991	2.248	0.335

^aStandard uncertainty: $u(T) = 0.01$ K, $u(p) = 0.3$ kPa, $u(x_1) = 0.005$, $u(y_1) = 0.005$.

and y_1 are the liquid- and vapor phase mole fractions of butyl acetate and T is the equilibrium temperature. The corresponding activity coefficients and relative volatility values were calculated from these data. The Antoine parameters used to obtain the pure-component vapor pressures are listed in Table 3, and the detailed calculation equations are provided in the Experimental Section. Measurement uncertainties in T , p , x_1 , and y_1 are given in the footnote to Table 2.

The equilibrium data for the ternary systems containing ionic liquid are summarized in Tables 4, 5, and 6. In each data set, the ionic liquid mole fraction was fixed at $x_3 = 0.02$, 0.04, or 0.06, while the composition of component 1 was varied systematically across the accessible range. To facilitate comparison across different ionic-liquid loadings, the composition of component 1 is reported both on an ionic-liquid-free basis and as the true mole fraction, accounting for x_3 . The same calculation scheme (eqs 1–3) was applied to obtain γ_i and α_{12} for the ternary mixtures.

3.2. Phase Equilibrium Calculation

Thermodynamic correlation of the measured VLE data was performed using the nonrandom two-liquid (NRTL) model, which is widely applied to alcohol–ester systems and mixtures containing ionic liquids.^{37–39} At $p = 101.3$ kPa, the vapor phase was assumed to behave ideally, and the model parameters were primarily regressed from the liquid phase nonideality, as reflected in γ_i .⁴⁰

The thermodynamic models used for data correlation, together with the corresponding equations and parameter definitions, are described in the Experimental Section. The

Table 3. Antoine Parameters of Butyl Acetate (1) + Butanol (2)

component	C_{1i}	C_{2i}	C_{3i}	C_{4i}	C_{5i}	C_{6i}	C_{7i}
butyl acetate	117.9272	−9253.2	0	0	−14.9900	1.05×10^{-05}	2
butanol	101.39723	−9866.4	0	0	−11.655	1.08×10^{-17}	6

Table 4. Vapor–Liquid Equilibrium Data of Butyl Acetate (1) + Butanol (2) + [EMIM][OAC] (3) at Temperature T , Liquid Composition x , Gas Composition y , and Pressure $p = 101.3 \text{ kPa}$ ^a

T/K	$100x_3$	x_1	x_1'	y_1	γ_1	γ_2	α_{12}
391.05	2.007	0.102	0.100	0.123	1.557	0.992	1.234
390.80	2.009	0.191	0.187	0.213	1.452	0.997	1.146
390.65	2.006	0.303	0.297	0.315	1.358	1.013	1.056
390.75	2.001	0.406	0.398	0.411	1.318	1.018	1.018
391.00	2.001	0.494	0.484	0.479	1.255	1.047	0.942
391.65	2.001	0.604	0.592	0.554	1.162	1.121	0.812
392.45	2.023	0.695	0.681	0.633	1.129	1.162	0.758
394.05	2.009	0.804	0.788	0.754	1.108	1.146	0.749
396.60	2.032	0.913	0.894	0.884	1.060	1.116	0.728
391.65	4.015	0.101	0.097	0.130	1.671	0.982	1.333
391.35	4.001	0.196	0.188	0.232	1.546	0.980	1.238
391.25	4.011	0.317	0.304	0.342	1.415	0.991	1.121
391.30	3.991	0.388	0.373	0.410	1.381	0.991	1.093
391.60	3.995	0.490	0.471	0.496	1.312	1.005	1.024
392.30	3.984	0.602	0.578	0.598	1.260	1.003	0.981
393.40	3.998	0.708	0.679	0.684	1.188	1.031	0.895
394.70	3.998	0.793	0.762	0.777	1.158	0.983	0.910
397.20	3.985	0.909	0.873	0.892	1.077	0.998	0.824
392.30	6.041	0.097	0.091	0.125	1.675	0.982	1.333
391.95	5.990	0.183	0.172	0.227	1.625	0.970	1.310
391.80	5.990	0.276	0.259	0.311	1.484	0.981	1.184
391.85	5.997	0.382	0.359	0.420	1.445	0.966	1.172
392.10	6.011	0.469	0.441	0.509	1.416	0.943	1.173
392.65	6.039	0.569	0.535	0.596	1.346	0.937	1.119
393.45	6.009	0.660	0.620	0.680	1.290	0.917	1.093
394.80	5.996	0.767	0.721	0.789	1.238	0.841	1.136
396.65	6.009	0.871	0.818	0.894	1.170	0.716	1.250

^a x_1' means the mole fraction of butyl acetate with no [EMIM][OAC] contained, and x_1' means the real mole fraction, which can be calculated as follows: $x_1' = x_1 \times (1 - x_3)$. γ_1 , activity coefficient; α_{12} , relative volatility. Standard uncertainty: $u(T) = 0.01 \text{ K}$, $u(p) = 0.3 \text{ kPa}$, $u(x_1) = 0.005$, $u(y_1) = 0.005$, $u(x_3) = 0.005$.

Results and Discussion section, therefore, focuses on the obtained correlation results and their analyses (Table 7).

The equations used for deviation analysis and thermodynamic consistency evaluation are described in the Experimental Section. In the Results and Discussion section, only the corresponding calculated results are presented and discussed.

The deviation statistics obtained from the model correlation are summarized in Table 8. In addition, the thermodynamic consistency test results for the binary and ternary systems are given in Table 9.

The low ARD values, along with small temperature and composition deviations, indicate that the NRTL model accurately reproduces the measured VLE behavior. The consistency test results further confirm the reliability of the experimental data and fitted parameters, supporting subsequent analysis based on the correlated thermodynamic models.

In order to further evaluate the applicability of different thermodynamic models to the investigated systems, the UNIQUAC model was also employed to correlate the experimental VLE data. Similar to the NRTL treatment, the correlation performance of the UNIQUAC model was assessed using the average relative deviation (ARD) together with the

mean absolute deviations and standard deviations of temperature and vapor phase composition. The corresponding model parameters and deviation statistics are summarized in Tables 10 and 11, respectively.

For further comparison, the Wilson model was also used to correlate the experimental VLE data of the binary and ternary systems. The correlation accuracy of the Wilson model was evaluated by using the same statistical criteria as those adopted for the NRTL and UNIQUAC models, including ARD, temperature deviation, and vapor phase composition deviation. The relevant model parameters and deviation results are given in Tables 12 and 13, respectively.

In summary, compared with the UNIQUAC and Wilson models, the NRTL model provided the most satisfactory overall correlation for the present systems, particularly for the ternary VLE data, where consistently lower ARD values were obtained. Therefore, the NRTL model was selected as the most appropriate model for describing the phase equilibrium behavior of the investigated systems.

3.3. Analysis and Discussion

Figure 1 presents a comparison of the vapor–liquid equilibrium data for the butyl acetate (1) butanol (2) binary

Table 5. Vapor–Liquid Equilibrium Data of Butyl Acetate (1) + Butanol (2) + [EMIM][Cl] (3) at Temperature T , Liquid Composition x , Gas Composition y , and Pressure $p = 101.3 \text{ kPa}$ ^a

T/K	$100x_3$	x_1	x_1'	y_1	γ_1	γ_2	α_{12}
391.05	1.991	0.110	0.108	0.124	1.456	0.999	1.145
390.80	2.018	0.200	0.196	0.215	1.403	1.005	1.099
390.65	2.018	0.313	0.307	0.315	1.315	1.027	1.008
390.75	2.012	0.412	0.404	0.402	1.272	1.044	0.959
391.00	1.995	0.502	0.492	0.472	1.218	1.077	0.890
391.60	1.983	0.615	0.603	0.554	1.143	1.155	0.776
392.45	1.996	0.704	0.690	0.625	1.098	1.227	0.699
394.15	2.013	0.815	0.799	0.748	1.080	1.241	0.674
396.85	2.016	0.919	0.900	0.884	1.046	1.188	0.673
391.60	4.001	0.109	0.104	0.124	1.484	0.999	1.164
391.35	3.945	0.206	0.197	0.231	1.466	0.992	1.159
391.25	3.993	0.325	0.312	0.334	1.344	1.016	1.038
391.35	4.024	0.399	0.383	0.407	1.335	1.011	1.036
391.65	4.098	0.498	0.478	0.490	1.274	1.034	0.965
392.35	4.000	0.615	0.590	0.587	1.210	1.063	0.889
393.40	4.003	0.721	0.692	0.674	1.149	1.115	0.800
394.65	3.988	0.800	0.769	0.764	1.129	1.082	0.806
397.15	3.985	0.913	0.877	0.894	1.076	1.025	0.802
392.30	6.024	0.106	0.099	0.121	1.486	0.996	1.166
391.95	5.832	0.196	0.185	0.238	1.592	0.970	1.285
391.80	6.016	0.276	0.260	0.304	1.449	0.991	1.145
391.85	6.043	0.379	0.356	0.397	1.378	1.000	1.079
392.10	5.991	0.468	0.440	0.498	1.388	0.962	1.128
392.65	5.995	0.585	0.550	0.581	1.274	1.010	0.984
393.45	5.995	0.674	0.633	0.682	1.268	0.949	1.038
394.80	6.015	0.758	0.712	0.761	1.209	0.917	1.018
396.65	6.053	0.874	0.821	0.886	1.155	0.792	1.117

^a x_1' means the mole fraction of butyl acetate with no [EMIM][Cl] contained, and x_1 means the real mole fraction, which can be calculated as follows: $x_1' = x_1 \times (1 - x_3)$. γ_1 , activity coefficient; α_{12} , relative volatility. Standard uncertainty: $u(T) = 0.01 \text{ K}$, $u(p) = 0.3 \text{ kPa}$, $u(x_1) = 0.005$, $u(y_1) = 0.005$, $u(x_3) = 0.005$.

system obtained in this study with literature values. The good agreement observed demonstrates the reliability of the experimental apparatus and the methodology. The obtained data are thus accurate and valid, providing a reliable foundation for subsequent investigations of the ternary systems.

As shown in Figure 2, as the mole fraction of the three ionic liquids (ILs) increases from 0.00 to 0.06, the y – x curve gradually deviates from the diagonal, and the azeotrope shifts upward. This trend quantitatively indicates an enhancement in separation performance with increasing ionic liquid concentration. For the systems containing [EMIM][OAC] and [BMIM][OAC], the azeotropic point progressively shifts and eventually disappears within the investigated concentration range, which is consistent with the increase in relative volatility shown in Figure 5. In contrast, [EMIM][Cl] does not break the azeotrope at a mole fraction of 0.06, indicating a weaker effect on the separation driving force. Compared with Figure 2b,c, the deviation of the y – x curve in Figure 2a is more pronounced, suggesting that [EMIM][OAC] provides the strongest enhancement among the three ionic liquids studied.

As depicted in Figure 3, the equilibrium temperature increases significantly with the mole fraction of the ionic liquid (IL). This effect is particularly pronounced in areas with a higher mole fraction of butyl acetate located on the right side of the figure. This indicates that while ionic liquids improve separation as distillation extractants, they also demand more heat during the distillation process. Additionally, as shown in Figure 3c, among the three ionic liquids, [BMIM][OAC]

causes a larger temperature increase than the other two. From a structural point of view, the larger temperature increase caused by [BMIM][OAC] is associated with the longer butyl chain in the [BMIM]⁺ cation compared with the ethyl-substituted [EMIM]⁺ cation. The longer alkyl chain increases the molecular size and hydrophobic character of the ionic liquid, which leads to a stronger perturbation of the liquid phase environment and a more pronounced increase in the equilibrium temperature. This structural difference is likely one of the main reasons that [BMIM][OAC] exhibits a more pronounced temperature-increasing effect under the present conditions.

As shown in Figure 4a–c, the addition of the three ionic liquids (ILs) leads to an overall increase in γ_1 , whereas γ_2 decreases markedly, indicating a pronounced redistribution of nonideality in the system upon IL introduction. This trend suggests stronger specific interactions between the IL and the component corresponding to γ_2 (butanol), which substantially suppress the activity coefficient of butanol. In contrast, the IL–butyl acetate interactions appear weaker, resulting in only limited changes in the corresponding activity coefficient. Notably, in the composition region with a high mole fraction of butyl acetate, the rapid decline in γ_2 further implies that the IL exhibits stronger selective solvation and/or complexation toward butanol. From a chemical perspective, whether an ionic liquid can break the azeotrope depends on its ability to interact selectively with butanol rather than butyl acetate and thereby modify the relative nonideality of the two components in the

Table 6. Vapor–Liquid Equilibrium Data of Butyl Acetate (1) + Butanol (2) + [BMIM][OAC] (3) at Temperature T , Liquid Composition x , Gas Composition y , and Pressure $p = 101.3 \text{ kPa}$ ^a

T/K	$100x_3$	x_1	x_1'	y_1	γ_1	γ_2	α_{12}
391.05	2.001	0.112	0.109	0.123	1.421	1.003	1.114
390.80	2.007	0.190	0.187	0.210	1.438	0.999	1.133
390.65	1.999	0.286	0.281	0.299	1.364	1.012	1.061
390.75	1.985	0.376	0.369	0.374	1.294	1.030	0.989
391.00	2.003	0.487	0.477	0.467	1.240	1.058	0.921
391.60	2.022	0.585	0.573	0.547	1.187	1.088	0.855
392.45	1.993	0.679	0.665	0.622	1.134	1.139	0.777
394.15	2.005	0.793	0.777	0.739	1.097	1.148	0.740
396.85	2.003	0.903	0.885	0.870	1.046	1.117	0.716
391.60	4.016	0.112	0.108	0.132	1.519	0.995	1.197
391.35	4.017	0.198	0.190	0.234	1.542	0.980	1.234
391.25	3.996	0.303	0.291	0.328	1.419	0.992	1.123
391.35	3.971	0.388	0.373	0.412	1.385	0.986	1.102
391.65	4.004	0.481	0.462	0.496	1.335	0.986	1.061
392.35	4.002	0.590	0.566	0.588	1.264	0.994	0.993
393.40	4.022	0.690	0.662	0.679	1.209	0.989	0.949
394.65	3.990	0.781	0.750	0.771	1.168	0.958	0.941
397.15	4.009	0.894	0.858	0.898	1.104	0.810	1.040
392.65	5.998	0.094	0.088	0.127	1.728	0.965	1.397
392.35	6.014	0.197	0.185	0.238	1.567	0.959	1.275
392.20	5.985	0.298	0.280	0.328	1.430	0.973	1.148
392.30	5.987	0.385	0.362	0.411	1.384	0.970	1.114
392.50	5.984	0.463	0.435	0.496	1.382	0.943	1.144
393.30	6.008	0.597	0.561	0.605	1.277	0.958	1.036
394.15	6.025	0.681	0.640	0.687	1.237	0.933	1.027
395.60	5.999	0.782	0.735	0.787	1.183	0.882	1.032
397.30	5.999	0.865	0.814	0.882	1.140	0.747	1.164

^a x_1' means the mole fraction of butyl acetate with no [BMIM][OAC] contained, and x_1' means the real mole fraction, which can be calculated as follows: $x_1' = x_1 \times (1 - x_3)$. γ_1 , activity coefficient; α_{12} , relative volatility. Standard uncertainty: $u(T) = 0.01 \text{ K}$, $u(p) = 0.3 \text{ kPa}$, $u(x_1) = 0.005$, $u(y_1) = 0.005$, $u(x_3) = 0.005$.

Table 7. Binary Interaction Parameters g_{ij} and g_{ji} and Nonrandom Activity Parameter α_{ij} in the NRTL Model

component i	component j	Δg_{ij}	Δg_{ji}	α_{ij}
butyl acetate	butanol	4481.9	−1670.8	0.3
butyl acetate	[EMIM][OAC]	17093.7	14518.1	0.47
butanol	[EMIM][OAC]	−3755.2	885.2	0.2
butyl acetate	[EMIM][Cl]	13060.7	2528.3	0.47
butanol	[EMIM][Cl]	−6185.2	1457.1	0.2
butyl acetate	[BMIM][OAC]	−578.1	12178.8	0.47
butanol	[BMIM][OAC]	−26390.2	−4507.6	0.2

Table 8. Deviation Between Experimental Data and Model Predictions (NRTL)

systems	δ_T	σ_T	δ_y	σ_y	ARD (%)
butyl acetate (1) + butanol (2)	0.1299	0.1539	0.0087	0.0096	4.80
butyl acetate (1) + butanol (2) + [EMIM][OAC](3)	0.0228	0.0281	0.0058	0.0071	3.48
butyl acetate (1) + butanol (2) + [EMIM][Cl](3)	0.0872	0.1288	0.0069	0.0085	3.65
butyl acetate (1) + butanol (2) + [BMIM][OAC](3)	0.1030	0.1377	0.0063	0.0079	3.57

liquid phase. Stronger ionic liquid–butanol interactions suppress the activity of butanol more effectively, while butyl

Table 9. Thermodynamic Consistency Test (NRTL)

	butyl acetate + butanol	butyl acetate + butanol + [EMIM][OAC]	butyl acetate + butanol + [EMIM][Cl]	butyl acetate + butanol + [BMIM][OAC]
Fredenslund test	0.0087	0.0058	0.0069	0.0063
request: $\Delta y < 0.01$				
result	passed	passed	passed	passed

Table 10. Binary Interaction Parameters g_{ij} and g_{ji} and Nonrandom Activity Parameter α_{ij} in the UNIQUAC Model

component i	component j	Δg_{ij}	Δg_{ji}
butyl acetate	butanol	2580.5	−1500.6
butyl acetate	[EMIM][OAC]	1674.5	472.3
butanol	[EMIM][OAC]	−4759.3	30870.5
butyl acetate	[EMIM][Cl]	9362.5	−3922.1
butanol	[EMIM][Cl]	12124.9	−5490.4
butyl acetate	[BMIM][OAC]	3016.9	−440.7
butanol	[BMIM][OAC]	−3848.3	32503.8

acetate is less strongly affected, resulting in an increase in the relative volatility of butyl acetate with respect to butanol. This is the fundamental reason why azeotropic behavior is weakened or eliminated after ionic-liquid addition. Among the three ionic liquids studied, [EMIM][OAC] showed the best performance because the acetate anion has strong

Table 11. Deviation between Experimental Data and Model Predictions (UNIQUAC)

systems	δ_T	σ_T	δ_y	σ_y	ARD (%)
butyl acetate (1) + butanol (2)	0.007	0.008	0.13	0.15	4.16
butyl acetate (1) + butanol (2) + [EMIM][OAC](3)	0.006	0.008	0.09	0.11	3.67
butyl acetate (1) + butanol (2) + [EMIM][Cl](3)	0.010	0.013	0.31	0.42	6.14
butyl acetate (1) + butanol (2) + [BMIM][OAC](3)	0.006	0.008	0.38	0.50	7.17

Table 12. Binary Interaction Parameters g_{ij} and g_{ji} and Nonrandom Activity Parameter α_{ij} in the Wilson Model

component i	component j	Δg_{ij}	Δg_{ji}
butyl acetate	butanol	−2056.7	4827.2
butyl acetate	[EMIM][OAC]	33,769	48,657
butanol	[EMIM][OAC]	−2559	−6493
butyl acetate	[EMIM][Cl]	2110	37,188
butanol	[EMIM][Cl]	−1888	−30,280
butyl acetate	[BMIM][OAC]	3949	33,660
butanol	[BMIM][OAC]	−2468	−39,067

Table 13. Deviation between Experimental Data and Model Predictions (Wilson)

systems	δ_T	σ_T	δ_y	σ_y	ARD (%)
butyl acetate (1) + butanol (2)	0.003	0.009	0.16	0.14	4.45
butyl acetate (1) + butanol (2) + [EMIM][OAC](3)	0.006	0.008	0.23	0.26	4.20
butyl acetate (1) + butanol (2) + [EMIM][Cl](3)	0.008	0.009	0.20	0.23	4.67
butyl acetate (1) + butanol (2) + [BMIM][OAC](3)	0.007	0.009	0.18	0.28	4.19

hydrogen-bond-accepting ability toward butanol, and the shorter ethyl chain of the [EMIM]⁺ cation causes less steric hindrance than the butyl chain in [BMIM][OAC]. As a result, [EMIM][OAC] can interact more effectively with butanol and produce a stronger separation enhancement. In contrast,

although [EMIM][Cl] also affects the phase behavior, its interaction pattern is less favorable for azeotrope breaking under the present conditions, so its separation effect is weaker.

As shown in Figure 5a,c, the addition of the ionic liquids [EMIM][OAC] and [BMIM][OAC] markedly increases the relative volatility of butyl acetate with respect to butanol (α_{12}). The resulting α_{12} curves remain above $\alpha = 1$ over the entire composition range, indicating that the azeotropic behavior is substantially weakened or even eliminated. For the [EMIM]-[OAC]-containing system, α_{12} is consistently higher than that of the corresponding binary system without ionic liquid, and no intersection with $\alpha = 1$ is observed in the low-butanol (high-butyl acetate) region, suggesting a more effective enhancement of the separation driving force. In contrast, after adding [EMIM][Cl], α_{12} does not stay above $\alpha = 1$ across the full composition range, implying that the azeotropic feature is not completely removed; this trend is consistent with the conclusions drawn from Figure 2a–c. The separation behavior observed in this work is closely related to the different types of intermolecular interactions present in the ternary systems. The main interactions include hydrogen bonding between butanol and the ionic liquid, ion–dipole interactions, and selective solvation of butanol by the ionic liquid. Because butanol contains a hydroxyl group, it can interact much more strongly with the ionic liquid than butyl acetate, particularly when the anion has strong hydrogen-bond-accepting ability. As a result, the activity of butanol is more strongly suppressed, whereas butyl acetate is affected to a much smaller extent. This selective interaction changes the relative nonideality of the two components, increases the relative volatility of butyl acetate with respect to butanol, and thus weakens or even eliminates the azeotropic behavior. In acetate-based ionic liquids, this effect is more pronounced because the acetate anion can interact more effectively with butanol. In addition, the cation structure also affects the accessibility of the interaction sites. For example, the shorter alkyl chain in [EMIM][OAC] leads to less steric hindrance than in [BMIM][OAC], making the selective interaction with butanol more effective and thereby producing a stronger separation enhancement. From a structural point of view, the difference mainly arises from the

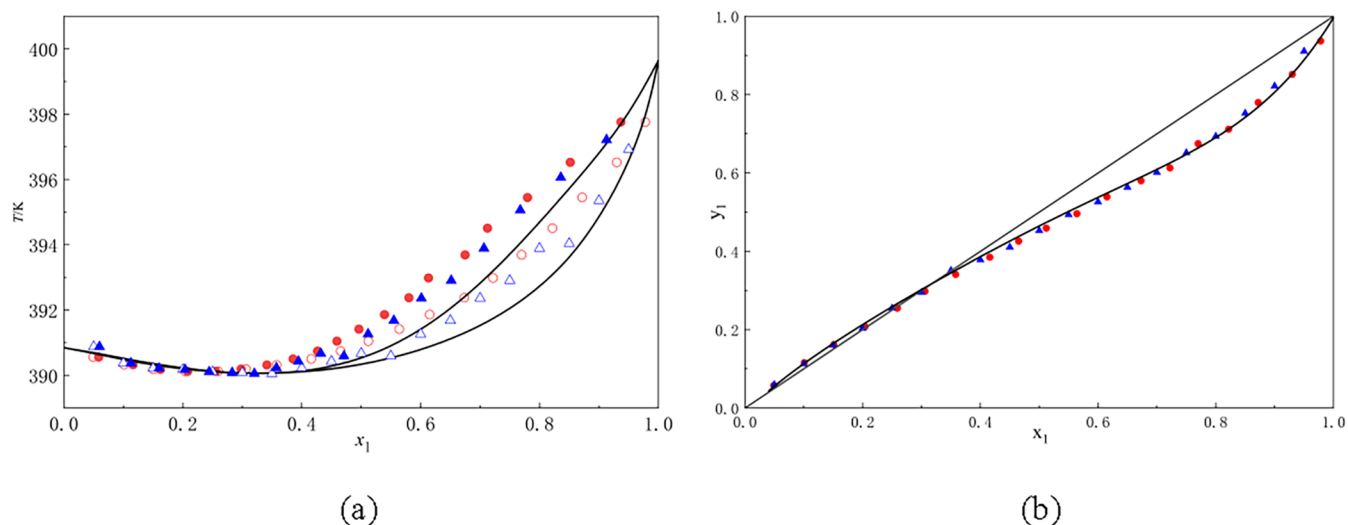


Figure 1. (a) T - x , y diagram for the butyl acetate, (1) butanol (2) system; and (b) x - y diagram for the same system. ●○ is this experimental data, ▲△ ref 41; black continuous line, fitted by NRTL (system at $P = 101.3$ kPa).

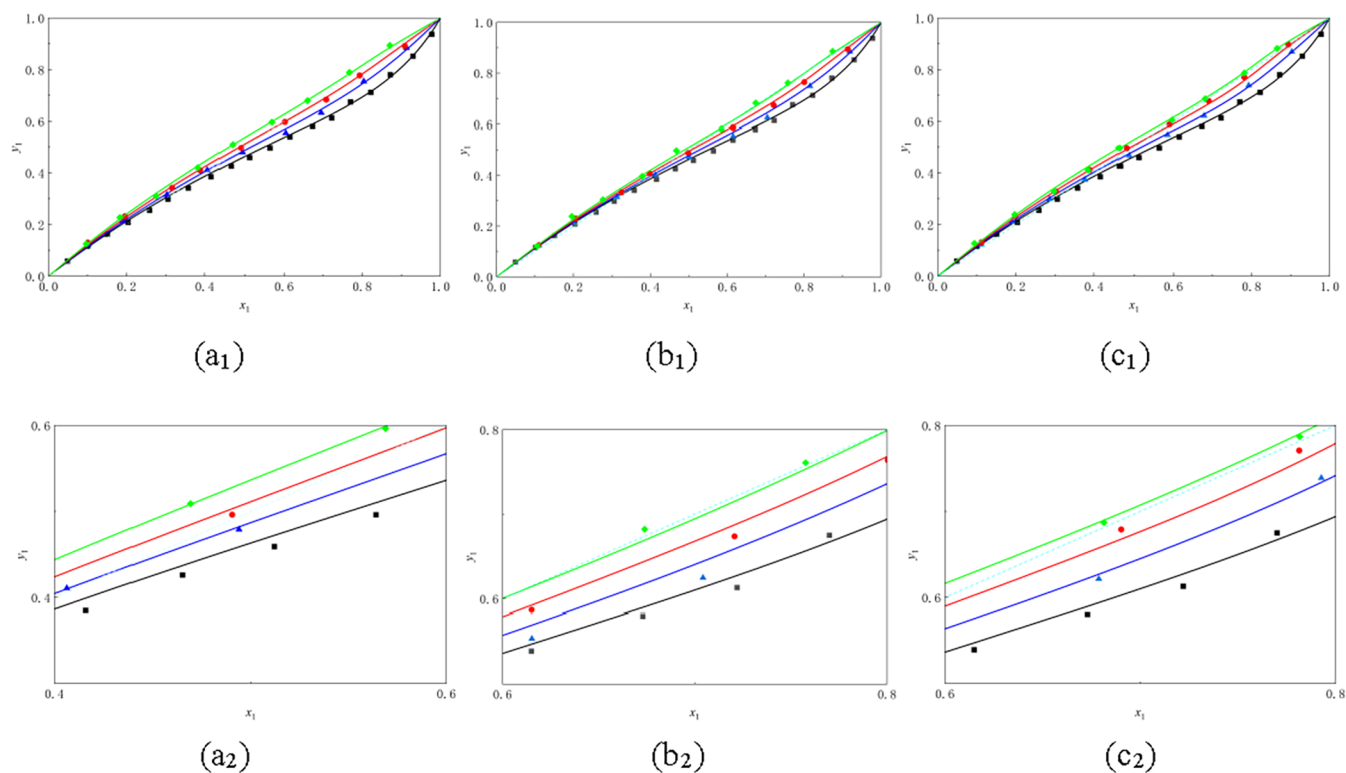


Figure 2. y – x diagram for butyl acetate, (1) butanol (2) + IL (3). (a) IL: [EMIM][OAC]; (b) IL: [EMIM][Cl]; and (c) IL: [BMIM][OAC]. ■, $x_3 = 0$; ▲, $x_3 = 0.02$; ●, $x_3 = 0.04$; ◆, $x_3 = 0.06$; solid line, NRTL model fit (system at $P = 101.3$ kPa).

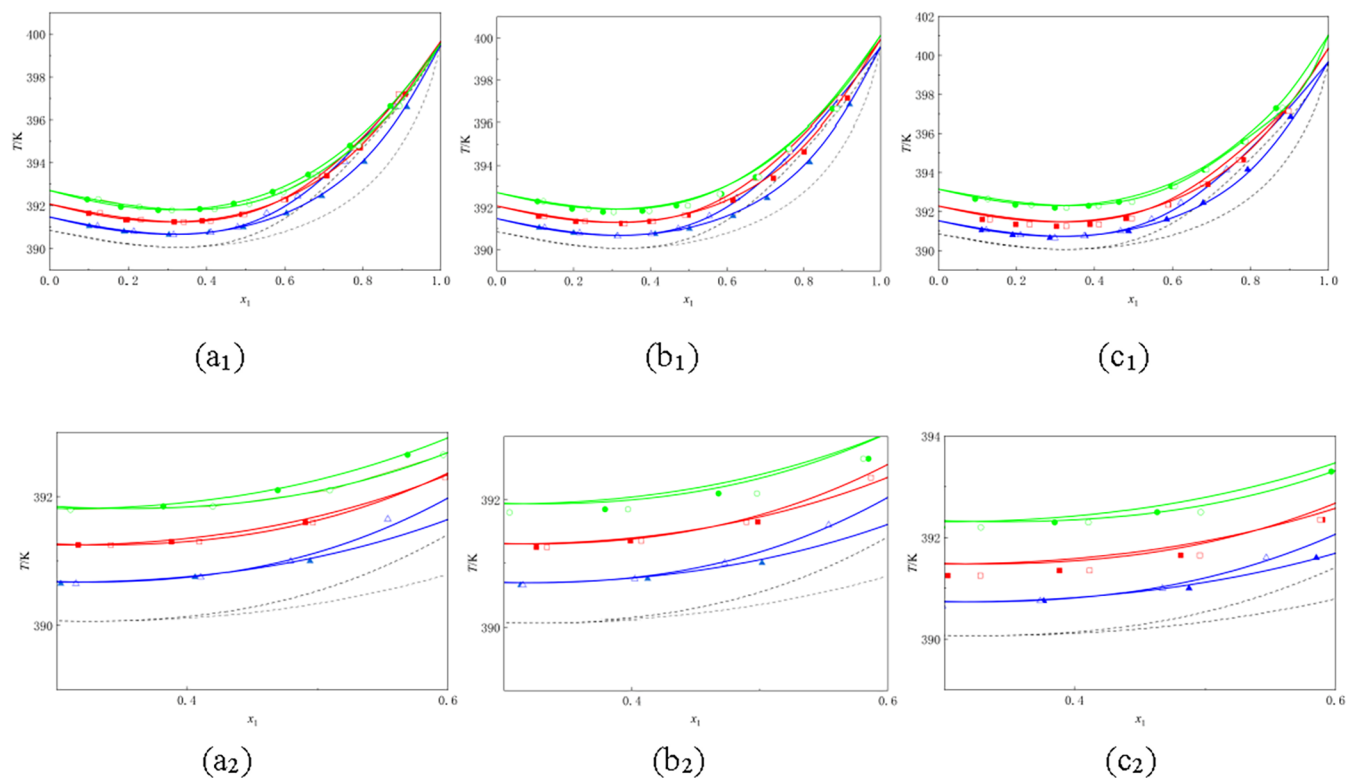


Figure 3. T – x , y diagram for butyl acetate, (1) butanol (2) + IL (3). (a) IL: [EMIM][OAC]; (b) IL: [EMIM][Cl]; and (c) IL: [BMIM][OAC]. ▲, $x_3 = 0.02$; ●, $x_3 = 0.04$; ◆, $x_3 = 0.06$; solid line, dashed line ($x_3 = 0$) NRTL model fit (system at $P = 101.3$ kPa).

anion. Although [EMIM][Cl] and [EMIM][OAC] share the same [EMIM]⁺ cation, the chloride anion is less effective than the acetate anion in producing the selective interaction

required for azeotrope breaking under the present conditions. Consequently, the ability of [EMIM][Cl] to suppress the activity of butanol is weaker, and the increase in the relative

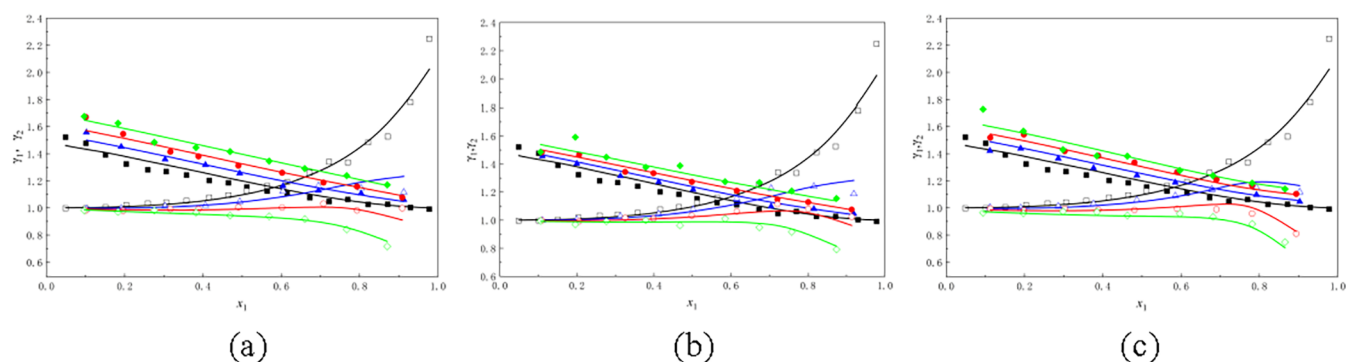


Figure 4. γ - x diagram for butyl acetate, (1) butanol (2) + IL (3). (a) IL: [EMIM][OAC]; (b) IL: [EMIM][Cl]; and (c) IL: [BMIM][OAC]. ■, $x_3 = 0$; ▲, $x_3 = 0.02$; ●, $x_3 = 0.04$; ◆, $x_3 = 0.06$; solid line, NRTL model fit (system at $P = 101.3$ kPa).

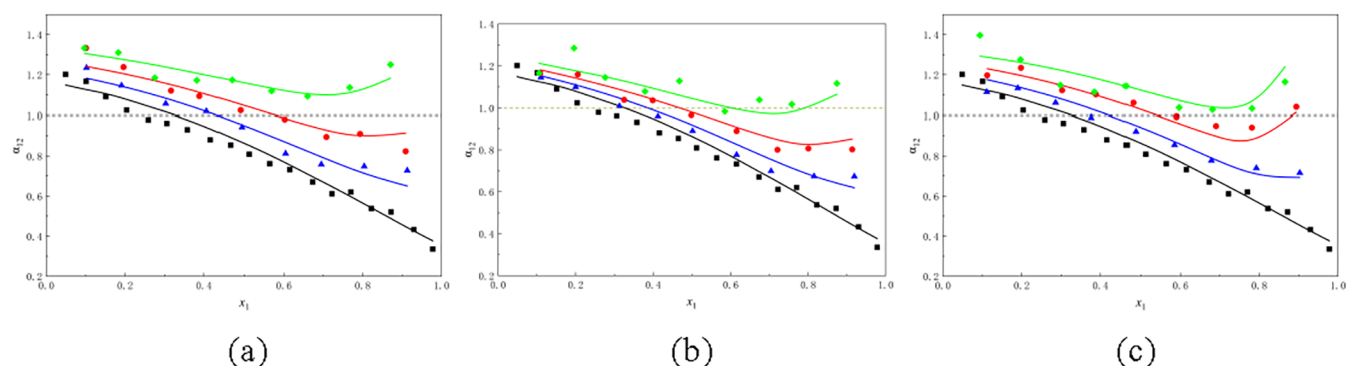


Figure 5. α - x diagram for butyl acetate, (1) butanol (2) + IL (3). (a) IL: [EMIM][OAC]; (b) IL: [EMIM][Cl]; and (c) IL: [BMIM][OAC]. ■, $x_3 = 0$; ▲, $x_3 = 0.02$; ●, $x_3 = 0.04$; ◆, $x_3 = 0.06$; solid line, NRTL model fit (system at $P = 101.3$ kPa).

volatility of butyl acetate is not large enough to maintain α_{12} above unity throughout the whole composition range. Therefore, the azeotropic behavior is weakened, but not completely eliminated, in the presence of [EMIM][Cl].

4.. CONCLUSIONS

This work systematically investigated the vapor–liquid equilibrium behavior of the butyl acetate + butanol binary system and the corresponding ternary systems containing [EMIM][OAC], [EMIM][Cl], and [BMIM][OAC] at 101.3 kPa. The results showed that the addition of ionic liquids changed the phase behavior of the system to different extents, with [EMIM][OAC] and [BMIM][OAC] showing much stronger separation enhancement than [EMIM][Cl]. Among the three ionic liquids, [EMIM][OAC] exhibited the best overall performance in improving the relative volatility and promoting azeotrope breaking. The experimental data were satisfactorily correlated by the NRTL model, with ARD values of 4.80% for the binary system and 3.48, 3.65, and 3.57% for the ternary systems containing [EMIM][OAC], [EMIM][Cl], and [BMIM][OAC], respectively, confirming the reliability of the model for describing the investigated systems. From a practical viewpoint, [EMIM][OAC] appears to be the most promising entrainer for the separation of the butyl acetate–butanol azeotrope. Nevertheless, further studies on economic feasibility, solvent recovery, and the detailed effect of ionic-liquid concentration are still needed before industrial application, and process scale-up should also be addressed in future work.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.6c00116>.

The details of GC; schematic diagram of modified Othmer; ternary VLE diagrams for butyl acetate + butanol + ionic liquids (PDF)

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Notes

The authors declare no competing financial interest.

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