

(Liquid + liquid) equilibria of (water + propionic acid + diethyl phthalate) at several temperatures

Süheyla Çehreli, Dilek Özmen *, Beşir Tatlı

Istanbul University, Engineering Faculty, Department of Chemical Engineering, 34320 Istanbul, Turkey

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Abstract

(Liquid + liquid) equilibrium (LLE) data for (water + propionic acid + diethyl phthalate) were measured under atmospheric pressure and at $T = (298.2, 303.2, 308.2, \text{ and } 313.2)$ K. Phase diagrams were obtained by determining solubility and tie-line data. The UNIFAC model was used to correlate the experimental tie-line data. The average root-mean-square deviation between the observed and calculated mass fraction was 0.03. Distribution coefficients and separation factors were evaluated over the immiscibility regions.

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1. Introduction

Propionic acid has many applications in chemical and biochemical industries. It is largely used as a mould inhibitor in baking, as an esterifying agent in the production of thermoplastics, and in the manufacture of flavours and perfume bases [1]. Propionic acid and its salts can be obtained by chemical reactions or by fermentation with bacteria of the genus *Propionibacterium* [2]. Recovery of the organic acid from aqueous solutions that are resulted from fermentation processes is also of considerable economic importance. Many solvents have been used to enhance the extraction of propionic acid from aqueous solutions and reported in the literature [3–9].

The LLE data of (water + diethyl phthalate) [10] and (water + acetic acid + diethyl phthalate) [11] sys-

tems have been presented previously. Diethyl phthalate has a high boiling point and in addition it is one of very few substances which makes partially miscible mixtures with water. The objective of this work is to determine LLE data of (water + propionic acid + diethyl phthalate) at several temperatures. Complete phase diagrams were obtained by solubility and tie-line data simultaneously for each temperature. Selectivity values (S) were also determined from the tie-line data to establish the feasibility of the use of these liquid for the separation of (water + propionic acid) binary mixture. The experimental LLE data were predicted with the UNIFAC method [12]. The UNIFAC method for estimation of activity coefficients works on the concept that a liquid mixture may be considered a solution of structural units from which the molecules are formed rather than a solution of the molecules themselves. This procedure is known as group contribution method. It has the advantage of being able to form a very large number of molecules from a relatively small set of structural units.

* Corresponding author. Tel.: +90 212 473 7070; fax: +90 212 473 7180/79.

E-mail addresses: cehrel@istanbul.edu.tr (S. Çehreli), dilekus@istanbul.edu.tr (D. Özmen).

This study is a part of a research program on the recovery of propionic acid from dilute aqueous solutions using phthalic esters.

2. Experimental

2.1. Chemicals

Propionic acid and diethyl phthalate (mass fraction purity > 0.99) were supplied by Merck and were used without further purification. The purity of these materials was checked by gas chromatography. Deionised water was further distilled before use. Refractive indexes were measured with an Abbé–Hilger refractometer; its stated accuracy is $\pm 5 \cdot 10^{-4}$. Densities were measured using a temperature controlled Anton Paar DMA 4500 density meter in an accuracy of $\pm 1 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. Boiling points were measured with a Fischer boiling-point apparatus. The estimated temperature uncertainties in the density and boiling point measurements were $T = 0.01 \text{ K}$. The measured physical properties together with the literature data are presented in table 1.

2.2. Apparatus and procedure

Solubility data for the ternary systems were determined by the cloud-point method. The data measurements were made in an equilibrium cell equipped with a magnetic stirrer and isothermal fluid jacketed beaker to keep the temperature of the stock solution constant. The mixture temperature was regulated by a thermostatic certified Fischer thermometer with an accuracy of $\pm 0.2 \text{ K}$. The cell, designed to contain a solution from (50 to 200) cm^3 , was filled with homogeneous (propionic acid + water) mixtures prepared by mass. An electronic Sauter balance with an accuracy of $\pm 0.1 \text{ mg}$ was used. The solvent was progressively added by means of an automatic microburet with an accuracy of $\pm 5 \cdot 10^{-3} \text{ cm}^3$. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. This pattern was convenient for providing the water-rich side of the

curves. The data for the solvent-rich side of the curves were therefore obtained by titrating the homogeneous (propionic acid + solvent) with water until turbidity appeared.

The tie-line data were obtained by preparing ternary mixtures of known overall compositions lying within the two-phase region, and after being allowed to reach equilibrium, samples were carefully taken from each phase and analysed. The liquid samples were analysed using a gas chromatography (HP 6890), equipped with flame ionisation (FI) and thermal conductivity (TC) detectors. *n*-Propanol was used as an internal standard. A 15-m long HP Plot Q column (0.32 mm i.d., 0.2 μm film thickness) for TCD, and HP-Innowax polyethylene glycol capillary column (30 m long, 0.32 mm i.d., 0.5 μm film thickness) for FID were utilized to separate organic components of samples at tailorized oven programs. The detector temperature was kept $T = 523.15 \text{ K}$, while injection port temperature was held at $T = 473.15 \text{ K}$. Injections were performed on the split 1/100 mode. Nitrogen was used as a carrier at a rate of $1 \text{ cm}^3 \cdot \text{min}^{-1}$. The composition of water was determined by means of thermal conductivity detector (TCD).

2.3. Prediction of LLE using the UNIFAC method

The experimental LLE can be predicted with the UNIFAC (universal quasi-chemical functional group activity coefficient) method [12]. The UNIFAC method can be used in predicting activity coefficients, γ_i . At LLE, the activities of the component of *i* on both phases are equal and the mole fractions x_i^E , x_i^R of LLE phases can be calculated using the following equations:

$$(\gamma_i x_i)^E = (\gamma_i x_i)^R, \quad (1)$$

where γ_i^E and γ_i^R are the corresponding activity coefficients of *i* in extract (solvent) and raffinate (aqueous) phase. The interaction parameters between each of the main groups can be used to calculate activity coefficients of component *i*. The values of the UNIFAC parameters for LLE predictions can be taken from a UNIFAC table [14].

TABLE 1
Densities (ρ) and refractive indexes (n_D) at $T = 293.15 \text{ K}$ and boiling temperatures at atmospheric pressure of the pure components [13]

| Component | $\rho/(\text{g} \cdot \text{cm}^{-3})$ | | Boiling point (K) | | n_D | |
|-------------------|--|---------|-------------------|-------|--------|---------------------------|
| | Exp. | Lit. | Exp. | Lit. | Exp. | Lit. |
| Water | 0.9984 | 0.99823 | 373.23 | 373.2 | 1.3326 | 1.33299 |
| Propionic acid | 0.9927 | 0.99300 | 414.10 | 414.2 | 1.3811 | 1.38090 |
| Diethyl phthalate | 1.1172 | 1.11750 | 571.17 | 571.2 | 1.5003 | 1.50000 ^{294,15} |

TABLE 2

The solubility curve data for {1water (1) + propionic acid (2) + diethyl phthalate (3)} at each temperature

| w_1 | w_2 | w_3 |
|-----------------------|--------|--------|
| $T = 298.2 \text{ K}$ | | |
| 0.0461 | 0.1921 | 0.7618 |
| 0.0677 | 0.2507 | 0.6816 |
| 0.0828 | 0.2814 | 0.6358 |
| 0.1033 | 0.3206 | 0.5761 |
| 0.1441 | 0.3714 | 0.4845 |
| 0.1997 | 0.3991 | 0.4012 |
| 0.2558 | 0.4099 | 0.3343 |
| 0.3015 | 0.4174 | 0.2811 |
| 0.3426 | 0.4139 | 0.2435 |
| 0.3806 | 0.4063 | 0.2131 |
| 0.4250 | 0.3993 | 0.1757 |
| 0.4799 | 0.3875 | 0.1326 |
| 0.5486 | 0.3648 | 0.0866 |
| 0.5963 | 0.3419 | 0.0618 |
| 0.6638 | 0.3024 | 0.0338 |
| $T = 303.2 \text{ K}$ | | |
| 0.0205 | 0.0671 | 0.9124 |
| 0.0349 | 0.1563 | 0.8088 |
| 0.0494 | 0.2078 | 0.7428 |
| 0.0788 | 0.2672 | 0.6540 |
| 0.1296 | 0.3336 | 0.5368 |
| 0.1734 | 0.3738 | 0.4528 |
| 0.2361 | 0.4001 | 0.3638 |
| 0.3211 | 0.4057 | 0.2732 |
| 0.3938 | 0.3995 | 0.2067 |
| 0.5022 | 0.3760 | 0.1218 |
| 0.5756 | 0.3489 | 0.0755 |
| 0.6360 | 0.3169 | 0.0471 |
| 0.7017 | 0.2740 | 0.0243 |
| $T = 308.2 \text{ K}$ | | |
| 0.0335 | 0.1266 | 0.8399 |
| 0.0496 | 0.1850 | 0.7654 |
| 0.0758 | 0.2437 | 0.6805 |
| 0.1067 | 0.3034 | 0.5899 |
| 0.1520 | 0.3547 | 0.4933 |
| 0.2012 | 0.3841 | 0.4147 |
| 0.2709 | 0.4027 | 0.3264 |
| 0.3665 | 0.3999 | 0.2336 |
| 0.4628 | 0.3830 | 0.1542 |
| 0.5552 | 0.3540 | 0.0908 |
| 0.6106 | 0.3309 | 0.0585 |
| 0.6352 | 0.3177 | 0.0471 |
| 0.6939 | 0.2790 | 0.0271 |
| $T = 313.2 \text{ K}$ | | |
| 0.0300 | 0.0738 | 0.8962 |
| 0.0546 | 0.1702 | 0.7752 |
| 0.0808 | 0.2360 | 0.6832 |
| 0.1133 | 0.2968 | 0.5899 |
| 0.1469 | 0.3433 | 0.5098 |
| 0.2236 | 0.3861 | 0.3903 |
| 0.2858 | 0.3968 | 0.3174 |
| 0.3541 | 0.3940 | 0.2519 |
| 0.4244 | 0.3854 | 0.1902 |
| 0.4750 | 0.3768 | 0.1482 |
| 0.5342 | 0.3611 | 0.1047 |
| 0.6167 | 0.3241 | 0.0592 |
| 0.6853 | 0.2823 | 0.0324 |

3. Results and discussion

The experimental solubility curve data of (water + propionic acid + diethyl phthalate) at $T = (298.2, 303.2, 308.2, \text{ and } 313.2) \text{ K}$ were reported in table 2, in which w_i denotes the mass fraction of the i th component. The experimental tie-lines for each temperature were given in table 3, for which w_{i1} and w_{i3} refer to mass fraction of the i th component in the aqueous and solvent phase, respectively. The predicted LLE data were plotted in figures 1–4 along with the experimental values. From the LLE phase diagrams (figures 1–4) and the literature [10], (water + diethyl phthalate) mixture is partially miscible and two liquid pairs (propionic acid + water) and (propionic acid + diethyl phthalate) are completely miscible.

Distribution coefficients, D_i , for water ($i = 1$) and propionic acid ($i = 2$) and separation factors, S , were determined as follows:

$$D_i = w_{i3}/w_{i1}, \quad (2)$$

$$S = D_2/D_1, \quad (3)$$

where D_2 and D_1 ; distribution coefficients of propionic acid (w_{23}/w_{21}) and distribution coefficients of water (w_{13}/w_{11}), respectively. The distribution coefficients and separation factors for the each temperature were given in table 4. The effectiveness of extraction of propionic acid by diethyl phthalate is given by its separation factor (S), which is an indication of the ability of diethyl phthalate to separate from water. This quantity is found to be greater than 1 (separating factors varying between 2.2825 and 37.8790) for the systems reported here means extraction of propionic acid by diethyl phthalate is feasible. Diagrams of selectivity on a solvent-free basis were plotted at each temperatures in figure 5. The effect of the temperature change on the selectivity values was found to be insignificant.

The UNIFAC model was used to predict the experimental tie-lines for the ternary mixture reported here. The calculated tie-lines (dashed lines) together with experimental data (solid lines) were presented in figures 1–4. The root-mean-square deviation (RMSD) was calculated from the difference between the experimental data and the predictions of the UNIFAC method at each temperature according to the following formula:

$$\text{RMSD} = \left[\sum_k \left(\sum_j \sum_i (w_{i,\text{exp}} - w_{i,\text{calcd}})^2 / 6N \right) \right]^{1/2}, \quad (4)$$

where N is the number of tie-lines, $w_{i,\text{exp}}$ indicates experimental mass fraction, $w_{i,\text{calcd}}$ is the calculated

TABLE 3
Experimental tie-line data for {water (1) + propionic acid (2) + diethyl phthalate (3)} at each temperature

| Overall | | | Water-rich phase (mass fraction) | | | Solvent-rich phase (mass fraction) | | |
|-----------------------|--------|--------|----------------------------------|----------|----------|------------------------------------|----------|----------|
| w_1 | w_2 | w_3 | w_{11} | w_{21} | w_{31} | w_{13} | w_{23} | w_{33} |
| $T = 298.2 \text{ K}$ | | | | | | | | |
| 0.4718 | 0.0600 | 0.4682 | 0.9382 | 0.0593 | 0.0025 | 0.0239 | 0.0528 | 0.9233 |
| 0.4552 | 0.0999 | 0.4449 | 0.9010 | 0.0963 | 0.0027 | 0.0345 | 0.0990 | 0.8665 |
| 0.4330 | 0.1408 | 0.4262 | 0.8730 | 0.1238 | 0.0032 | 0.0451 | 0.1443 | 0.8106 |
| 0.4014 | 0.2000 | 0.3986 | 0.8227 | 0.1719 | 0.0054 | 0.0723 | 0.2158 | 0.7119 |
| 0.3738 | 0.2600 | 0.3662 | 0.7681 | 0.2209 | 0.0110 | 0.0941 | 0.2810 | 0.6249 |
| 0.3573 | 0.2992 | 0.3435 | 0.7228 | 0.2581 | 0.0191 | 0.1134 | 0.3241 | 0.5625 |
| 0.3246 | 0.3490 | 0.3264 | 0.6691 | 0.3000 | 0.0309 | 0.1540 | 0.3731 | 0.4729 |
| 0.3034 | 0.3969 | 0.2997 | 0.5526 | 0.3680 | 0.0794 | 0.2775 | 0.4218 | 0.3007 |
| $T = 303.2 \text{ K}$ | | | | | | | | |
| 0.4727 | 0.0634 | 0.4639 | 0.9332 | 0.0633 | 0.0035 | 0.0209 | 0.0537 | 0.9254 |
| 0.4543 | 0.1027 | 0.4430 | 0.8928 | 0.1030 | 0.0042 | 0.0366 | 0.0995 | 0.8639 |
| 0.4323 | 0.1420 | 0.4257 | 0.8706 | 0.1251 | 0.0043 | 0.0504 | 0.1446 | 0.8050 |
| 0.4032 | 0.2000 | 0.3968 | 0.8194 | 0.1731 | 0.0075 | 0.0620 | 0.2075 | 0.7305 |
| 0.3692 | 0.2608 | 0.3700 | 0.7567 | 0.2311 | 0.0122 | 0.1011 | 0.2816 | 0.6173 |
| 0.3578 | 0.2998 | 0.3424 | 0.7234 | 0.2544 | 0.0222 | 0.1410 | 0.3196 | 0.5394 |
| 0.3218 | 0.3478 | 0.3304 | 0.6605 | 0.2977 | 0.0418 | 0.1891 | 0.3766 | 0.4343 |
| 0.3036 | 0.3945 | 0.3019 | 0.5754 | 0.3401 | 0.0845 | 0.2655 | 0.4006 | 0.3339 |
| $T = 308.2 \text{ K}$ | | | | | | | | |
| 0.4730 | 0.0627 | 0.4643 | 0.9195 | 0.0709 | 0.0096 | 0.0237 | 0.0575 | 0.9188 |
| 0.4545 | 0.1021 | 0.4434 | 0.9010 | 0.0944 | 0.0046 | 0.0293 | 0.0994 | 0.8713 |
| 0.4329 | 0.1419 | 0.4252 | 0.8631 | 0.1326 | 0.0043 | 0.0472 | 0.1509 | 0.8019 |
| 0.4041 | 0.2037 | 0.3922 | 0.8035 | 0.1883 | 0.0082 | 0.0744 | 0.2161 | 0.7095 |
| 0.3760 | 0.2602 | 0.3638 | 0.7590 | 0.2257 | 0.0153 | 0.0970 | 0.2748 | 0.6282 |
| 0.3536 | 0.3007 | 0.3457 | 0.7263 | 0.2523 | 0.0214 | 0.1261 | 0.3116 | 0.5623 |
| 0.3254 | 0.3502 | 0.3244 | 0.6573 | 0.3073 | 0.0354 | 0.1620 | 0.3600 | 0.4780 |
| 0.3030 | 0.3980 | 0.2990 | 0.5830 | 0.3454 | 0.0716 | 0.2416 | 0.3948 | 0.3636 |
| $T = 313.2 \text{ K}$ | | | | | | | | |
| 0.4707 | 0.0634 | 0.4659 | 0.9401 | 0.0582 | 0.0017 | 0.0230 | 0.0520 | 0.9250 |
| 0.4523 | 0.1021 | 0.4456 | 0.9081 | 0.0898 | 0.0021 | 0.0312 | 0.0922 | 0.8766 |
| 0.4288 | 0.1427 | 0.4285 | 0.8791 | 0.1175 | 0.0034 | 0.0453 | 0.1355 | 0.8192 |
| 0.3999 | 0.2012 | 0.3989 | 0.8234 | 0.1704 | 0.0062 | 0.0663 | 0.2041 | 0.7296 |
| 0.3670 | 0.2635 | 0.3695 | 0.7621 | 0.2235 | 0.0144 | 0.0946 | 0.2741 | 0.6313 |
| 0.3491 | 0.3046 | 0.3463 | 0.7332 | 0.2490 | 0.0178 | 0.1212 | 0.3198 | 0.5590 |
| 0.3214 | 0.3526 | 0.3260 | 0.6708 | 0.2972 | 0.0320 | 0.1550 | 0.3641 | 0.4809 |

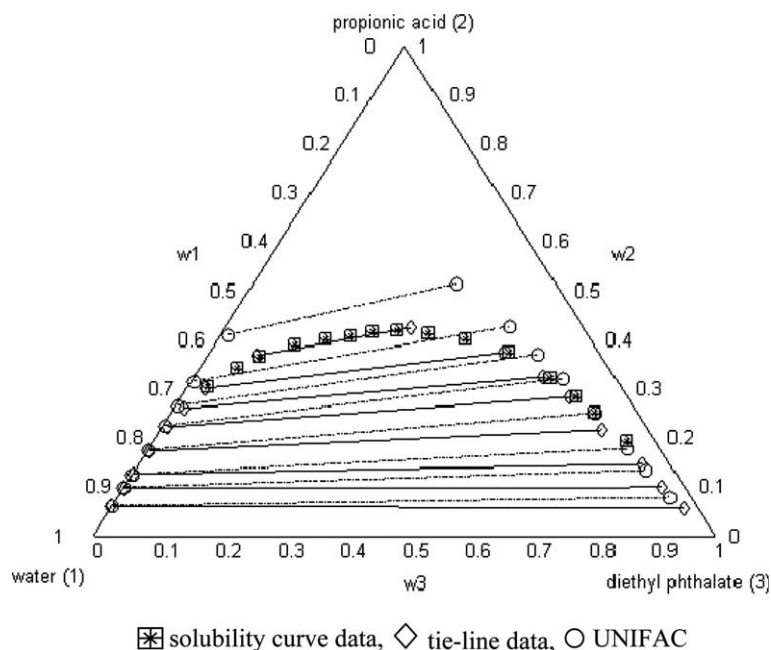


FIGURE 1. Solubility curve and tie-lines of (water + propionic acid + diethyl phthalate) at $T = 298.2 \text{ K}$.

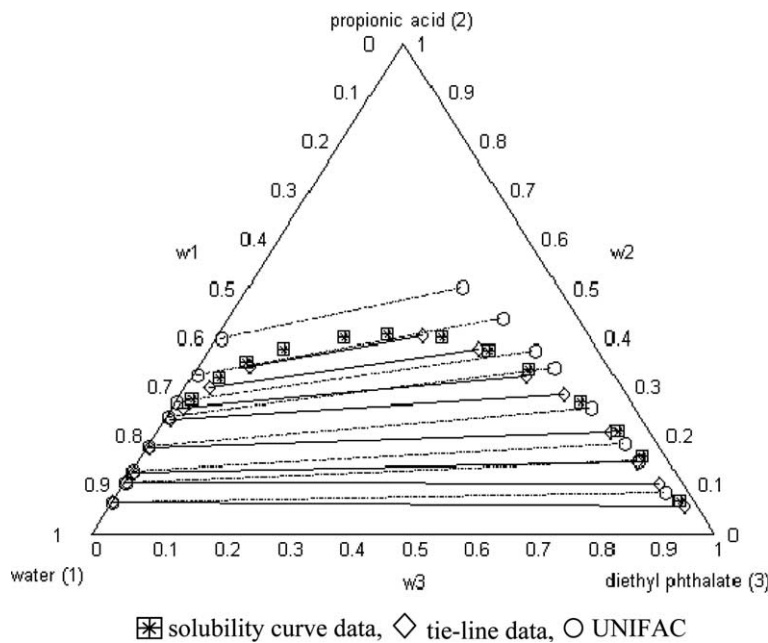


FIGURE 2. Solubility curve and tie-lines of (water + propionic acid + diethyl phthalate) at $T = 303.2$ K.

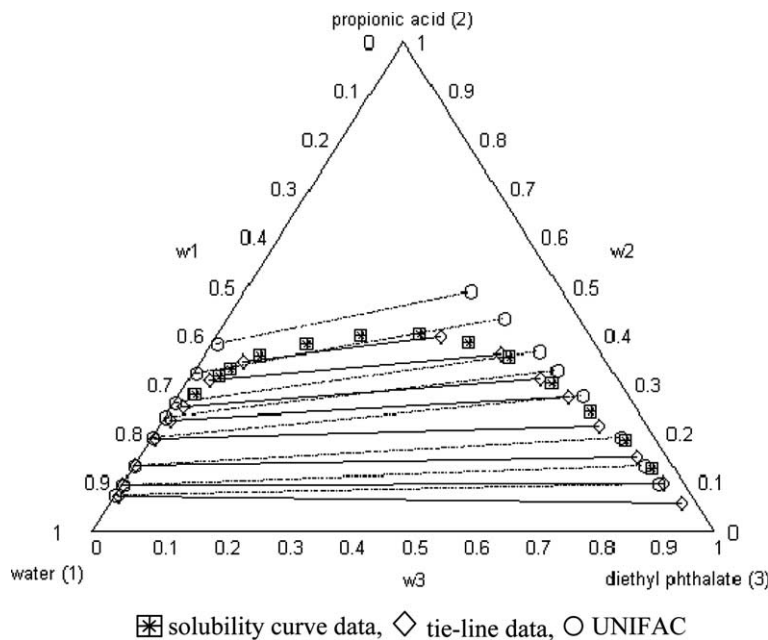


FIGURE 3. Solubility curve and tie-lines of (water + propionic acid + diethyl phthalate) at $T = 308.2$ K.

mass fraction, and subscript i indexes components, j indexes phases, and $k = 1, 2, 3, \dots, N$ (tie-lines). The UNIFAC method was used to correlate the experimental data at $T = (298.2, 303.2, 308.2, \text{ and } 313.2)$ K with RMSD values of 0.03, 0.04, 0.04, 0.02, respectively.

4. Conclusion

The LLE data for (water + propionic acid + diethyl phthalate) were measured under atmospheric pressure and at $T = (298.2, 303.2, 308.2, \text{ and } 313.2)$ K. It was observed that the effect of the temperature changes on the

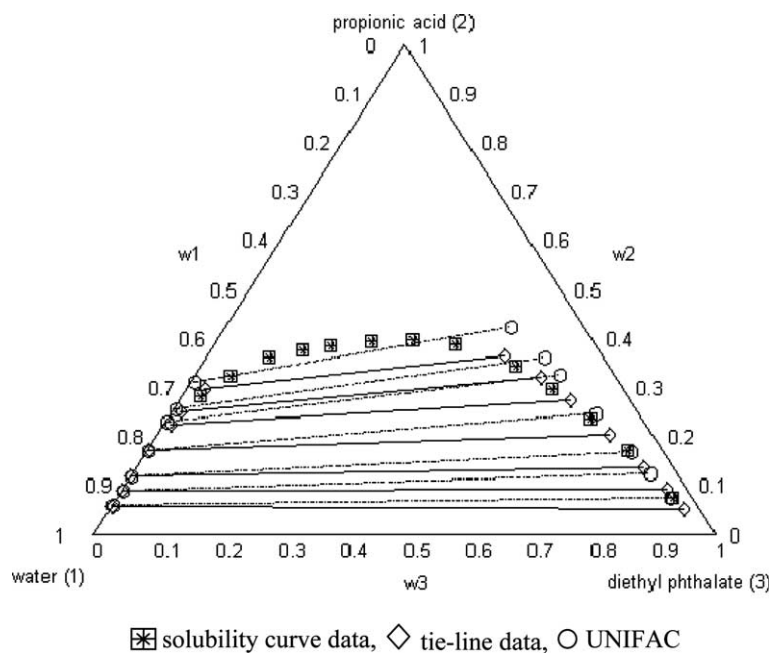


FIGURE 4. Solubility curve and tie-lines of (water + propionic acid + diethyl phthalate) at $T = 313.2$ K.

TABLE 4
Experimental distribution coefficients (D_i) of the (water and propionic acid) and separation factors (S)

| D_1 | D_2 | S |
|---------------|--------|---------|
| $T = 298.2$ K | | |
| 0.0255 | 0.8904 | 34.9524 |
| 0.0383 | 1.0280 | 26.8482 |
| 0.0517 | 1.1656 | 22.5623 |
| 0.0879 | 1.2554 | 14.2850 |
| 0.1225 | 1.2721 | 10.3834 |
| 0.1569 | 1.2557 | 8.0038 |
| 0.2302 | 1.2437 | 5.4035 |
| 0.5022 | 1.1462 | 2.2825 |
| $T = 303.2$ K | | |
| 0.0224 | 0.8483 | 37.8790 |
| 0.0410 | 0.9660 | 23.5645 |
| 0.0579 | 1.1559 | 19.9664 |
| 0.0757 | 1.1987 | 15.8426 |
| 0.1336 | 1.2185 | 9.1202 |
| 0.1949 | 1.2563 | 6.4454 |
| 0.2863 | 1.2650 | 4.4186 |
| 0.4614 | 1.1779 | 2.5528 |
| $T = 308.2$ K | | |
| 0.0258 | 0.8110 | 31.4648 |
| 0.0325 | 1.0530 | 32.3796 |
| 0.0547 | 1.1380 | 20.8097 |
| 0.0926 | 1.1476 | 12.3942 |
| 0.1278 | 1.2175 | 9.5270 |
| 0.1736 | 1.2350 | 7.1135 |
| 0.2465 | 1.1715 | 4.7532 |
| 0.4144 | 1.1430 | 2.7582 |
| $T = 313.2$ K | | |
| 0.0245 | 0.8935 | 36.5196 |
| 0.0344 | 1.0267 | 29.8837 |
| 0.0515 | 1.1532 | 22.3790 |
| 0.0805 | 1.1978 | 14.8755 |
| 0.1241 | 1.2264 | 9.8799 |
| 0.1653 | 1.2843 | 7.7696 |
| 0.2311 | 1.2251 | 5.3019 |

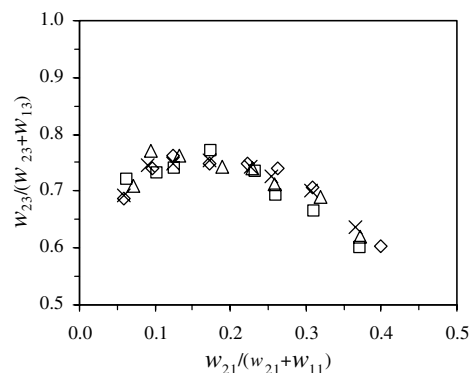


FIGURE 5. Selectivity diagram (solvent-free basis) of (water + propionic acid + diethyl phthalate) at $T = (\diamond, 298.2; \square, 303.2; \triangle, 308.2; \text{and } \times, 313.2)$ K.

shape and the size of the immiscibility gap was insignificant over the investigated range. Experimental tie-line data of this work were analysed and predicting using UNIFAC method. The average RMSD value between the measured and calculated mass fractions was 0.03. It can be concluded that diethyl phthalate has high separation factor, very low solubility in water, high boiling point may be an adequate solvent to extract propionic acid from its dilute solutions.

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References

- [1] M.J. Playne, in: M. Moo Young (Ed.), *Comprehensive Biotechnology*, Pergamon Press, Oxford, 1985 (Chapter 37).
- [2] P. Boyaval, J. Seta, C. Gavach, *Enzyme Microb. Technol.* 15 (1993) 683–686.
- [3] Sh. Hashemi, C. Ghotbi, V. Taghikhani, B. Behzadi, *Fluid Phase Equilib.* 226 (2005) 251–259.
- [4] V. Taghikhani, G.R. Vakili-Nezhaad, M.K. Khoshkbarchi, M. Shariaty-Niassar, *J. Chem. Eng. Data* 46 (2001) 1107–1109.
- [5] D. Özmen, U. Dramur, B. Tatlı, *Braz. J. Chem. Eng.* 21 (2004) 647–657.
- [6] A. Arce, A. Blanco, P. Souza, I. Vidal, *J. Chem. Eng. Data* 38 (1993) 201–203.
- [7] A. Badakhshan, A.I. Chowdhury, R. Leung, *J. Chem. Eng. Data* 30 (1985) 416–421.
- [8] A. Arce, A. Blanco, P. Souza, I. Vidal, *J. Chem. Eng. Data* 40 (1995) 225–229.
- [9] S. Çehreli, B. Tatlı, U. Dramur, *Chim. Acta Turcica* 27 (2) (1999) 53–61.
- [10] K. Řehák, J. Matouš, J.P. Novák, M. Bendová, *J. Chem. Thermodyn.* 32 (2000) 393–400.
- [11] U. Dramur, B. Tatlı, *J. Chem. Eng. Data* 38 (1993) 23–25.
- [12] A. Fredenslund, R.L. Jones, J.M. Prausnitz, *AIChE J.* 21 (1975) 1086–1099.
- [13] R.C. Weast, *Handbook of Chemistry and Physics*, 17th ed., CRC Press, Boca Raton, FL, 1989–1990.
- [14] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, fourth ed., McGraw-Hill Inc., Mexico, 1987.

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