# Azeotropic Behavior of the 2-Methylpropan-2-ol + water + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide System

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Vapor-liquid equilibrium data were measured isothermally in the near-azeotropic region of the 2-methylpropan-2-ol + water + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide system at 333.15, 343.15, and 353.15 K. The data were processed using a recently developed method based on a small number of experiments that provides a complete thermodynamic description of the azeotropic behavior. The parameters of the third-order Redlich-Kister equation were correlated with the ionic liquid concentration to determine an analytical dependence of both the azeotropic composition and the pressure.

*Keywords*
alcohol-water system, azeotropy, correlation, ionic liquid, vapor-liquid equilibrium

## Introduction

The addition of an entrainer, which affects the phase equilibrium, is in many cases essential for a successful distillation or rectification. As a consequence, an average of 20 new articles have been published each year over the past two decades. For example, 15 papers have been published in the last six months on using ionic liquids only to separate azeotropic systems. Listing even a portion of these papers does not make much sense. However, an example of such a list was published in our previous paper[1]. A variety of ionic liquids have already been used, each with different properties, availability, and cost. These are highly indicative and require further investigation.

In addition to measuring new vapor-liquid equilibrium (VLE) data, our study aimed to test the recently developed method for the quantitative thermodynamic description of azeotropic behavior based on minimal input of experimental data, which are usually difficult to obtain. This work is part of a research project in which theoretical and experimental methods are used to study the effects of azeotrope breakers. In a previous study[1], the water and 2-propanol system was examined. The same approach will be used in this study to verify the proposed correlation. The new experimental data of the system water + 2-methylpropan-2-ol (= tert.-butanol) containing the same ionic liquid were measured, and their processing is presented. Compared to the water + 2-propanol system, the results of the

thermodynamic correlation were obtained more smoothly, and some relationships could even be simplified, which speaks in favor of the new approach.

## Experimental

### Materials

The chemicals used for the measurements are listed together with their properties in Table 1. 2-Methylpropan-2-ol, p. a., with a declared purity of > 99.85 %, was kept at a temperature slightly above its melting point (298 K) over a 5A molecular sieve, while the ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM NTf2, hereafter *IL*), was used as received. The water used was distilled twice.

### Equipment and procedure

We used our classical setup, as often reported earlier, e.g., in[2,3]. The equilibrium apparatus used was a dynamic all-glass still with a circulation of both phases; the volume of the liquid mixture was about 160 mL. The schematic drawing and the measurement procedure are recapitulated in the previous paper[1].

### Vapor-liquid equilibrium

Vapor-liquid equilibrium (VLE) data were measured isothermally at 333.15, 343.15, and 353.15 K. As a test of instrument functionality, the

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Table 1 – *Description of compounds*

| Chemical name | CAS No.[a] | Purification |
|---|---|---|
| 2-methylpropan-2-ol, purity >0.9985 [b] | 75-65-0 | dried with a molecular sieve 5A |
| 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 0.99[c] | 174899-82-2 | none |
| water | 7732-18-5 | re-distilled |

[a] CAS No.: Chemical Abstract Service Registry Number
[b] Manufacturer: Lach-Ner, Czech Republic
[c] Manufacturer: IOLITEC GmbH, Heilbronn, Germany. Sometimes denoted as EMIM NTf2
Purity is given in mass fractions

Table 2 – *Experimental saturated vapor pressures of the ionic liquid (IL) + 2-methylpropan-2-ol system in dependence on concentration $x_{IL}$*

| $x_{IL}$ | $P°$ (kPa) at 333.15 K | $P°$ (kPa) at 343.15 K | $P°$ (kPa) at 353.15 K |
|---|---|---|---|
| 0.0000 | 39.207 | 61.374 | 92.877 |
| 0.1198 | 38.120 | 59.526 | 89.840 |
| 0.1499 | 37.735 | 58.828 | 88.620 |
| 0.1999 | 37.100 | 57.635 | 86.529 |
| 0.2500 | 36.210 | 56.100 | 83.674 |
| 0.3000 | 35.056 | 54.091 | 80.771 |

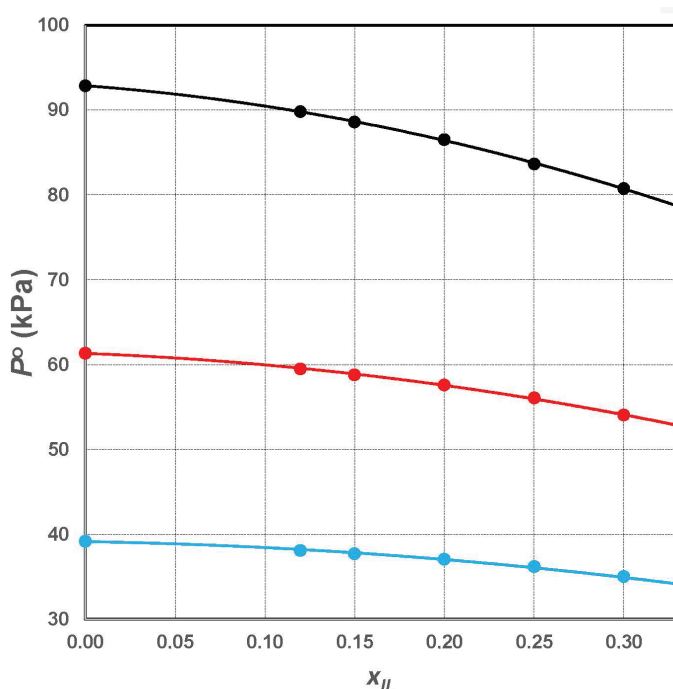$u(x_{IL}) = 0.001$, $u(P) = 0.001$ kPa, $u(T) = 0.01$ K



F i g . 1 – *Dependence of saturated vapor pressure of the 2-methylpropan-2-ol + IL mixtures on the IL mole fraction at three isotherms. Experimental points: ●— 333.15 K, ●— 343.15 K, ●— 353.15 K.*

phase equilibrium in the 2-methylpropan-2-ol + water system was determined and published elsewhere[1]. The vapor pressures of the 2-methylpropan-2-ol + 1-ethyl-3-methylimidazolium bis(trifluoromethyl-

sulfonyl)imide mixtures were measured (in the same setup as aforementioned) at these isotherms to cover the relevant composition range, which is necessary for subsequent data processing. Such vapor pressure data are presented in Table 2 and Fig. 1.

VLE data in the ternary system have always been determined for mixtures close to the expected azeotropic composition. The previous paper[1] provides detailed instructions on how to set the starting point for measurements. The newly measured data are summarized in Table 3.

## Data processing

The details of the correlation procedure are fully summarized in[1], but essential steps are repeated here. The third-order Redlich-Kister equation with two adjustable parameters *b* and *c* can be written for a binary system as follows,

$$\ln \gamma_1 = x_2^2 \left[ b + c \left( 4x_1 - 1 \right) \right] \tag{1}$$

$$\ln \gamma_2 = x_1^2 \left[ b - c \left( 4x_2 - 1 \right) \right] \tag{2}$$

which is also applicable to a pseudobinary system, with a known amount of the third component as a characteristic parameter.

From the thermodynamic point of view, only one $x - y - P$ equilibrium data point of a binary (pseudobinary) system and two vapor pressure points at both the concentration ends are sufficient to evaluate the two parameters *b* and *c*. Consequently, these parameters can be used to calculate the azeotropic point (assuming the ideal behavior of the vapor phase) from the relationships

$$P_{az} = \gamma_1 P_1^{\circ} = \gamma_2 P_2^{\circ} \tag{3}$$

where $P_1^{\circ}$ and $P_2^{\circ}$ represent the vapor pressures of the respective pure components 1 (2-methylpropan-2-ol) and 2 (water), respectively, and $P_{az}$ is the pressure of the azeotropic point. The mole fraction of the azeotrope $x_{1\,az}$ is then obtained by solving Equation (3).

The maximum likelihood method, as described in[5], was used to evaluate the parameters *b* and *c*. In

Table 3 – *Vapor-liquid equilibrium data in the 2-methylpropan-2-ol (1) + water (2) + 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (IL) system*

| $x_{IL}$ | $x_1$ | $y_1$ | $P$ (kPa) | $x_1$ | $y_1$ | $P$ (kPa) | $x_1$ | $y_1$ | $P$ (kPa) |
|---|---|---|---|---|---|---|---|---|---|
| | $T$ = 333.15 K | | | $T$ = 343.15 K | | | $T$ = 353.15 K | | |
| 0.0000 | 0.6704 | 0.6728 | 42.856 | 0.6605 | 0.6671 | 66.899 | 0.6752 | 0.6715 | 101.330 |
| 0.1013 | 0.7218 | 0.7205 | 40.667 | 0.7140 | 0.7158 | 63.260 | 0.7206 | 0.7181 | 95.466 |
| 0.1504 | 0.7289 | 0.7320 | 39.600 | 0.7384 | 0.7380 | 61.590 | 0.7361 | 0.7352 | 92.630 |
| 0.1992 | 0.7438 | 0.7494 | 38.330 | 0.7498 | 0.7523 | 59.601 | 0.7485 | 0.7495 | 89.545 |
| 0.2481 | 0.7524 | 0.7599 | 37.052 | 0.7561 | 0.7639 | 57.230 | 0.7662 | 0.7698 | 85.717 |
| 0.2999 | 0.7943 | 0.8009 | 35.316 | 0.7940 | 0.8023 | 54.471 | 0.7918 | 0.8020 | 80.866 |

$u(T)$ = 0.01 K, $u(P)$ = 0.001 kPa, $u(x_1)$ = $u(y_1)$ = 0.0005
Mole fractions $x_1$ and $y_1$ are on an *IL*-free-basis

addition to one $x - y - P$ data point, the Antoine equation parameters ($A$, $B$, and $C$) for the vapor pressures of the two pure components are also required. We used the data from the TRC Tables[6]. The vapor pressures were almost proportional to the ionic liquid concentration, but the quadratic equation fits the data perfectly (see Fig. 1). Therefore, the dependence of the vapor pressure $P°$ on the ionic liquid mole fraction in 2-methylpropan-2-ol mixtures can be expressed as

$$P° = p_2 x_{IL}^2 + p_1 x_{IL} + p_0 \qquad (4)$$

where the optimized coefficients $p_0$, $p_1$ and $p_2$ for the three isotherms are summarized in Table 4. No published vapor pressure data were found for this system. Equation (4) gives the saturated vapor pres-

Table 4 – *Optimized coefficients $p_0$, $p_1$, $p_2$ for the evaluation of saturated vapor pressures of the ionic liquid (IL) + 2-methyl-propan-2-ol system from equation (4)*

| $T$ (K) | $p_2$ | $p_1$ | $p_0$ |
|---|---|---|---|
| 333.15 | –35.1959 | –3.5179 | 39.1527 |
| 343.15 | –52.8819 | –8.2485 | 61.3384 |
| 353.15 | –82.5008 | –15.7610 | 92.8830 |

sure of the 2-methylpropan-2-ol + *IL* system for any ionic liquid concentration. The details of further processing are described in the previous work[1].

Tables 6 and 7 present simple polynomial expressions, similar to Equation (4), that can be used to evaluate the dependence of the adjustable parameters $b$ and $c$ on the concentration $x_{IL}$. Then, the Equations (1) to (3) make it easy to calculate the azeotropic behavior of mixtures containing a specified amount of ionic liquid.

## Discussion

The concept of "correlating the correlated values", as developed in our first paper[1], worked successfully despite the limited input data, namely, the vapor pressures of binary systems, one VLE data point with *IL* in the azeotropic region, and two vapor pressure points at both the concentration ends. Although any VLE data point is theoretically sufficient to correlate the phase equilibrium over the entire concentration range, it is more reliable to use the one not too far from the azeotrope for consistency.

The Redlich-Kister equation was chosen for its simplicity due to its polynomial form, which was the essential prerequisite for both the previous and present work. Fig. 4 shows that the calculated lines of azeotropic composition versus ionic liquid mole fraction differ slightly from the expected behavior at low ionic liquid concentrations. In the higher ionic
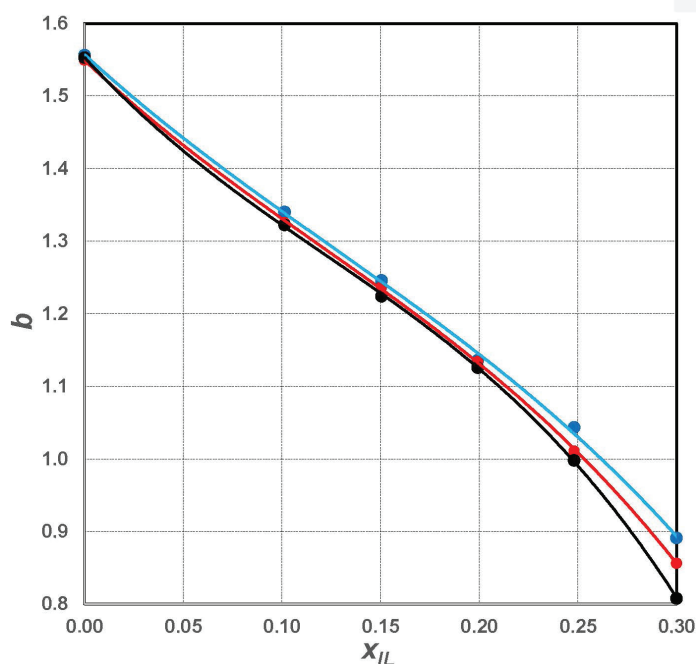
Fig. 2 – *Dependence of Redlich-Kister parameter b on the mole fraction of an ionic liquid at three isotherms. Experimental points:* ●— 333.15 K, ●— 343.15 K, ●— 353.15 K.

Table 5 – *Parameters of the Redlich-Kister equation for the 2-methylpropan-2-ol + water system in dependence on 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide concentration*

| $x_{IL}$ | $b$ | $c$ | $b$ | $c$ | $b$ | $c$ |
|---|---|---|---|---|---|---|
| | $T = 333.15$ K | | $T = 343.15$ K | | $T = 353.15$ K | |
| 0.0000 | 1.5566 | −0.4114 | 1.5498 | −0.4327 | 1.5530 | −0.4586 |
| 0.1013 | 1.3403 | −0.3361 | 1.3256 | −0.3447 | 1.3224 | −0.3581 |
| 0.1504 | 1.2461 | −0.2951 | 1.2371 | −0.3033 | 1.2243 | −0.3141 |
| 0.1992 | 1.1361 | −0.2565 | 1.1342 | −0.2673 | 1.1257 | −0.2768 |
| 0.2481 | 1.0436 | −0.2305 | 1.0111 | −0.2392 | 0.9981 | −0.2514 |
| 0.2999 | 0.8910 | −0.2009 | 0.8563 | −0.2087 | 0.8077 | −0.2195 |

$u(x_{IL}) = 0.001$

Table 6 – *Optimized polynomial coefficients $b_0$, $b_1$, $b_2$, $b_3$ for the evaluation of parameter b in the Redlich-Kister equation from Equation $b = b_3 x_{IL}^3 + b_2 x_{IL}^2 + b_1 x_{IL} + b_0$*

| $T$ (K) | $b_3$ | $b_2$ | $b_1$ | $b_0$ |
|---|---|---|---|---|
| 333.15 | −12.108 | 4.5745 | −2.4951 | 1.5570 |
| 343.15 | −5.5240 | 5.5609 | −2.5829 | 1.5494 |
| 353.15 | −24.806 | 9.0591 | −2.9669 | 1.5533 |

Table 7 – *Optimized polynomial coefficients $c_0$, $c_1$, $c_2$ for the evaluation of parameter c in the Redlich-Kister equation from equation $c = c_2 x_{IL}^2 + c_1 x_{IL} + c_0$*

| $T$ (K) | $c_2$ | $c_1$ | $c_0$ |
|---|---|---|---|
| 333.15 | −0.4779 | 0.8553 | −0.4130 |
| 343.15 | −0.7359 | 0.9695 | −0.4332 |
| 353.15 | −1.0740 | 1.1159 | −0.4588 |

liquid concentrations region, the dependence shows a faster convergence to the non-azeotropic state, i.e. to $x_{1az} = 1$.

## Conclusions

In conclusion, the thermodynamic description of the phase equilibrium in this complex system is very reasonable. The presented correlations and subsequent calculations accurately predict the effect of the ionic liquid used as an azeotrope breaker. Fig. 4 clearly shows that the azeotrope of the 2-methylpropan-2-ol (1) + water (2) system is eliminated at the mole fraction of an ionic liquid in the interval of the three investigated isotherms. Furthermore, it is now possible to calculate azeotropic data at any temperature within the investigated range and for
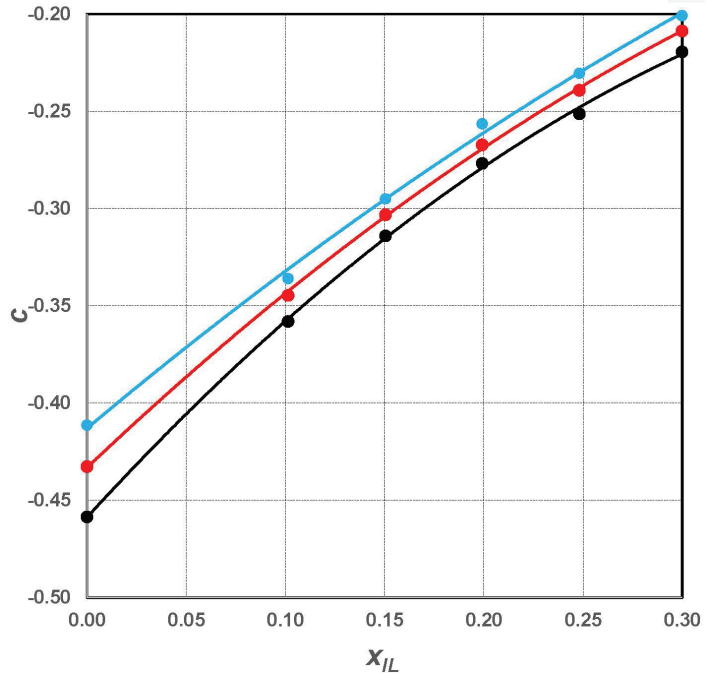


Fig. 3 – *Dependence of Redlich-Kister parameter c on the mole fraction of an ionic liquid at three isotherms. Experimental points:* ●— *333.15 K,* ●— *343.15 K,* ●— *353.15 K.*
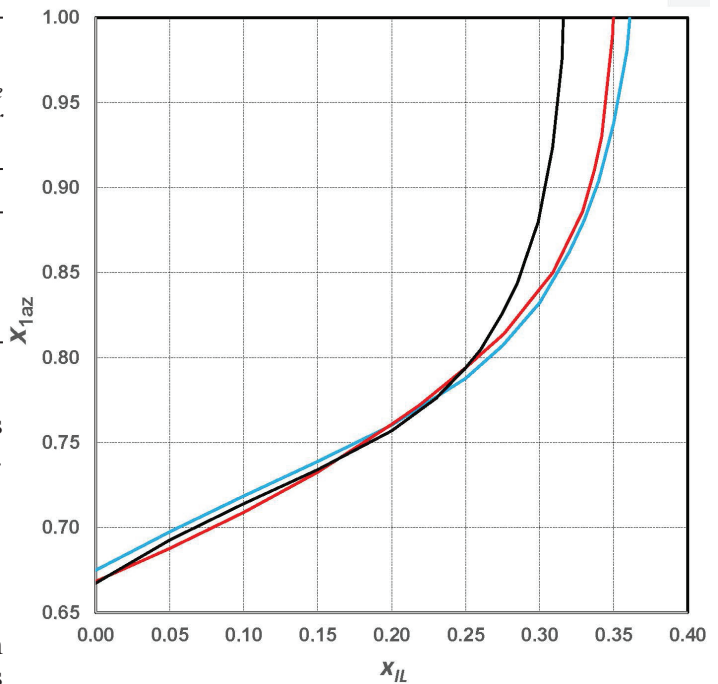


Fig. 4 – *Calculated dependence of the azeotrope composition, $x_{1az}$, of the 2-methylpropan-2-ol + water system on the mole fraction of ionic liquid, $x_{IL}$.* — *333.15 K,* — *343.15 K,* — *353.15 K*

any IL concentration using the evaluated relationships and simple interpolation. It is strongly believed that even a slight extrapolation would not result in a significant error.

## List of symbols and abbreviations

| | | |
|---|---|---|
| *az* | – | azeotrope |
| *A, B, C* | – | parameters of Antoine equation |
| *b, c* | – | parameters of Redlich-Kister equation |
| $b_i$ | – | constants of polynomial equation for *b* (Table 6) |
| $c_i$ | – | constants of polynomial equation for *c* (Table 7) |
| $\gamma_i$ | – | activity coefficient of component *i* |
| *P* | – | pressure |
| $P_i^\circ$ | – | saturated vapor pressure of pure component *i* |
| $p_i$ | – | constants of polynomial Equation (4) for saturated vapor pressure |
| $x_i$ | – | mole fraction of component *i* in liquid phase on *IL*-free-basis |
| $y_i$ | – | mole fraction of component *i* in vapor phase on *IL*-free-basis |
| *IL* | – | ionic liquid (here: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) |
| *u* | – | standard uncertainty of measured quantities |
| VLE | – | vapor-liquid equilibrium |

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