



Measurement and correlation of phase equilibria for ternary aqueous mixtures of two carboxylic acids with isobutyl acetate at T= 298.2 K

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Abstract

Experimental tie-line results and phase diagrams were obtained for the ternary systems of [water + carboxylic acids + isobutyl acetate] at T=298.2 K and atmospheric pressure. The carboxylic acids were propionic acid and butyric acid. These two ternary systems exhibit type-1 behavior of LLE. The experimental tie-line data were also compared with those correlated by the UNIQUAC and NRTL models. The consistency of the values of the experimental tie-lines was determined through the Hand correlation equation. Distribution coefficients and separation factors were evaluated over the immiscibility regions and a comparison of the extracting capabilities of the isobutyl acetate was made with respect to distribution coefficients and separation factors.

Keywords: LLE data, Ternary mixture, NRTL model, UNIQUAC model, Extraction processes.

Introduction

Liquid-phase equilibrium data of aqueous mixtures with organic solvents play an important role in the design and development of separation processes. In particular, liquid-liquid equilibria (LLE) investigations for ternary mixtures are important in the evaluation of industrial units for solvent extraction processes. The accurate interpretation of phase equilibria and thermodynamic behavior for the different ternary mixtures is a fundamental and important key to improving solvent extraction techniques. As in many separation processes, the type of solvent and temperature, which influence the equilibrium characteristics of the solute extraction from aqueous solutions, play an essential role in the effectiveness of the separation. Distribution coefficients and separation factors were determined from the tie-line data to establish the extracting capability of the solvent and the possibility of the use of this solvent for the separation of (water + propionic acid and butyric acid) mixtures. The experimental data were correlated using the UNIQUAC and NRTL equations [1, 2], and the values for the interaction parameter were obtained and compared. In general, according to these



comparisons, the UNIQUAC and NRTL models are applicable for the LLE calculations of the investigated system.

Experimental

At each system, the individual bimodal curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. The mixture temperature was regulated by a thermostatic certified Fischer thermometer with an accuracy of ± 0.1 K. A binary mixture of known composition was titrated with the third component at each system at 298.2 K using non sealed glass vessels. The transition point is taken as the appearance/ disappearance of turbidity in the sample and it is defined as a cloud point.

We determined the equilibrium values preparing the ternary mixtures of known compositions. For this process and measuring the LLE values was used a 250 cm³ glass cell connected to a thermostat at T= 298.2 K. A water jacket was used to control the temperature of the cell to within $\pm 0.1\%$. The prepared mixtures were placed in the extraction cell and were vigorously agitated by a magnetic stirrer for 4 h. The mixtures were then settled for 4h at constant system temperature to separate completely into two liquid phases. After separation, samples of both phases were transparent and were carefully collected from each phase and analyzed to determine their compositions. The concentrations of carboxylic acid in both phases were determined by potentiometric NaOH titration in the presence of phenol phthale in as an indicator. The water content of the organic phase was measured by the Karl - Fisher method using Mettler Toledo DL 38 Karl – Fisher titrator. The content in the aqueous phase and the amount of the organic solvent in both phases were determined by using a material balance. All weighting was carried out with an analytical balance accurate to within ± 0.0001 g. The estimated uncertainties in the mole fractions were about 0.0005.

Results and Discussion

The experimental tie - line data for the ternary systems {water + carboxylic acid (propionic acid and butyric acid) + isobutyl acetate } were determined at T= 298.2 K. The experimental and the correlated values for each ternary system are listed in Table 1 and shown in Figures 1, 2.

Table 1. Calculated UNIQUAC and NRTL ($\alpha = 0.3$) tie - line values in mole fraction for {water (1) + carboxylic acids (2) + isobutyl acetate (3)} at T = 298.2 K.

| | | | | | | | | | | | |
|--|--------|--------|-----------------------|--------|--------|-----------------------------|--------|--------|-----------------------|--------|--------|
| 0.9490 | 0.9463 | 0.9463 | 0.0472 | 0.0466 | 0.0437 | 0.3249 | 0.3255 | 0.3276 | 0.3352 | 0.3336 | 0.3276 |
| 0.9434 | 0.9341 | 0.9334 | 0.0537 | 0.0581 | 0.0557 | 0.3858 | 0.3851 | 0.3862 | 0.3453 | 0.3443 | 0.3393 |
| Aqueous phase mole fraction | | | | | | Organic phase mole fraction | | | | | |
| 0.9255 | 0.9201 | 0.9159 | 0.0736 | 0.0711 | 0.0720 | 0.4487 | 0.4493 | 0.4492 | 0.3418 | 0.3423 | 0.3432 |
| x ₁ (water) | | | x ₂ (acid) | | | x ₁ (water) | | | x ₂ (acid) | | |
| Exp. 14 | UNIQ. | NRTL | Exp. 50 | UNIQ. | NRTL | Exp. 00 | UNIQ. | NRTL | Exp. 00 | UNIQ. | NRTL |
| <i>water (1) + propionic acid (2) + isobutyl acetate (3)</i> | | | | | | | | | | | |
| 0.9990 | 0.9990 | 0.9990 | 0.0010 | 0.0010 | 0.0010 | 0.1928 | 0.1929 | 0.1929 | 0.1161 | 0.1160 | 0.1160 |
| 0.9949 | 0.9788 | 0.9693 | 0.0050 | 0.0072 | 0.0062 | 0.2857 | 0.2843 | 0.2827 | 0.2321 | 0.2332 | 0.2346 |
| 0.9875 | 0.9779 | 0.9714 | 0.0100 | 0.0103 | 0.0094 | 0.3144 | 0.3143 | 0.3138 | 0.2667 | 0.2668 | 0.2674 |
| 0.9800 | 0.9757 | 0.9711 | 0.0150 | 0.0144 | 0.0136 | 0.3443 | 0.3466 | 0.3475 | 0.3000 | 0.2976 | 0.2964 |
| 0.9700 | 0.9683 | 0.9656 | 0.0260 | 0.0243 | 0.0238 | 0.4100 | 0.4100 | 0.4119 | 0.3400 | 0.3407 | 0.3373 |
| 0.9500 | 0.9511 | 0.9490 | 0.0390 | 0.0436 | 0.0444 | 0.5060 | 0.5048 | 0.5042 | 0.3629 | 0.3629 | 0.3657 |
| <i>water (1) + butyric acid (2) + isobutyl acetate (3)</i> | | | | | | | | | | | |
| 0.9736 | 0.9736 | 0.9736 | 0.0175 | 0.0175 | 0.0175 | 0.1800 | 0.1800 | 0.1800 | 0.1495 | 0.1495 | 0.1494 |
| 0.9571 | 0.9602 | 0.9584 | 0.0350 | 0.0336 | 0.0323 | 0.2600 | 0.2595 | 0.2582 | 0.2989 | 0.3000 | 0.3044 |

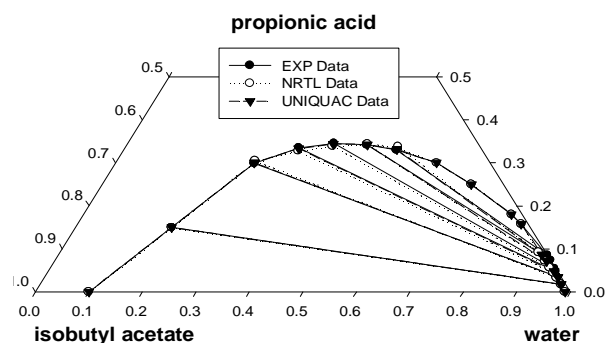


Figure 1. Ternary phase diagram for LLE of {water (1) + propionic acid (2) + isobutyl acetate (3)} at T=298.2K.

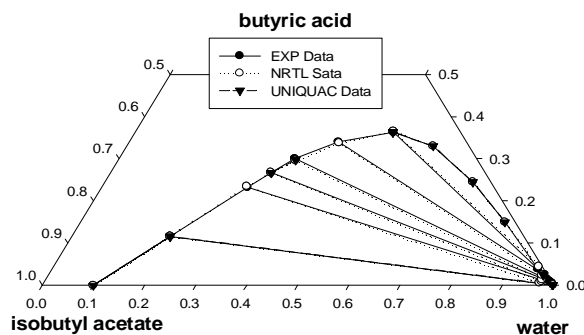


Figure 2. Ternary phase diagram for LLE of {water (1) + butyric acid (2) + isobutyl acetate (3)} at T=298.2K.

The efficient separation of carboxylic acid from aqueous solutions is an important concept in the chemical industries. In order to evaluate the extracting capability of the solvent (isobutyl acetate) for the separation of carboxylic acid from aqueous solutions with (liquid + liquid) extraction, the separation factor (S) was calculated.

The separation factor is defined as the ratio of distribution coefficients of the acid (D_2) to water (D_1), as follows:

$$S = \frac{D_2}{D_1}, \quad (1)$$

Where D_1 and D_2 are the distribution coefficients of water and the acid, respectively.

The distribution coefficients of water and carboxylic acid were calculated from the experimental results as follows:

$$D_1 = \frac{x_{13}}{x_{11}}, \quad \text{and} \quad D_2 = \frac{x_{23}}{x_{21}}, \quad (2)$$

A comparison of the extracting capability of the solvent was made with respect to separation factor values. This factor is found to be greater than 1 ($S > 1$) for the systems investigated. The separation factors are not constant over the completely two-phase region. The variation of experimental separation factor and the distribution coefficient of the acids as a function of the mole fraction of the solute in aqueous phase for the ternary systems are shown in Figures 3 and 4 and Table 2.



Table 2. Separation factors (S) and distribution coefficients of acid (D_2) and water (D_1) at $T = 298.2\text{K}$.

| D_2 | D_1 | S |
|--|--------|---------|
| <i>water (1) + propionic acid (1) + isobutyl acetate (3)</i> | | |
| 8.5400 | 0.2716 | 31.4370 |
| 7.1017 | 0.3424 | 20.7433 |
| 6.4302 | 0.4089 | 15.7237 |
| 4.6440 | 0.4848 | 9.5789 |
| 3.8824 | 0.5577 | 6.9608 |
| <i>water (1) + butyric acid (2) + isobutyl acetate (3)</i> | | |
| 46.4200 | 0.2872 | 161.653 |
| 26.6700 | 0.3183 | 83.7778 |
| 20.0000 | 0.3513 | 56.9271 |
| 13.0769 | 0.4227 | 30.9381 |
| 9.3051 | 0.5326 | 17.4701 |

For the systems investigated, the experimental results indicate that isobutyl acetate has a larger separation factor for butyric acid (varying between 161.653 and 17.4701) than the propionic acid. The experimental results indicate the superiority of isobutyl acetate as the preferred solvent for the extraction of butyric acid from its aqueous solutions. The biphasic region was found to be larger when the butyric acid was used as an acid.

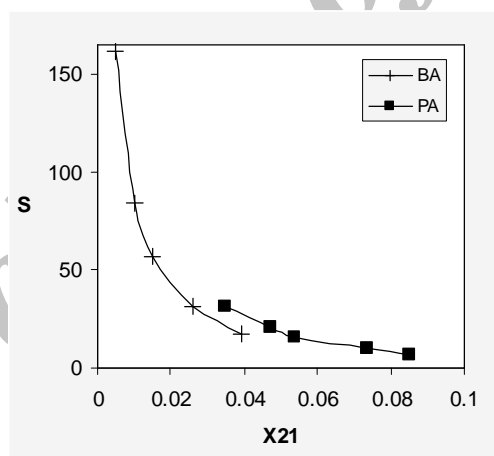


Figure 3. Plot of the separation factor (S) of carboxylic acid as a function of the mole fraction (x_{21}) of acid in the aqueous phase.

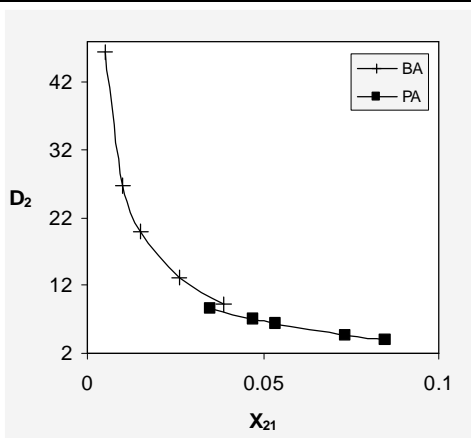


Figure 4. Plot of the distribution coefficient (D_2) of carboxylic acid as a function of the mole fraction (x_{21}) of acid in the aqueous phase.

The UNIQUAC and NRTL models were used to correlate the raw experimental LLE values. The UNIQUAC model was used to correlate the raw experimental LLE values. The UNIQUAC structural parameters r (the number of segments per molecules) and q (the relative surface area per molecules) were computed from the number of molecular groups and the individual values of the van der Waals volume and area of the molecule by the Bondi method. In the present work, the value of the non-randomness α was fixed at 0.3.

The objective function developed by Sorensen was used to optimize the equilibrium models. The objective function is the sum of the squares of the difference between the experimental and calculated mole fractions. The correlated results together with the experimental values for this ternary system of (water + carboxylic acid + isobutyl acetate) were plotted and are shown in Figures 1 and 2 and Table 1. The observed results were also used to determine the optimum UNIQUAC (a_{ij}) and NRTL (b_{ij}) binary interaction energy between an $i-j$ pair of molecules or between each pair of compounds (tables 4). The detailed description of the meaning of parameters and equations is widely defined in the current literature. The values r and q used for these ternary systems are presented in Table 3.

Table 3. The UNIQUAC structural parameters (r and q) for pure components.

| Components | r | q |
|-------------------|--------|--------|
| Water | 0.9200 | 1.4000 |
| Propionic acid | 2.8768 | 2.6120 |
| Butyric acid | 3.5510 | 3.1520 |
| iso-Butyl acetate | 4.8266 | 4.1918 |



Table 4. UNIQUAC and NRTL binary interaction parameters (a and b) and root-mean square deviation (RMSD) values for LLE data of the ternary systems at T = 298.2 K.

| $i-j$ | a_{ij}/K | a_{ji}/K | RMSD% | b_{ij}/K | b_{ji}/K | RMSD% |
|--|------------|------------|-------|------------|------------|-------|
| <i>water (1) + propionic acid (2) + isobutyl acetate (3)</i> | | | | | | |
| 1-2 | 0.289 | -0.619 | 0.39 | 693.944 | -40.962 | 0.68 |
| 1-3 | -0.134 | -1.731 | | 1135.072 | 975.122 | |
| 2-3 | -10.410 | 1.477 | | -430.070 | 301.681 | |
| <i>water (1) + butyric acid (2) + isobutyl acetate (3)</i> | | | | | | |
| 1-2 | -0.310 | -0.210 | 0.51 | 917.010 | -79.740 | 0.85 |
| 1-3 | 0.310 | -2.463 | | 573.400 | 363.300 | |
| 2-3 | 0.912 | -0.624 | | -858.900 | 60.513 | |

The quality of the correlation is measured by the root-mean square deviation (RMSD). The RMSD value was calculated from the difference between the experimental and calculated mole fractions according to the following equation:

$$RMSD \% = 100 \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 (x_{ijk} - \hat{x}_{ijk})^2}{6n}}, \quad (3)$$

where n is the number of tie-lines, x indicates the experimental mole fraction, \hat{x} is the calculated mole fraction, and the subscript i indexes components, j indexes phases and k = 1, 2, ..., n (tie-lines). The RMSD values in the correlation by UNIQUAC and NRTL models for the systems studied at T=298.2 K are also listed in Table 5 and 6.

The reliability of experimental tie-line data can be determined using the Hand equation (4) for each solvent, as shown in the following equation:

$$\ln \left(\frac{x_{21}}{x_{11}} \right) = A + B \ln \left(\frac{x_{23}}{x_{33}} \right), \quad (4)$$

Where x_{11} , mole fraction of water in the aqueous phase; x_{33} mole fraction of solvent in organic phase; A and B, the parameters of the Hand correlation.

The parameters of the Hand correlation are listed in Table 6 at T=298.2K. For these two systems, the Hand plots are also shown in figures 5. The correlation factor (R^2) being approximately unity and the linearity of the plots indicate the degree of consistency of the measured LLE values in this study.

Table 5. Hand equation constants (A, B) and the correlation factor (R^2) for the ternary systems (water + propionic acid + isobutyl acetate) and (water + butyric acid + isobutyl acetate) at T= 298.2K.

| acids | Hand correlation | | |
|----------------|------------------|--------|--------|
| | A | B | R^2 |
| Propionic acid | -2.9776 | 0.8556 | 0.9979 |
| Butyric acid | -4.0125 | 1.5633 | 0.9649 |

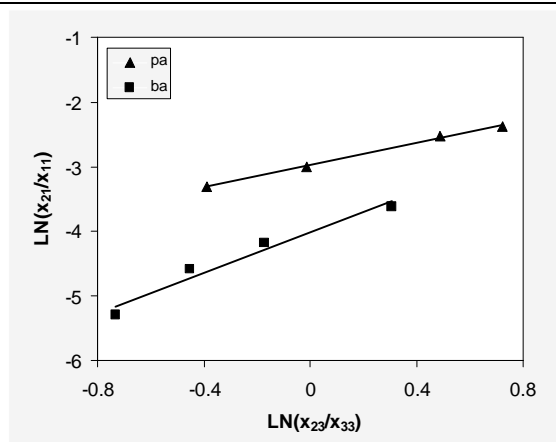


Figure 5. Hand plot for the (water + carboxylic acid + isobutyl acetate) ternary systems at T= 298.2K.

Conclusions

Tie-line data for the {water (1) + propionic acid (2) + isobutyl acetate (3)} and {water (1) + butyric acid (2) + isobutyl acetate (3)} ternary systems were obtained at T= 298.2K. Each ternary system exhibits Type-1 behaviour of the LLE. The UNIQUAC and NRTL solution models were used to correlate the experimental LLE results and to calculate the phase compositions of the mixtures studied. The corresponding optimized binary interaction parameters were also calculated. The UNIQUAC and NRTL models give the good results for these systems. The separation factor and distribution coefficient for each of these systems used in this work were calculated and compared. The experimental results indicate the superiority of isobutyl acetate as the preferred solvent for the extraction of butyric acid from its aqueous solutions. The immiscibility region was found to be large when the isobutyl acetate was used as an organic solvent for extraction of butyric acid.

Acknowledgements

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اندازه گیری و بررسی همبستگی داده های تعادل فازي مخلوطهای آبی سه جزئی دو کربوکسیلیک اسید به کمک ایزو بوتیل استات در دمای 298,2 کلوین

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چکیده

نتایج آزمایشگاهی خطوط گره برای سیستم { آب + پروپیونیک و بوتیریک اسید + ایزو بوتیل استات } در دمای 298,2 کلوین و در فشار یک اتمسفر ارائه شده است. این سیستم سه تایی رفتار نوع 1- دارد. داده های آزمایشگاهی خطوط گره با داده های حاصل از مدل NRTL و UNIQUAC مقایسه شده اند و میزان نزدیکی این داده ها به هم توسط انراف استاندارد گزارش شده است. همبستگی این داده ها با استفاده از رابطه اتمر - تویاس محاسبه و ضرایب توزیع و فاکتور انتخاب پذیری حلال برای منطقه دو فازي برای دو اسید با یکدیگر مقایسه شده است. با توجه به نتایج بدست آمده ایزو بوتیل استات توانایی خوبی برای جداسازی هر دو اسید به کار برده شده دارد ولی نتایج بدست آمده برای بوتیریک اسید حاکی از توانایی خوب ایزو بوتیل استات از محیط آبی می باشد.

واژه های کلیدی: داده های LLE، سیستم سه تایی، مدل NRTL، مدل UNIQUAC، فرایند استخراج

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