# Investigation of Water/Ethanol Mixture Separation by 2-Butanone and Diethyl Ether at 291.15 K: Experimental Results and Theoretical Correlation

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This study describes the separation of ethanol from an aqueous solution using liquid-liquid extraction. Two ternary systems, water–ethanol–2–butanone and water–ethanol–diethyl ether, were investigated at 291.15 K and atmospheric pressure using the cloud point method. Both ternary systems had a type 1 liquid-liquid equilibrium diagram. The experimental tie-line data were correlated using the non-random two-liquid (NRTL) thermodynamic model and the Hand correlation. The separation factors and distribution coefficients were calculated to evaluate the separation performance. The selectivity diagram was also used to determine the most suitable solvent for ethanol separation. Among the two solvents studied, diethyl ether exhibited the best capability for extracting ethanol from aqueous solution in this study.

*Keywords*

liquid-liquid extraction, ethanol, 2-butanone, diethyl ether, NRTL model, Hand correlation, selectivity

## Introduction

In the 21st century, alcohol-derived fuels have increasingly been recognised as a potential solution for promoting clean energy, aiming to combat climate change and limiting greenhouse gas emissions.[1] They are therefore recognised as valuable alternatives to fossil-derived liquid fuels[2] and as crucial components in the manufacture of other biofuels, including biodiesel and bioethers.[3] The most frequently used alcohol-based fuels are methanol, ethanol, and biobutanol.[1]

Ethanol is produced by fermenting agricultural products such as corn, sugarcane and manioc.[4,5] However, one of the main challenges is that bioethanol is produced in an aqueous solution and must be dehydrated before it can be used as fuel.[3] The recovery of anhydrous ethanol from the fermentation broth by distillation requires a considerable amount of energy.[6,7] Moreover, it is not possible to obtain a degree of purity greater than 95 % by distillation because of the azeotropic peak.[5] One possible method for achieving higher purity is liquid-liquid extraction, or solvent extraction. Solvent extraction processes provide considerable energy savings in the recovery of fermentation products and the separation of azeotropes.[7,8] The choice of highly selective and effective solvents is therefore important for such extraction processes.

Liquid-liquid equilibrium data are also necessary for the design and simulation of extraction processes. Previous studies have reported liquid-liquid equilibrium data (LLE) for ternary systems comprising ethanol and water with different solvents and at different temperatures.[3,9,10] However, no LLE data have previously been reported for the ternary systems of water–ethanol–solvent at 291.15 K. The selection for 291.15 K in this work represents realistic ambient operating conditions in industrial extraction units, allowing process performance to be evaluated without the energy penalty associated with artificial heating or cooling. Moreover, although more effective structural solvents exist for ethanol separation, diethyl ether and 2-butanone were strategically selected due to their high volatil-

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ity (boiling points of 34.6 °C and 79.6 °C, respectively).[11] This low boiling point drastically facilitates subsequent solvent recovery by low-temperature flash distillation, thereby minimising the overall thermal energy demand of the separation process. Regarding alternative separation methods, extractive or azeotropic distillations are widely applied but are highly energy-intensive and often involve highly toxic entrainers. Liquid-liquid extraction at 291.15 K can serve as an energy-efficient primary concentration step for dilute aqueous streams, such as fermentation broths, by avoiding the need to vaporise bulk water and enabling the design of less energy-intensive hybrid separation processes. Although several studies have investigated the liquid–liquid equilibrium (LLE) or vapor–liquid–liquid equilibrium (VLLE) of the ternary systems involving water–ethanol–2-butanone[12,13] and water–ethanol–diethyl ether[14,15] across various temperature ranges, experimental data at exactly 291.15 K remain unavailable in the literature. Although thermodynamic models with temperature-dependent parameters allow the mathematical extrapolation of LLE at lower temperatures, such predictive calculations often exhibit nonlinear deviations near the binodal curve due to the strengthening of competitive hydrogen bonding at 291.15 K. Therefore, the new experimental data reported herein provide a critical validation benchmark for verifying the accuracy of such simulated recalculations.

In this study, the LLE data for the two ternary systems: water–ethanol–2-butanone and water–ethanol–diethyl ether were experimentally determined at 291.15 K under atmospheric pressure using the cloud point method. The experimental LLE data for the ternary systems were correlated using the NRTL thermodynamic model and the Hand equation. The distribution coefficients and separation factors were calculated to assess the extraction capability of 2-butanone and diethyl ether for separating ethanol from aqueous solutions. A comparison of the two solvents, 2-butanone and diethyl ether, at 291.15 K was also performed. Thus, this study provides valuable insights for the design and simulation of water–ethanol separation processes.

## Experimental

### Materials

All materials used in this study were of analytical grade, as shown in Table 1. The purity of all materials was provided by the supplier and confirmed by refractive index measurements. Distilled water with a GFL 2001/4 distiller was used for all experiments.

### Experimental procedure

The solubility curves for the two ternary systems, water–ethanol–2-butanone and water–ethanol–diethyl ether, were determined at 291.15 K and atmospheric pressure using the cloud point method.[19] The cloud point of the water-rich phase or side was determined by titrating the binary water–ethanol mixture with the solvent (2-butanone or diethyl ether). The mixture was stirred in a glass equilibrium vessel fitted with an isothermal double jacket to maintain a constant temperature. The equilibrium vessel was magnetically agitated, and the temperature was measured using a mercury thermometer with a precision of ± 0.1 K. The cloud point of the solvent-rich phase or side was obtained by titrating the binary solvent–ethanol mixture with water in the same equilibrium vessel. The endpoint of titration was determined by observing the transition of the mixture from a clear to a turbid state. Cloud-point stability was verified by allowing the mixture to stand for five minutes at the endpoint. The refractive index ($n_D$) of the turbid mixtures, representing points on the mutual-solubility curve, was measured using a refractometer type OPTi® Digital Handheld ± 0.2 Brix and recorded as a function of composition. The mixtures were carefully weighed using an analytical precision balance (KERN ABJ220-4NM) with an accuracy of ±0.0001 g.

The tie-line data were obtained by vigorously mixing a known compositions of the pure components (water, ethanol, and solvent) in the equilibrium vessel, which was maintained at a constant temperature of 291.15 K for 2 h. The mixtures were then allowed to stand for 24 h until two phases,

Table 1 – *Physicochemical of the pure materials*

| Component | Supplier | Purity (%) | Molecular weight (g mol$^{-1}$) | Density (kg m$^{-3}$) | Refractive index ($n_D$) | |
|---|---|---|---|---|---|---|
| | | | | | Exp | Lit |
| Ethanol | Biochem | 99.9 | 46.07 | 0.789 | 1.3640 | 1.3621 [16] |
| 2-Butanone | Honeywell | ≥ 99 | 72.11 | 0.805 | 1.3800 | 1.3768 [17] |
| Diethyl ether | Merck | ≥ 99.5 | 74.12 | 0.714 | 1.3560 | 1.3524 [15] |
| Water | – | – | 18.02 | 1.000 | 1.3329 | 1.3330 [18] |

aqueous and organic, appeared at equilibrium. Samples were subsequently taken from each phase at equilibrium, and the refractive index of the two phases, in equilibrium, was measured. Three independent samples were taken from each phase and subsequently measured to ensure repeatability.

### Standard deviation

To evaluate the uncertainty of the measurement, the standard deviation was determined in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM).[20] The appropriate calculation formulas are given as follows:[20,21]

$$\overline{q} = \frac{1}{n}\sum_{k=1}^{n} q_k \tag{1}$$

$$S^2 = \frac{\sum_{j=1}^{n}\left(q_j - \overline{q}\right)^2}{n-1} \tag{2}$$

$$u^2 = \frac{S^2}{n} \tag{3}$$

where $S$ represents the experimental standard deviation, $u$ is the standard uncertainty, $n$ is the number of experiments, $q_j$ is to the $j^{th}$ experimental value, $\overline{q}$ is the average value of $q_k$ (of the experiments).

## Results and discussion

### Liquid-liquid equilibrium results

Tables 2—3 list the data for the solubility curves and the experimental tie lines for the ternary systems water–ethanol–2-butanone, water–ethanol–diethyl ether at 291.15 K under atmospheric pressure, where $w_i^{I}$ and $w_i^{II}$ refer to mass fraction of the $i$th component in the water-rich phase (aqueous or raffinate phase) and solvent-rich phase (organic or extract phase), respectively.

The phase diagrams of the ternary systems water–ethanol–2-butanone and water–ethanol–diethyl ether are presented in Figs. 1 and 2. As classified by Treybal,[22] the two ternary systems studied exhibited type I behaviour. Indeed, two distinct regions can be identified: one homogeneous and the other heterogeneous, separated by the solubility curve. Both water–2-butanone and water–diethyl ether were partially miscible, while the liquid pairs ethanol–water and ethanol–solvent were miscible.

The tie-lines in Figs. 1 and 2 have a positive slope towards the solvent-rich phase, indicating that both solvents, 2-butanone and diethyl ether, have greater affinity for ethanol than for water. Therefore, both 2-butanone and diethyl ether are suitable for the liquid–liquid extraction of ethanol from aqueous solutions.

Table 2 – *Experimental binodal-curve data in mass fractions for water (1)- ethanol (2)- 2- butanone or diethyl ether (3) ternary systems at 291.15 K*

| water (1)-ethanol (2)- 2-butanone (3) | | | water (1)-ethanol (2)- diethyl ether (3) | | |
|---|---|---|---|---|---|
| $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ |
| 0.7564 | 0.0000 | 0.2436 | 0.8751 | 0.0000 | 0.1249 |
| 0.6888 | 0.0340 | 0.2772 | 0.8321 | 0.0492 | 0.1187 |
| 0.6403 | 0.0565 | 0.3032 | 0.7789 | 0.0904 | 0.1307 |
| 0.5966 | 0.0672 | 0.3362 | 0.6992 | 0.1491 | 0.1517 |
| 0.5456 | 0.0828 | 0.3716 | 0.6396 | 0.1893 | 0.1711 |
| 0.4994 | 0.0985 | 0.4021 | 0.5652 | 0.2169 | 0.2179 |
| 0.4492 | 0.1042 | 0.4466 | 0.4547 | 0.2314 | 0.3139 |
| 0.3865 | 0.1080 | 0.5055 | 0.3467 | 0.2303 | 0.4230 |
| 0.3005 | 0.0948 | 0.6047 | 0.2341 | 0.2010 | 0.5649 |
| 0.2440 | 0.0825 | 0.6735 | 0.1639 | 0.1616 | 0.6745 |
| 0.2205 | 0.0696 | 0.7099 | 0.1289 | 0.1356 | 0.7355 |
| 0.1628 | 0.0413 | 0.7959 | 0.0984 | 0.0870 | 0.8146 |
| 0.1092 | 0.0115 | 0.8793 | 0.0579 | 0.0527 | 0.8894 |
| 0.0765 | 0.0000 | 0.9235 | 0.0273 | 0.0000 | 0.9727 |
| [a]Standard uncertainties u are u($T$) = 0.1 K, u($w_1$) = 0.06 %, u($w_2$) = 0.009 %, u($w_3$) = 0.064 % | | | [a]Standard uncertainties u are u($T$) = 0.1 K, u($w_1$) = 0.54 %, u($w_2$) = 0.34 %, u($w_3$) = 0.80 % | | |

Table 3 – *Experimental tie-line data in mass fractions for water (1)- ethanol (2)-2- butanone or diethyl ether (3) ternary systems at 291.15 K*

| water (1) -ethanol (2) -2-butanone (3) | | | | | |
|---|---|---|---|---|---|
| Water-rich phase (raffinate phase) | | | Butanone-2-rich phase (extract phase) | | |
| $w_1^I$ | $w_2^I$ | $w_3^I$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ |
| 0.7503 | 0.0062 | 0.2435 | 0.1750 | 0.0452 | 0.7798 |
| 0.7459 | 0.0092 | 0.2449 | 0.2072 | 0.0604 | 0.7324 |
| 0.7436 | 0.0107 | 0.2457 | 0.2313 | 0.0749 | 0.6938 |
| 0.7419 | 0.0121 | 0.2460 | 0.2411 | 0.0814 | 0.6775 |
| 0.7382 | 0.0148 | 0.2470 | 0.2834 | 0.0912 | 0.6254 |
| 0.7332 | 0.0183 | 0.2485 | 0.3024 | 0.1014 | 0.5962 |

[a]Standard uncertainties u are u($T$) = 0.1 K, u($w_1$) = 0.19 %, u($w_2$) = 0.002 %, u($w_3$) = 0.20 % in raffinate phase, u($w_1$) = 0.019 %, u($w_2$) = 0.019 %, u($w_3$) = 0.0039 % in extract phase.

| water (1)-ethanol (2)- diethyl ether (3) | | | | | |
|---|---|---|---|---|---|
| Water rich phase (raffinate phase) | | | Diethyl ether rich phase (extract or phase) | | |
| $w_1^I$ | $w_2^I$ | $w_3^I$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ |
| 0.8564 | 0.0249 | 0.1187 | 0.0456 | 0.0482 | 0.9062 |
| 0.8388 | 0.0425 | 0.1187 | 0.0955 | 0.0805 | 0.8240 |
| 0.8135 | 0.0637 | 0.1228 | 0.1102 | 0.1063 | 0.7835 |
| 0.7886 | 0.0809 | 0.1305 | 0.1278 | 0.1335 | 0.7387 |
| 0.7584 | 0.1063 | 0.1353 | 0.1792 | 0.1708 | 0.6500 |
| 0.7243 | 0.1304 | 0.1453 | 0.2363 | 0.1955 | 0.5682 |

[a]Standard uncertainties u are u($T$) = 0.1 K, u($w_1$) = 0.99 %, u($w_2$) = 0.039 %, u($w_3$) = 0.13 % in raffinate phase, u($w_1$) = 0.079 %, u($w_2$) = 0.019 %, u($w_3$) = 0.099 % in extract phase.

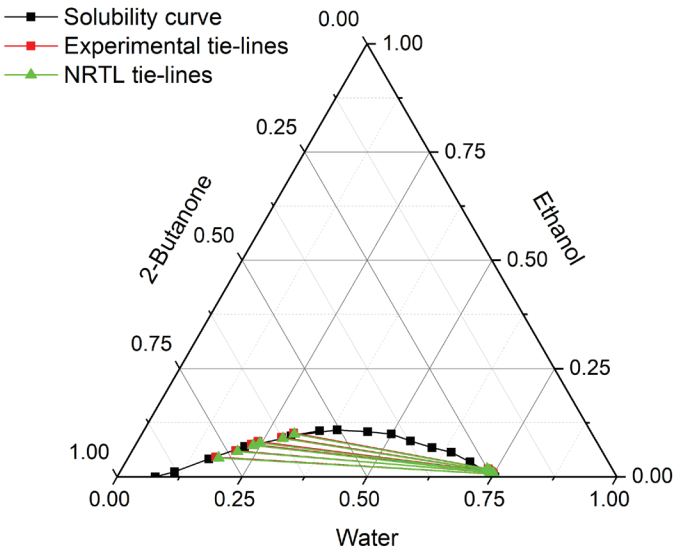



Fig. 1 – *LLE phase diagram for water (1) – ethanol (2) – 2-butanone (3) system at 291.15 K*

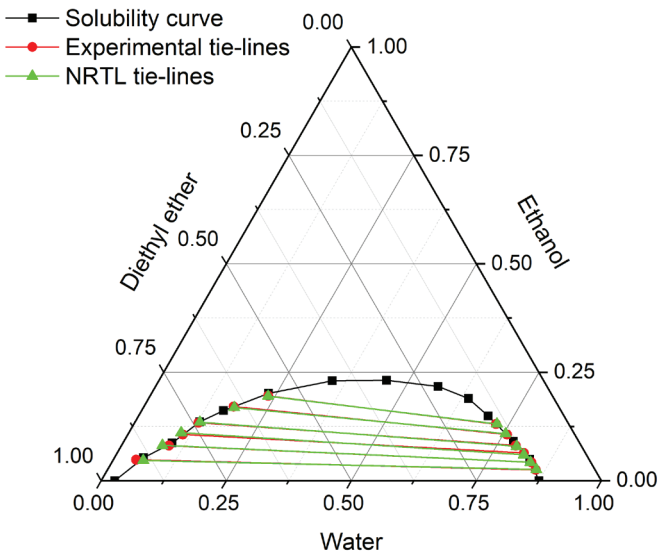



Fig. 2 – *LLE phase diagram for water (1) – ethanol (2) – diethyl ether (3) system at 291.15 K*

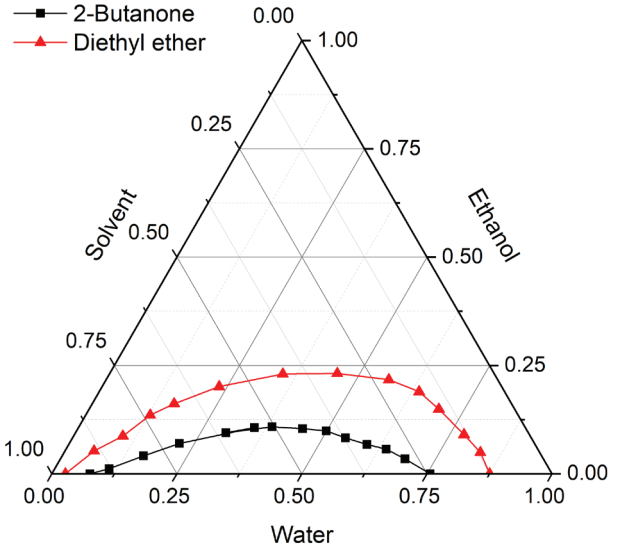



Fig. 3 – *Ternary LLE diagrams at 291.15 K for the water–ethanol–2-butanone and water–ethanol–diethyl ether systems*

Fig. 3 shows a graphical comparison of the solubility curves of the two systems studied. The surface area of the immiscibility region decreases in the following order: diethyl ether > 2-butanone.

A decrease in the solvent dielectric constant polarity (dielectric constants $e_{2\text{–butanone}} = 18.56$, $e_{\text{diethyl ether}} = 4.27$)[11] led to an increase in the area of the two-phase region (heterogeneous phase), reflecting a reduction in mutual solubility of the components (high dielectric constants indicate increased solvent polarity). Furthermore, water was more soluble in the (2-butanone–ethanol) mixture than in the (diethyl ether–ethanol) mixture.

## Liquid-liquid equilibrium calculation (correlation)

The non-random two-liquid (NRTL) equation was developed by Renon and Prausnitz;[23] it is widely used in chemical thermodynamic studies to calculate phase equilibrium and analyse material behavior.[24] This model accurately reproduces the experimental data. For multi-component systems, the NRTL model is represented by the following equations:

$$\ln\gamma_i = \frac{\sum_{j=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n}G_{ki}x_k} + \sum_{j=1}^{n}\frac{x_jG_{ij}}{\sum_{k=1}^{n}G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{i=1}^{n}x_i\tau_{ij}G_{ij}}{\sum_{k=1}^{n}G_{kj}x_k}\right) \quad (4)$$

$$G_{ij} = \exp\left(-\alpha_{ji}\tau_{ji}\right), \quad (\alpha_{ij} = \alpha_{ji}) \quad (5)$$

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

where $g_{ji}$–$g_{ii}$ are the fitting interaction parameters, and $\alpha_{ij}$ is the non-randomness parameter which was fixed at 0.2.

The quality of the fit was verified by calculating the root mean square deviation (RMSD) according to the following Equation:[24]

$$\text{RMSD} = \left[\frac{\sum_{k=1}^{M}\sum_{j=1}^{2}\sum_{i=1}^{3}\left(x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}}\right)^2}{6M}\right]^{1/2} \quad (7)$$

The binary interaction parameters for the NRTL model were estimated from the experimental LLE data by minimising a suitable objective function (Equation 8), defined as the difference between the squared experimental and calculated mole fractions for each of the components.[25,26]

$$\text{OF} = \sum_{k=1}^{M}\sum_{j=1}^{2}\sum_{i=1}^{3}\left(x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}}\right)^2 \quad (8)$$

where $x_{ijk}^{\text{exp}}$ represents the experimental mole fraction, $x_{ijk}^{\text{cal}}$ is the calculated mole fraction, *i, j* and *k* represent the component, phase, and tie-line, respectively, and *M* represents the number of tie-lines.

The RMSD value and all binary interaction parameters obtained for the ternary systems studied using the NRTL model are given in Table 4.

The tie-line data calculated using the NRTL model are also provided in Figs. 1 and 2. These figures show good agreement between the experimental and calculated (predicted) tie-line data.

To ensure the physical reliability and mathematical robustness of the regressed binary interaction parameters presented in Table 4, a global thermodynamic stability analysis was carried out. Following the topological criteria and methodology

Table 4 – *NRTL parameters and root-mean-square deviation (RMSD) for water-ethanol- solvents systems studied at 291.15 K*

| Component | | | RMSD |
|---|---|---|---|
| *i-j* | $A_{ij}$ | $A_{ji}$ | |
| water (1)-ethanol (2)-2-butanone (3) | | | |
| 1–2 | 7.363 | –3.363 | |
| 1–3 | 1.602 | 18.166 | $3.449\cdot10^{-2}$ |
| 2–3 | 1.600 | 0.301 | |
| water (1)-ethanol (2)-diethyl ether (3) | | | |
| 1–2 | 4.354 | –0.718 | |
| 1–3 | 4388.734 | 5.840 | $8.099\cdot10^{-2}$ |
| 2–3 | 3.089 | –3.384 | |

Table 5 – *Constants of Hand correlation for the ternary systems water – ethanol -solvents*

| Hand correlation | | | |
|---|---|---|---|
| Solvent | *a* | *b* | $R^2$ |
| 2-butanone | 1.8315 | 0.9626 | 0.9806 |
| diethyl ether | 0.6279 | 1.0077 | 0.9949 |

emphasized in recent literature,[27] the Gibbs energy of mixing expressions was evaluated over the complete range of operational compositions.

The analysis confirmed that the calculated NRTL parameters reliably described the phase behaviour of the studied systems without generating false solutions or spurious phase splits (Figs. S1-S6 of the Supplementary Information, available from the authors upon request).

To further verify the experimental methodology employed in this study, the measured liquid–liquid equilibrium (LLE) data at 291.15 K were benchmarked against available literature values for the exact same ternary systems at temperatures close to the experimental temperature.

For the water (1) –ethanol (2) –diethyl ether (3) system, the experimental binodal curve was evaluated alongside the literature values reported by Merzougui et *al.*[15] at a slightly higher temperature of 293.15 K (Fig. S7 of the Supplementary Information, available from the authors upon request).

Both datasets consistently exhibit a Type I behaviour according to Treybal's[22] classification, with a single partially miscible binary pair (water–diethyl ether). The systematic overlay displays excellent geometric harmony and strict parallelism between the two binodal curves.

The high proximity and topographical agreement of the experimental points across this narrow temperature interval ($\Delta T$ = 2 K) successfully confirmed the accuracy and reproducibility of the cloud-point technique used in this study.

For the water (1) –ethanol (2) –2-butanone (3) system, the comparative analysis with the data of Katayama and Amano[12] at 298.15 K and 308.15 K revealed a distinct temperature-dependent behaviour (Fig. S8 of the Supplementary Information, available from the authors upon request). As the temperature decreased to our experimental condition of 291.15 K, a noticeable shrinkage of the heterogeneous two-phase region was observed, resulting in a lower binodal curve profile. This trend is in perfect agreement with the well-known thermophysical behaviour of the binary water–2-butanone system, which exhibited an inverse mutual solubility relationship within this temperature range. At lower temperatures, the mutual solubility between water and 2-butanone increased, thereby requiring a significantly lower concentration of ethanol to completely homogenize the ternary system. This logical thermodynamic sequence and smooth continuity with established literature curves provide strong evidence for the soundness and validity of our experimental measurements.

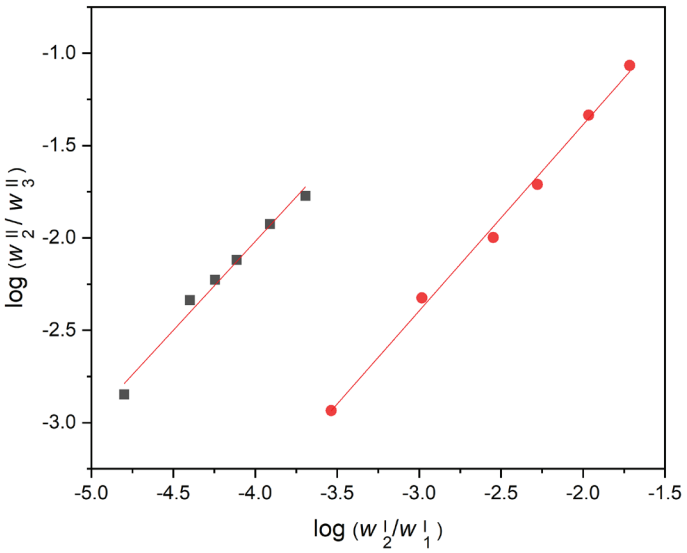



Fig. 4 – *Hand plots of ternary systems at T = 291.15 K*

Hand correlation was used additionally to test the experimental tie-line data, defined as follows[17,28]

$$\log\left(\frac{w_2^{II}}{w_3^{II}}\right)=a+b\log\left(\frac{w_2^{I}}{w_1^{I}}\right) \tag{9}$$

where $a$ and $b$ are the parameters of Hand (the fitting parameters), $w$ is the mass fraction, subscripts 1, 2, and 3 correspond to water, ethanol and solvent, respectively, and superscripts I and II refer to the water-rich phase (raffinate) and the solvent-rich phase (extract).

The fitting parameters for Equation (9) for each studied system are presented in Table 5. The Hand plots are shown in Fig. 4. The high linearity in Hand plots, in addition to the high values of regression factors, confirmed the absence of serious flaws or outliers in the experimental tie-line data.

## Efficiency of ethanol extraction

The efficiency of ethanol extraction from aqueous solutions using 2-butanone and diethyl ether as solvents is determined in terms of the separation factor ($S$) as follows:[29]

$$S=\frac{D_1}{D_2}=\frac{w_{23}/w_{13}}{w_{21}/w_{11}} \tag{10}$$

where $D_1$ and $D_2$ are the distribution coefficients of ethanol and water, respectively, $w_{23}$ and $w_{13}$ are the mass fractions of ethanol and water in the sol-

vent-rich phase, respectively, $w_{21}$ and $w_{11}$ are the mass fractions of ethanol and water in the water-rich phase.

The experimental results for the separation factors and distribution coefficients are shown in Table 6.

The separation factor values are greater than 1 (varying between 4.6 and 36.3), meaning that the solvents were more selective for the solute than for the diluent. Thus, the extraction of ethanol using 2-butanone and diethyl ether is feasible. Higher separation factors were achieved with the diethyl ether system, suggesting a superior quantitative separation capacity. To evaluate this behaviour, solvent-free selectivity diagrams were generated by plotting, in rectangular coordinates, the solute composition in the solvent-rich phase (extract) against the solute composition in the water-rich phase (raffinate) without the solvent, for each ternary system (Fig. 5). Fig. 5 reveals that both solvents exhibit close and comparable selectivity profiles across the composition range. The higher numerical values of the separation factors, combined with the wider immiscibility gap of the ether-containing system, indicate that diethyl ether offers a slight advantage for the primary concentration of ethanol from aqueous solutions under the conditions studied.

To evaluate the industrial applicability and extraction efficiency of the solvents investigated in this work (2-butanone and diethyl ether at 291.15 K), their thermodynamic performance was compared with that of alternative solvents reported in the literature at similar temperatures (293.15 K and 303.2 K). The benchmarked systems included 3-methyl-1-butanol;[30] 1-octanol, methyl isobutyl ketone (MIBK), ethyl acetate;[5] and the hydrophobic ionic liquid 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([dmim][Tf2N]).[31] The corresponding comparative plots for the distribution coefficient ($D_2$) and separation factor ($S$), expressed on a mass fraction basis, are provided in Figs. S9 and S10 of the Supplementary Information, available from the authors upon request.

As illustrated in Fig. S9, diethyl ether exhibits an high distribution coefficient for ethanol ($D_2$), ranging from 5.5 to 7.3, significantly outperforming

Table 6 – *Experimental distribution coefficients of the (ethanol and water) and separation factors for the ternary systems water (1)-ethanol (2)-solvents (3)*

| water (1)-ethanol (2)- 2-butanone (3) | | |
|---|---|---|
| $D_1$ | $D_2$ | $S$ |
| 7.2903 | 0.2332 | 31.2620 |
| 6.5652 | 0.2778 | 23.6328 |
| 7.0000 | 0.3111 | 22.5008 |
| 6.7273 | 0.3250 | 20.6994 |
| 6.1622 | 0.3839 | 16.0516 |
| 5.5410 | 0.4124 | 13.4360 |
| water (1)-ethanol (2)- diethyl ether (3) | | |
| 1.9322 | 0.0532 | 36.3195 |
| 1.8968 | 0.1138 | 16.6678 |
| 1.6696 | 0.1354 | 12.3309 |
| 1.6500 | 0.1621 | 10.1789 |
| 1.6073 | 0.2363 | 6.8019 |
| 1.4987 | 0.3263 | 4.5930 |

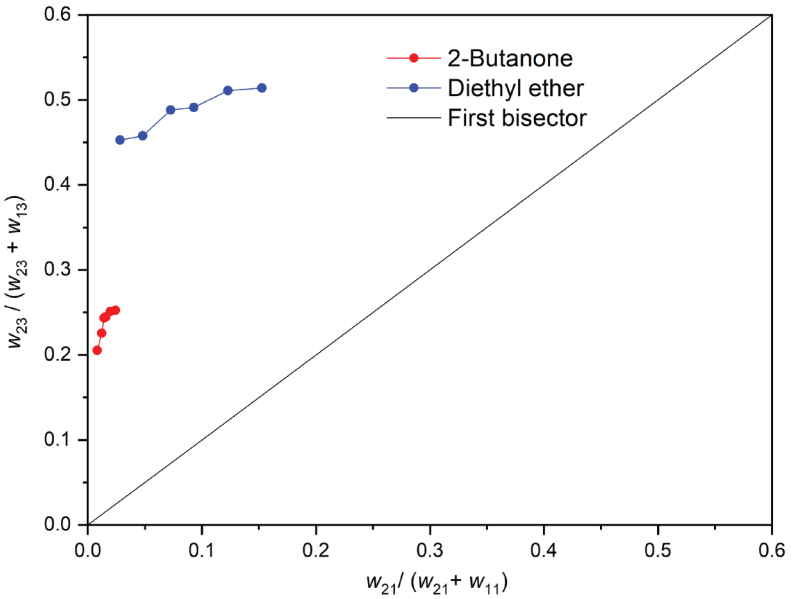



Fig. 5 – *Solvent-free selectivity diagram of water–ethanol–solvents at 291.15 K*

all other solvents considered. For 2-butanone, the distribution coefficient was comparable to those of conventional organic solvents.

In terms of separation capability (Fig. S10), diethyl ether demonstrates remarkably high separation factors in the dilute region. While MIBK maintains competitive selectivity at intermediate concentrations, the separation factor of 2-butanone is comparable to those of conventional organic solvents reported in the literature, particularly in the high-concentration region where its selectivity aligns with the general decreasing trend observed for alternative extraction solvents. The solvents investigated in this study offer a balance between a high distribution coefficient and high selectivity, specifically in the case of diethyl ether. This outstanding selectivity guarantees the extraction of ethanol with highly minimised water co-extraction, which is a crucial requirement to efficiently bypass the water–ethanol azeotrope.

## Conclusion

In this study, the liquid-liquid equilibrium for ternary systems water–ethanol–2-butanone and water–ethanol–diethyl ether was investigated at $T$ = 291.15 K and atmospheric pressure. According to the experimental results, both ternary systems exhibit type I behaviour according to the Treybal classification. The heterogeneous region decreases in the follow order: diethyl ether > 2-butanone, which is consistent with the higher mutual solubility of 2-butanone and water compared to diethyl ether. The positive slope of the tie-lines for the two studied systems towards the solvent-rich phase shows that both solvents are suitable for extraction of ethanol.

The NRTL model was used to predict the experimental data, where good agreement was found between the experimental and calculated tie-line data with an average RMSD of $3.449 \cdot 10^{-2}$ and $8.099 \cdot 10^{-2}$ for the ternary systems water-ethanol-2-butanone and water-ethanol-diethyl ether, respectively. The experimental tie-line data (LLE data) were verified by the Hand equation. All separation factors exceeded unity. The higher separation factor values, reaching a maximum of 36.3, reflect that diethyl ether is an effective solvent for extracting ethanol from its aqueous solution among the investigated systems, as confirmed by the solvent-free selectivity diagram.

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### Nomenclature

$a, b$ – Hand's parameters
$D_1$ – distribution coefficients of ethanol
$D_2$ – distribution coefficients of water
$g$ – fitting parameters
$i$ – component
$j$ – experience; phase
$k$ – tie-line
OF – objective function
$\overline{q}$ – average values of the experiments, $q_k$
$R^2$ – regression factor
$S$ – separation factor
$T$ – temperature
$u$ – standard uncertainty
$w$ – mass fraction
$x$ – mole fraction
$\alpha$ – non-randomness parameter
$\varepsilon$ – dielectric constant

### Abbreviations

NRTL – non-random two-liquid
RMSD – root mean square deviation

### References

1. *Yun, Y.,* Alcohol Fuels: Current Technologies and Future Prospect, IntechOpen, London, 2020, pp 45–47. doi: https://doi.org/10.5772/intechopen.77645
2. *Erdiwansyah, Mamat, R., Sani, M. S. M., Sudhakar, K., Kadarohman, A., Sardjono, R. E.,* An overview of higher alcohol and biodiesel as alternative fuels in engines, Energy Reports **5** (2019) 467. doi: https://doi.org/10.1016/j.egyr.2019.04.009
3. *Mejía, A., Cartes, M., Chaparro, G.,* Isobaric vapor –liquid –liquid equilibrium for water + MTBE + alcohol (ethanol or 1-butanol) mixtures, Fluid Phase Equilib. **523** (2020) 112768. doi: https://doi.org/10.1016/j.fluid.2020.112768
4. *Coelho, S. T., Goldemberg, J.,* Alternative transportation Fuels: Contemporary case studies, Encycl. Energy **1** (2004) 67. doi: https://doi.org/10.1016/B0-12-176480-X/00177-7
5. *Bacha, O., Baka, O., Hasseine, A., Korichi, M., Selloum, D., Henni, A.,* A Comparative study on water and ethanol separation mixture by different solvents: New experimental and correlation data, Phys. Chem. Res. **9** (2012) 689. doi: https://doi.org/10.22036/PCR.2021.274620.1890
6. *Rahman, M. A., Rahman, M. S., Nabi, M. N., Rahman, M. M. S., Azad, M. A. K.,* Extraction of ethanol from aqueous solution using 1-hexanoic acid and 1-nonanoic acid, Khulna Univ. Stud. **9** (2008) 41. doi: https://doi.org/10.53808/kus.2008.9.1.0725-1
7. *Kirbaslar, I., Cehreli, S., Ustun, D., Keskinocak, E.,* Equilibrium data on ethanol-water-solvent ternaries, Braz. J. Chem. Eng. **17** (2000). doi: https://doi.org/10.1590/S0104-66322000000200007

8. *Zhu, Z., Bai, W., Xu, Y., Gong, H., Wang, Y., Xu, D., Gao, J.*, Liquid-liquid extraction of methanol from its mixtures with hexane using three imidazolium-based ionic liquids, J. Chem. Thermodyn. **138** (2019) 189. doi: https://doi.org/10.1016/j.jct.2019.06.024
9. *Follegatti-Romero, L. A., Lanza, M., Batista, F. R. M., Batista, E. A. C., Oliveira, M. B., Coutinho, J. A. P., Meirelles, A. J. A.,* Liquid-liquid equilibrium for ternary systems containing ethyl esters, anhydrous ethanol and water at 298.15, 313.15, and 333.15 K, Ind. Eng. Chem. Res. **49** (2010) 12613. doi: https://doi.org/10.1021/ie101611j
10. *Cháfer, A., Lladosa, E., Montón, J. B., De la Torre, J.,* Measurements and correlation of liquid-liquid equilibria of 4-methyl-2-pentanone + ethanol + water and 4-methyl-2-pentanone + n-butanol + water ternary systems between 283.2 and 323.2 K, Fluid Phase Equilib. **317** (2012) 89. doi: https://doi.org/10.1016/j.fluid.2012.01.009
11. *Haynes, W. M.*, CRC Handbook of Chemistry and Physics, 97th Ed., CRC Press, Boca Raton, FL, USA, 2016.
12. *Katayama, H., Amano, K.,* Liquid-liquid equilibria of three ternary systems: water+2-butanone+ aliphatic alcohols (ethanol, 2-propanol and 1-propanol), J. Chem. Eng. Jpn. **38** (2005) 459. doi: https://doi.org/10.1252/jcej.38.459
13. *Brits, L., Kouakou, A. C., Burger, A. J., Schwarz, C. E.,* Isobaric vapor−liquid−liquid phase equilibria measurements of three ternary water + 2-butanone + aliphatic alcohol (ethanol, 1-propanol, 2-propanol) systems at 101.3 kPa, J. Chem. Eng. Data. **62** (2017) 1767. doi: https://doi.org/0.1021/acs.jced.6b00725
14. *Qasim, F., Choi, H. C., Shin, J. S., Park, S. J.,* Liquid-liquid equilibrium data for water-ethanol-entrainer ternary system with entrainers: Cyclohexane, n-pentane, DEE (diethyl ether), DIPE (di-isopropyl ether), ETBE (ethyl tert-butyl ether), Korean J. Chem. Eng. **33** (2016) 2179. doi: https://doi.org/10.1007/s11814-016-0066-x
15. *Merzougui, A., Hasseine, A., Kabouche, A., Korichi, M.,* LLE for the extraction of alcohol from aqueous solutions with diethyl ether and dichloromethane at 293.15 K, parameter estimation using a hybrid genetic based approach, Fluid Phase Equilib. **309** (2011) 161. doi: https://doi.org/10.1016/j.fluid.2011.07.011
16. *Lide, D. R., Baysinger, G., Berger, L. I.,* CRC handbook of chemistry and physics, J. Am. Chem. Soc. **129** (2007) 724. doi: https://doi.org/10.1021/ja069813z
17. *Pereiro, A. B., Rodrõ Âguez, A.,* Ternary liquid-liquid equilibria ethanol + 2-butanone + 1-butyl-3-methylimidazolium hexafluorophosphate, 2-propanol + 2-butanone + 1-butyl-3-methylimidazolium hexafluorophosphate, and 2-butanone + 2-propanol + 1,3-dimethylimidazolium methyl sulfate at 298.15 K, J. Chem. Eng. Data. **52** (2007) 2138. doi: https://doi.org/10.1021/je700119m
18. *Trofimova, M., Sadaev, A., Samarov, A., Golikova, A., Tsvetov, N., Toikka, M., Toikka, A.,* Liquid-liquid equilibrium of acetic acid – ethanol – ethyl acetate – water quaternary system: Data review and new results at 323.15 K and 333.15 K, Fluid Phase Equilib. **503** (2020) 112321. doi: https://doi.org/10.1016/j.fluid.2019.112321
19. *Rogers, D. W., Scher, J.,* Cloud-point analysis of microlitre samples—determination of water in six common solvents, Talanta **16** (1969) 1579. doi: https://doi.org/10.1016/0039-9140(69)80219-5
20. JCGM. 100:2008., GUM 1995 with Minor Corrections. Evaluation of Measurement Data-Guide to the Expression of Uncertainty in Measurement, JCGM. 2008, pp 08—10. doi: https://doi.org/10.59161/JCGM100-2008E
21. *Borecka, M., Bielińska, A. B., Siedlewicz, G., Kornowska, K., Kumirska, J., Stepnowski, P., Pazdro, K.,* A new approach for the estimation of expanded uncertainty of results of an analytical method developed for determining antibiotics in seawater using solid-phase extraction disks and liquid chromatography coupled with tandem mass spectrometry technique, J. Chromatogr. A. **1304** (2013) 138. doi: https://doi.org/10.1016/j.chroma.2013.07.018
22. *Treybal, R. E.*, Liquid Extraction, First Ed. McGraw-Hill., New York, 1951, pp 12–18.
23. *Renon, H., Prausnitz, J. M.,* Local composition in thermodynamic excess functions for mixtures, AICHE J. **14** (1968) 135. doi: https://doi.org/10.1002/aic.690140124
24. *Yang, L., Xing, S., Teng, X., Liu, R., Wang, Z., Lin, B., Lv, P., Al-Haimi, A. A. N. M., Yehia, F., Luo, W.,* Liquid–liquid equilibrium behavior of ternary systems comprising biodiesel + glycerol and triglyceride + methanol: Experimental data and modelling, Catalysts **14** (2024) 320. doi: https://doi.org/10.3390/catal14050320
25. *Cháfer, A., De la Torre, J., Loras, S., Montón, J. B.,* Study of liquid–liquid extraction of ethanol + water azeotropic mixtures using two imidazolium-based ionic liquids, J. Chem. Thermodyn. **118** (2018) 92. doi: https://doi.org/10.1016/j.jct.2017.11.006
26. *Ruszczyński, Ł., Zubov, A., O'Connell, J. P., Abildskov, J.,* Reliable correlation for liquid–liquid equilibria outside the critical region, J. Chem. Eng. Data. **62** (2017) 2842. doi: https://doi.org/10.1021/acs.jced.7b00164
27. *Marcilla, A., Reyes-Labarta, J. A., Olaya, M. M.,* Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication, Fluid Phase Equilib. **476** (2018) 202. doi: https://doi.org/10.1016/j.fluid.2016.11.009
28. *Hand, D. B.,* Dineric distribution, J. Phys. Chem. **34** (1930) 1961. doi: https://doi.org/10.1021/j150315a009
29. *Stoicescu, C., Ulian, O., Isopescu, R.,* Liquid-liquid phase equilibria of (1-propanol + water + n-alcohol) ternary systems at 294.15 k. I. 1-propanol + water + 1-butanol or 1-pentanol or 1-hexanol, Rev. Roum. Chim. **56** (2011) 553.
30. *Kadir, S., Decloux, M., Giampaoli, P., Joulia, X.,* Liquid–liquid equilibria of the ternary systems 3-methyl-1-butanol + ethanol + water and 2-methyl-1-propanol + ethanol + water at 293.15 K, J. Chem. Eng. Data. **53** (2008) 910. doi: https://doi.org/10.1021/je700558x
31. *Cumplido, M. P., de la Torre, J., Arango, M. C., Cerisuelo, J. P., Chafer, A.,* Study of the viability of separating mixtures of water–bioethanol using a neoteric solvent: 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, Processes **13** (2025) 580. doi: https://doi.org/10.3390/pr13020580