Liquid-Liquid Equilibria in Two Systems Comprising Propionic Acid, Water and Organic Solvent

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Abstract: Liquid-liquid phase equilibria (LLE) in the systems H2O(1) – *n*-butyl acetate(2) – propionic acid(3) at 35°C and H2O(1) – dimethyl adipate(2) – propionic acid(3) at 25°C was experimentally determined with a combination of turbidimetric titration and refractometry methods. Experimental binodal curves were modeled with Hlavatý equation and tie lines with Othmer-Tobias equation to provide an excellent agreement with the data. UNIFAC LLE model was not found suitable for the prediction of LLE in the systems studied. NRTL and UNIQUAC model parameters were determined as well. The correlation was found fair, but much worse than that obtained by the empirical approach of Hlavatý and Othmer-Tobias.

Keywords: Liquid-liquid equilibria, propionic acid, *n*-butyl acetate, dimethyl adipate

Introduction

There is an increasing demand for propionic acid produced by the fermentation route, using whey lactose as a substrate and *Propionibacterium* microorganisms (Bodie et al., 1986; Goswami and Srivastava, 2000). The product may be classified as “natural” and may serve as a replacement for “artificial” chemical preservatives – fungistatic agents in the bakery industries. The same is valid for sodium, calcium and potassium propionates as food additives. Propionic acid finds other uses in the manufacturing of cellulose thermoplasts, artificial aromas and fragrances, etc., where it serves as an esterification agent (Playne, 1985).

The fermentation products are generally dilute water solutions of propionic acid, with many impurities. The product may be separated by liquid-liquid extraction, commonly performed at near ambient temperatures to reduce costs and avoid possible thermal degradation. Many solvents were investigated experimentally with this respect and phase diagrams in the system $H_2O(1)$ – solvent(2) – propionic acid(3) were derived. The list of solvents include aromatics, e.g. benzene (Utkin et al., 1971), toluene (Alessi et al., 1984; Ghanadzadeh et al., 2010; Badakhshan et al., 1985; Kim and Park, 2005) o-xylene (Kim and Park, 2005) and cumene (Çehreli, 2006); linear and cyclic aliphatics, such as petroleum ether (Utkin et al., 1971), *n*-heptane (Alessi et al., 1984), cyclohexane (Ghanadzadeh et al., 2010; Özmen et al., 2004; Badakhshan et al., 1985), methylcyclohexane (Ghanadzadeh et al., 2010), *n*-hexane (Özmen et al., 2004); alcohols: 1-butanol (Solimo et al., 1997; Zurita et al., 1998; Kim and Park, 2005), cyclohexanol (Özmen et al., 2004), 2-butanol (Radwan and Al Muhtaseb, 1997), longer-chain aliphatic alcohols (Senol, 2005; Ghanadzadeh et al., 2008, Bilgin and Arisoy, 2006; İsmail Kırbaşlar et al., 2006; Raja Rao et al., 1958); ketones: methyl isopropyl ketone (Vakili-Nezhaad et al., 2004; Roy et al., 2007; Taghikhani et al., 2001), methyl isobutyl ketone (Vakili-Nezhaad et al., 2004; Roy et al., 2007; Arce et al., 1993; Kim and Park, 2005), methyl *n*-butyl ketone (Taghikhani et al., 2001), methyl ethyl ketone (Arce et al., 1995), methyl *n*-propyl ketone (Arce et al., 1995), cyclohexanone (Çehreli et al., 2005b), methyl isoamyl ketone, diisobutyl ketone and ethyl isoamyl ketone (Özmen, 2006); ethers: di-*n*-propyl ether (Özmen, 2007) or di-*i*-propyl ether (Özmen et al., 2004) or nitriles: butanenitrile (Letcher and Redhi, 2002) or chlorinated solvents: dichlorometane (Mohsen-Nia et al., 2009). However, many of these solvents are toxic; downstream separation of propionic acid may be a very demanding task if products for the food industry are required.

Esters are among the most investigated solvents due to their low toxicity, such as monofunctional cyclohexyl acetate (Özmen et al., 2004), ethyl acetate(Utkin et al., 1971; Kim and Park, 2005), *n*-butyl acetate (Utkin et al., 1971; Çehreli et al., 1999), *n*-propyl acetate and *i*-propyl acetate (Çehreli et al., 1999), or bifunctional dimethyl phthalate (Özmen et al., 2005), diethyl phthalate (Çehreli et al., 2005a), dimethyl adipate, dimethyl succinate and dimethyl glutarate (İsmail Kırbaşlar et al., 2007a), diethyl succinate, diethyl glutarate and diethyl adipate (İsmail Kırbaşlar et al., 2007b), dimethyl maleate (Özmen, 2008). The problem of downstream separation remains, however, to be resolved.

In this article we contribute new data for the two systems, i.e. $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3) at 35°C (first data at this temperature) and $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3) at 25°C. The data are compared with literature findings and suitable model correlations and/or predictions.

Materials and Methods

Chemicals. Propionic acid (p.a. purity ≥99.8%, M=74.08 g mol^{-1}, ρ=0.990 g cm^{-3}, boiling point 141°C) was obtained from Fluka. *n*-butyl acetate (p.a. purity ≥99.5%,, M=116.16, ρ=0.880 g cm^{-3}, boiling point 126°C) was obtained from Kemika, Zagreb, Croatia. Dimethyl adipate (p.a. purity >99%, M=174.20) was obtained from Fluka. The chemicals were used without any further treatment. Milli-Q water (18 MΩ cm^{-1} water, Millipore, Bedford, MA, USA) was used in all experiments.

Solubility curve and refractive index measurements. All the measurements were performed at indicated temperatures, in a thermostated air bath. Solutions of propionic acid in water were carefully titrated by dropwise addition of *n*-butyl acetate or dimethyl adipate with a glass syringe through a silicone septum sleeve stopper to prevent evaporation of the components until incipient turbidity was observed. For other branch of solubility curves, the measurements were performed by titrating solutions of propionic acid in *n*-butyl acetate or dimethyl adipate with water in a similar manner. The overall volume of solutions never exceeded 4 ml (4 ml vials). After observing the initial turbidity, the solutions were left overnight at corresponding temperatures to settle into two layers. Refractive indices of the major layer were determined by an Abbe refractometer (RL3 type, PZO Warszawa, Poland), thermostated again at selected temperatures. Triplicate measurements were performed.

Tie lines. Two-phase three-component solutions (approx. 4 ml) were prepared by weighing the components. The solutions were shaken well and left in a thermostated air bath at 25°C or 35°C for a day to settle and reach equilibrium separation. The refractive indices of the two coexisting phases were determined (in triplicate) using the above mentioned instrument at corresponding temperatures.

Results

Solubility curve and refractive index measurements. Solubility curve data are presented in Table 1.

Table 1 – Experimentally determined binodal curve compositions and corresponding refractive indices (triplicate averages).

H2O(1) – n-butyl acetate(2) – propionic acid(3), 35°C			H2O(1) – dimethyl adipate(2) – propionic acid(3), 25°C		
w_2	w_3	n_D	w_2	w_3	n_D
0.0184	0.0627	1.3373	0.0345	0.0000	1.3358
0.0194	0.1278	1.3426	0.0280	0.0562	1.3411
0.0124	0.1854	1.3480	0.0404	0.1000	1.3454
0.0296	0.2169	1.3507	0.0451	0.1434	1.3500
0.0345	0.2605	1.3540	0.0641	0.1771	1.3545
0.0489	0.3089	1.3586	0.1025	0.2250	1.3612
0.0835	0.3399	1.3630	0.1422	0.2510	1.3651
0.0949	0.3622	1.3633	0.1840	0.2748	1.3732
0.2285	0.4330	1.3772	0.2385	0.2989	1.3789
0.2853	0.4352	1.3788	0.2845	0.3115	1.3840
0.3651	0.4432	1.3828	0.3377	0.3273	1.3900
0.4417	0.4222	1.3851	0.3184	0.3245	1.3871
0.4887	0.3936	1.3857	0.4033	0.3256	1.3940
0.5683	0.3494	1.3867	0.4582	0.3072	1.3974
0.6576	0.2988	1.3875	0.5383	0.2951	1.4016
0.7457	0.2280	1.3879	0.5750	0.2614	1.4047
0.8079	0.1765	1.3880	0.6458	0.2228	1.4091
0.8669	0.1209	1.3884	0.7280	0.1790	1.4111
0.9303	0.0612	1.3883	0.7621	0.1501	1.4139
			0.8369	0.1023	1.4184
			0.8973	0.0590	1.4209
			0.9610	0.0000	1.4223

Following the work of Hlavatý (Hlavatý, 1972), three equations have been fitted to the data, but with experimental mass instead of mole fractions as variables. These are the modified equations of Hlavatý:

$$w_3 = A_1 w_A \ln w_A + A_2 (1 - w_A) \ln w_A + A_3 w_A (1 - w_A), \tag{1}$$

β-function equation:

$$w_3 = B_1 (1 - w_A)^{B_2} w_A^{B_3} \tag{2}$$

as well as logγ-function equation:

$$w_3 = C_1\left(-\ln w_A\right)^{C_2} w_A^{C_3}. \tag{3}$$

where w_A is defined as:

$$w_A = \frac{w_2 + 0.5w_3 - w_2'}{w_2'' - w_2'} \tag{4}$$

and w_2' and w_2'' are the mass fractions of component 2 in the absence of component 3 (in this case mass fractions describe the mutual solubility of water and organic ester. The equation parameters, $A_{1\text{-}3}$, $B_{1\text{-}3}$ and $C_{1\text{-}3}$, were determined by minimizing the functions:

$$OF_1 = \sqrt{\frac{1}{n_b}\left(w_{3,\exp} - w_{3,\mathrm{mod}}\right)^2}, \tag{5}$$

and are shown in Table 2. n_b is the number of binodal data points. All the equations behave quite similarly in describing the binodal curves, the Hlavatý equation producing somewhat better results than the others. Therefore, this equation was selected for further calculations.

Table 2 – Model parameters of the empirical binodal curve correlations.

Hlavatý	□	log□
H_2O(1) – *n*-butyl acetate(2) – propionic acid(3), 35°C		
A_1=-0.395868	B_1=1.40078	C_1=1.28192
A_2=-0.429353	B_2=0.825051	C_2=0.785559
A_3=0.626771	B_3=0.83448	C_3=1.12037
w_2''=0.9833	w_2''=0.9833	w_2''=0.9833
w_2'=0.0300	w_2'=0.0300	w_2'=0.0300
OF_1=0.0105273	OF_1=0.0106949	OF_1=0.0121922
H_2O(1) – dimethyl adipate(2) – propionic acid(3), 25°C		
A_1=-0.294197	B_1=1.05564	C_1=0.961382
A_2=-0.184108	B_2=0.885395	C_2=0.842681
A_3=0.61914	B_3=0.833761	C_3=1.14201
w_2''=0.9661	w_2''=0.9661	w_2''=0.9661
w_2'=0.0240	w_2'=0.0240	w_2'=0.0240
OF_1=0.00818113	OF_1=0.00818337	OF_1=0.00882725

By examining refractive index, n_D, vs. composition plots corresponding to binodal curves, best sensitivity was observed for the lower (water) phase in both systems, with respect to the mass fraction of propionic acid, w_3. The proposed equations are:

$$n_D = -14.8514 + 11.1556\, w_3\,, \tag{6}$$

$$n_D = -196.748 + 283.119\, w_3 - 101.685\, w_3^2\,, \tag{7}$$

for the systems with *n*-butyl acetate at 35°C and dimethyl adipate at 25°C, respectively.

Tie lines. Overall compositions and refractive indices (triplicate averages) of equilibrium lower (water) phase are given in Table 3. Using the refractive indices, it was possible to determine the corresponding w_3 values for the water phase from Eqs. 6 and 7, respectively, w_2 values from the Hlavatý equation, and w_1 values from the mass balance requirement $w_1+w_2+w_3=1$. Compositions of the upper phase were deduced from the overall mass balance and Hlavatý equation. The results are added in Table 3.

Table 3 – Overall compositions, composition of equilibrium phases and refractive index values (triplicate averages) of water phase.

$H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3), 35°C						
Overall		Lower (water) phase			Upper (organic) phase	
w_2	w_3	n_D(35°C)	$w_{2,aq}$	$w_{3,aq}$	$w_{2,org}$	$w_{3,org}$
0.4560	0.0538	1.3359	0.0205	0.0513	0.9351	0.0565
0.4053	0.1365	1.3402	0.0170	0.0993	0.8117	0.1754
0.4079	0.1553	1.3415	0.0168	0.1138	0.7882	0.1956
0.4010	0.1781	1.3425	0.0169	0.1250	0.7505	0.2264
0.3742	0.2183	1.3443	0.0176	0.1450	0.6783	0.2808
0.3584	0.2523	1.3468	0.0197	0.1729	0.6273	0.3153
0.3494	0.2867	1.3483	0.0218	0.1897	0.5678	0.3514
0.3204	0.3330	1.3512	0.0273	0.2220	0.4828	0.3945
0.2895	0.3746	1.3546	0.0371	0.2600	0.4010	0.4253

$H_2O(1)$ – dimethyl adipate(2) – propionic acid(3), 25°C						
Overall		Lower (water) phase			Upper (organic) phase	
w_2	w_3	n_D(25°C)	$w_{2,aq}$	$w_{3,aq}$	$w_{2,org}$	$w_{3,org}$
0.4913	0.0309	1.3382	0.0247	0.0264	0.9272	0.0351
0.4792	0.0482	1.3397	0.0267	0.0426	0.9051	0.0534
0.4755	0.0808	1.3409	0.0288	0.0553	0.8426	0.1018
0.4492	0.1104	1.3426	0.0325	0.0727	0.7873	0.1410
0.4342	0.1324	1.3437	0.0352	0.0837	0.7430	0.1701
0.4261	0.1617	1.3454	0.0399	0.1001	0.6880	0.2035
0.4089	0.1978	1.3481	0.0484	0.1250	0.6197	0.2404
0.3980	0.2191	1.3496	0.0537	0.1382	0.5763	0.2610
0.3820	0.2496	1.3522	0.0636	0.1600	0.5132	0.2865
0.3721	0.2731	1.3543	0.0724	0.1766	0.4636	0.3026

Modeling and discussion

Comparison with literature data. The experimental results for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3) at 35°C are compared with available results of other authors (Utkin et al., 1971; Çehreli et al., 1999) available at different temperatures. The results are shown in Fig. 1. The position of binodal curve varies little with the temperature in the investigated range, seemingly by decreasing the homogeneous region with increasing temperature. All the data show higher mass fractions of propionic acid in the organic phase with comparable tie line slopes. The results for the system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3) at 25°C are compared with available literature data (İsmail Kırbaşlar et al., 2007a) in Fig. 2. In this case the match is fairly good, again pointing to higher mass fractions of propionic acid in the organic phase.

Plait Points. Plait points in the investigated systems may be determined by the Treybal method (Treybal et al., 1946), by intersecting the linear relationship of $\log(w_3/w_1)$ in the aqueous phase vs. $\log(w_3/w_2)$ in the organic phase (Hand, 1930), with the binodal curve (i.e. its Hlavatý's equation representation) as plotted by $\log(w_3/w_1)$ vs. $\log(w_3/w_2)$. The procedure is illustrated in Fig. 3. The determined

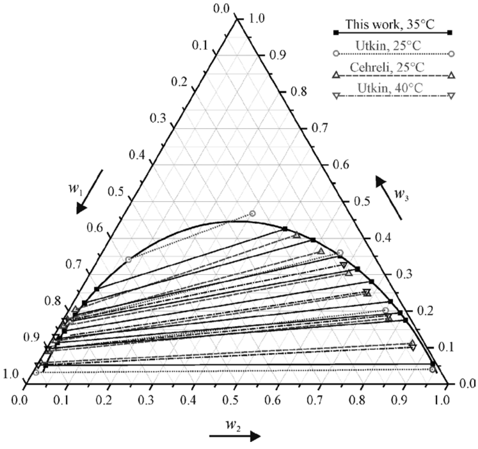

Fig. 1 – Comparison of experimentally determined binodal curve and tie lines with literature tie line data (Utkin et al., 1971; Çehreli et al., 1999) for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3).

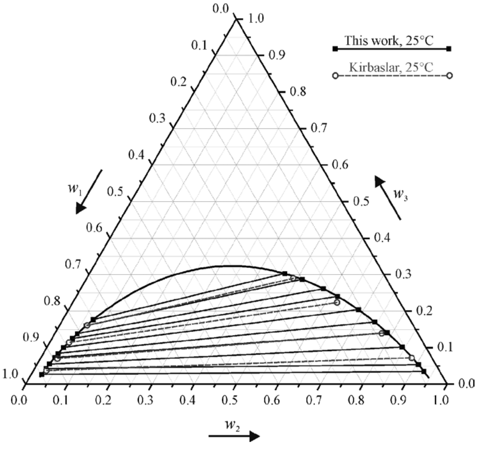

Fig. 2 – Comparison of experimentally determined binodal curve and tie lines with literature tie line data (İsmail Kırbaşlar et al., 2007a) for the system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3).

plait point coordinates are: $\{w_2=0.1104, w_3=0.3843\}$ and $\{w_2=0.1480, w_3=0.2649\}$ for the system with *n*-butyl acetate at 35°C and dimethyl adipate at 25°C, respectively.

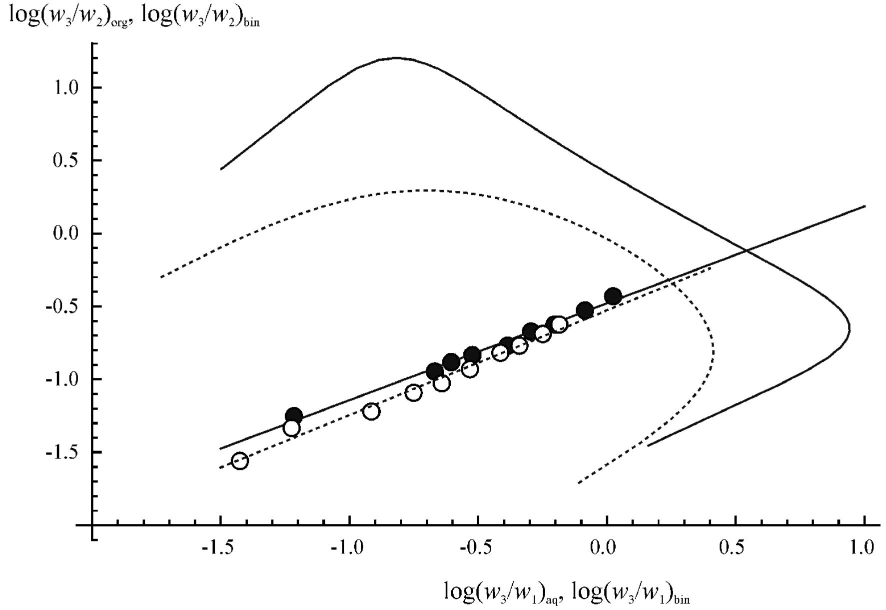

Fig. 3 – Treybal-Hand plot for determining plait points for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3) [black circles, solid lines] and system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3) [white circle, dotted lines].

Othmer Tobias correlation. Othmer-Tobias plot (Othmer and Tobias, 1942) is a revised version of Hand's plot that takes into account the mutual solubility of two (partially) immiscible solvents. Tie line data are approximated with the correlation of the form:

$$\frac{w_{2,\mathrm{aq}} + w_{3,\mathrm{aq}}}{w_{1,\mathrm{aq}}} = k\left(\frac{w_{1,\mathrm{org}} + w_{3,\mathrm{org}}}{w_{2,\mathrm{org}}}\right)^n \tag{8}$$

or, by applying mass balance for both phases:

$$\frac{1 - w_{1,\mathrm{aq}}}{w_{1,\mathrm{aq}}} = k\left(\frac{1 - w_{2,\mathrm{org}}}{w_{2,\mathrm{org}}}\right)^n . \tag{9}$$

with k being roughly the distribution coefficient and n, again roughly, describing the curvature of the equilibrium line in the Hand coordinates plot. Model parameters k and n are easily determined from the experimental data, by minimizing the function:

$$OF_2 = \sqrt{\frac{1}{n_\mathrm{d}}\sum_{i=1}^{n_\mathrm{d}}\left[\log\left(\frac{1 - w_{2,\mathrm{aq}}}{w_{2,\mathrm{aq}}}\right) - \log K - n\log\left(\frac{1 - w_{3,\mathrm{org}}}{w_{3,\mathrm{org}}}\right)\right]^2} . \tag{10}$$

Where, n_d is the number of experimental tie-lines. The results are shown in Fig. 4. The linearity of the plots indicates the consistency of data. The parameters are $\{K, n\}=\{0.315, 0.556\}$ and $\{K, n\}=\{0.288, 0.653\}$ for the systems with *n*-butyl

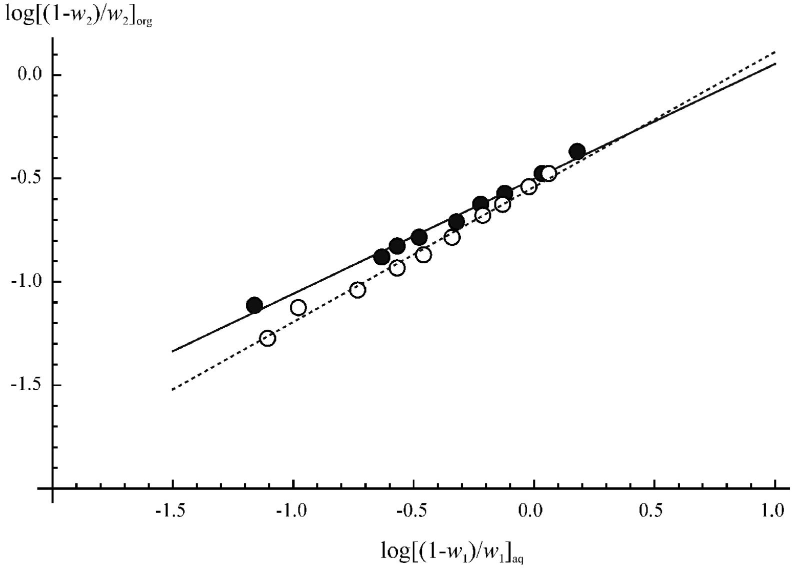

Fig. 4 – Othmer-Tobias plot for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3) [black circles, solid lines] and system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3) [white circle, dotted lines].

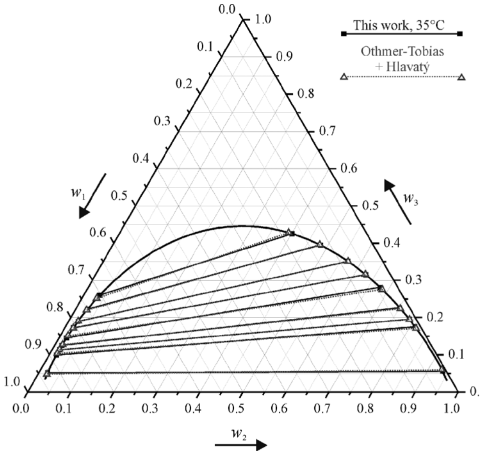

Fig. 5 – Comparison of experimentally determined binodal curve and tie lines with Othmer-Tobias correlation for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3).

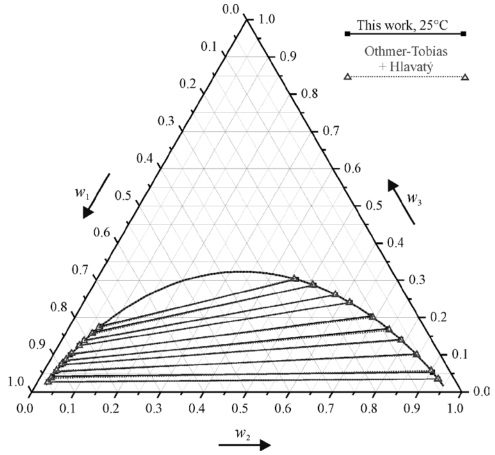

Fig- 6 – Comparison of experimentally determined binodal curve and tie lines with Othmer-Tobias correlation for the system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3)

acetate and dimethyl adipate, respectively. The parameters may serve, together with the Hlavatý parameters as given in Table 2, for the complete reconstruction of the phase diagram as presented in Figs. 5 and 6.

UNIFAC model. UNIFAC LLE model (Magnussen et al., 1981) as a group contribution model allows for the prediction of LLE data. Here, we used the ChemCAD

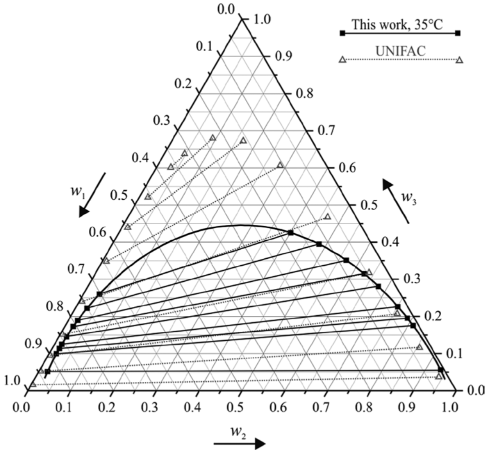

Fig. 7 – Comparison of experimentally determined binodal curve and tie lines with UNIFAC LLE prediction for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3).

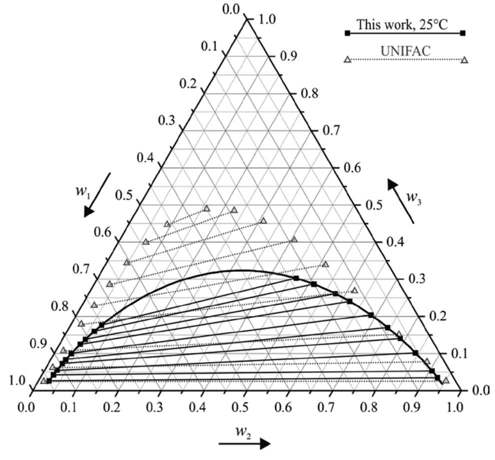

Fig. 8 – Comparison of experimentally determined binodal curve and tie lines with UNIFAC LLE prediction for the system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3).)

6.3.1. software with built-in thermodynamic data tables (UNIFAC LLE) to calculate the phase diagrams of the investigated systems. Dimethyl adipate was added as new component according to common rules of sectioning the components into functional groups. The results are shown in Figs. 7 and 8. For both systems, UNIFAC LLE predicts too large a region of immiscibility.

NRTL and UNIQUAC models. NRTL model (Renon and Prausnitz, 1968) takes into account local concentration variations as induced by differences between Gibbs interaction energies of the same and unlike species. Interaction energy parameters for pairs of species are t_{ij} and t_{ji}. The additional nonrandomness parameter $a_{ij}=a_{ji}$ is introduced into the model, giving a set of three parameters per pair of components. The excess Gibbs function, g^{ex}, is:

$$\frac{g^{\text{ex}}}{RT}=\sum_{i=1}^{n_\text{c}}x_i\left[\frac{\sum_{j=1}^{n_\text{c}}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n_\text{c}}G_{ki}x_k}\right], \tag{11}$$

with:

$$G_{ij}=\exp\left(-\alpha_{ij}\tau_{ij}\right), \tag{12}$$

n_c is the number of components. Commonly, α-parameters are set fixed; for the systems with water and propionic acid, fixed α-values are in most cases either all 0.2 or all 0.3. In this article we tested all eight possible combinations of three α-values set at either 0.2 or 0.3.

τ-parameters were regressed from the experimental data.

UNIQUAC model (Abrams and Prausnitz, 1975) gives excess Gibbs function as a sum of two contributions, combinatorial, $g^{\text{ex,C}}$, based on the lattice theory that accounts for the size and shape differences of the species:

$$\frac{g^{\text{ex,C}}}{RT}=\sum_{i=1}^{n_\text{c}}x_\text{i}\ln\frac{\Phi_i}{x_i}+\frac{z}{2}\sum_{i=1}^{n_\text{c}}q_ix_i\ln\frac{\Theta_i}{\Phi_i}, \tag{13}$$

and residual, $g^{\text{ex,R}}$, accounting for the interaction energies between molecules, expressed by:

$$\frac{g^{\text{ex,R}}}{RT}=-\sum_{i=1}^{n_\text{c}}q_ix_i\ln\left(\sum_{j=1}^{n_\text{c}}\Theta_j\tau_{ji}\right), \tag{14}$$

The model includes a set of two adjustable interaction parameters t_{ij} and t_{ji} per pair of components. F_i, Q_i and x_i are volume, area and molar fractions of component i, respectively, z is the lattice coordination number and q_i is the surface parameter of component i. The formulas for calculating F*i* and Q*i* from volume and surface parameters, r_i and q_i of the components, respectively, are:

$$\Phi_i = \frac{x_i r_i}{\sum_{j=1}^{n_\mathrm{c}} x_j r_j}, \tag{15}$$

$$\Theta_i = \frac{x_i q_i}{\sum_{j=1}^{n_\mathrm{c}} x_j q_j}. \tag{16}$$

r_i and q_i of the components are calculated using the group contribution approach and group parameters as given in (Magnussen et al., 1981), using the following formulae:

$$r_i = \sum_{k=1}^{n_\mathrm{g}} \nu_{ki} R_k , \tag{17}$$

$$q_i = \sum_{k=1}^{n_\mathrm{g}} \nu_{ki} Q_k . \tag{18}$$

where R_k and Q_k are volume and surface parameters of structural group k, respectively. Thus, both models have six adjustable interaction parameters to be determined from experimental data. In this paper, we have chosen the two-step Sorensen-Arlt method (Sorensen and Arlt, 1979). In the first step, function:

$$OF_3 = \sum_{j=1}^{n_\mathrm{d}} \sum_{i=1}^{n_\mathrm{c}} \left(\frac{x_i^\mathrm{I} \gamma_i^\mathrm{I} - x_i^\mathrm{II} \gamma_i^\mathrm{II}}{x_i^\mathrm{I} \gamma_i^\mathrm{I} + x_i^\mathrm{II} \gamma_i^\mathrm{II}} \right)_j^2 + Q\left(\tau_{12}^2 + \tau_{21}^2 + \tau_{13}^2 + \tau_{31}^2 + \tau_{23}^2 + \tau_{32}^2\right) \tag{19}$$

is minimized with respect to parameters. In the denominator of the first term on the right-hand side of equation (double sum with respect to number of components, $n_\mathrm{c}=3$, and number of tie-lines, n_d) one can recognize the liquid-liquid equilibrium equation, $a_i^\mathrm{I}=a_i^\mathrm{II}$ or $(x_i g_i)^\mathrm{I}=(x_i g_i)^\mathrm{II}$, written in terms of component activities, a_i, or activity coefficients, g_i. The second term is the so-called penalty function, used to penalize for the unrealistically large values of τ producing minima in OF3 in NRTL. Therefore, we used the empirical value of penalization factor $Q=0.001$ for NRTL and $Q=0$ for UNIQUAC.

The optimal set of τ-parameters describes the equilibrium fairly well, but does not provide the best possible tie line description, which is more important from the engineering point of view. Therefore, the obtained optimal set serves as an initiation for the second step, where the following function is minimized:

$$OF_4=\sum_{j=1}^{n_\mathrm{d}}\sum_{i=1}^{n_\mathrm{c}}\sum_{p=\mathrm{I}}^{\mathrm{II}}\left[\left(x_i^p\right)_\mathrm{exp}-\left(x_i^p\right)_\mathrm{mod}\right]_j^2+Q\left(\tau_{12}^2+\tau_{21}^2+\tau_{13}^2+\tau_{31}^2+\tau_{23}^2+\tau_{32}^2\right) \tag{20}$$

where the number of components is $n_\mathrm{c}=3$, n_d is again the number of tie lines and p takes values of I and II that denote the phases in the system. Penalty function is again used with $Q=0.001$ for NRTL and $Q=0$ for UNIQUAC.

Model parameters are summarized in Table 4, together with average absolute prediction errors in mole fractions as calculated by:

$$A=\sqrt{\frac{OF_4-Q\left(\tau_{12}^2+\tau_{21}^2+\tau_{13}^2+\tau_{31}^2+\tau_{23}^2+\tau_{32}^2\right)}{n_\mathrm{d}\cdot n_\mathrm{c}\cdot 2}}\,. \tag{21}$$

Table 4 – Optimal NRTL and UNIQUAC model parameters and prediction errors.

	H_2O(1) – *n*-butyl acetate(2) – propionic acid(3), 35°C		H_2O(1) – dimethyl adipate(2) – propionic acid(3), 25°C	
	NRTL	UNIQUAC	NRTL	UNIQUAC
A	0.01170	0.01840	0.01290	0.01206
α_{12}	0.3	–	0.3	–
α_{13}	0.3	–	0.3	–
α_{23}	0.3	–	0.3	–
τ_{12}	1.3754	0.4657	1.1720	0.1164
τ_{13}	4.3436	0.9066	3.6943	0.8341
τ_{21}	0.7579	1.1105	0.4594	2.5049
τ_{23}	–2.3066	0.7059	–2.9203	1.8967
τ_{31}	3.4223	$1.264\cdot10^{-5}$	0.7594	0.2237
τ_{32}	1.6619	0.8095	0.5813	0.2358

Experimental and calculated compositions are compared in Table 5. The agreement seems to be reasonably good, providing an accurate description of the size of the two-phase region, which was not the case for UNIFAC. NRTL model was found to be much better for the H_2O(1) – *n*-butyl acetate(2) – propionic acid(3) system at 35°C than UNIQUAC and UNIQUAC described the system H_2O(1) – dimethyl adipate(2) – propionic acid(3) at 25°C slightly better than NRTL. However, much more is revealed from the triangular diagrams plotted in weight fractions, Figs. 9

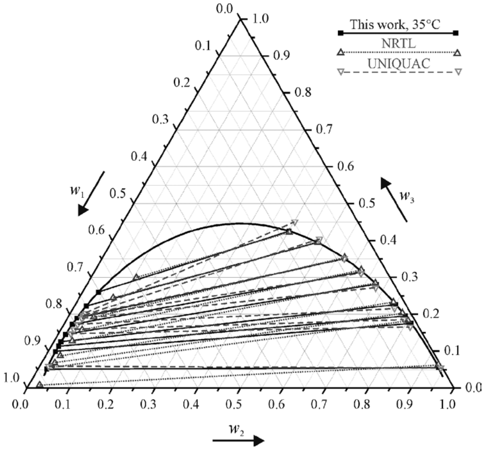

Fig. 9 – Comparison of experimentally determined binodal curve and tie lines with NRTL and UNIQUAC LLE correlation for the system $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3).

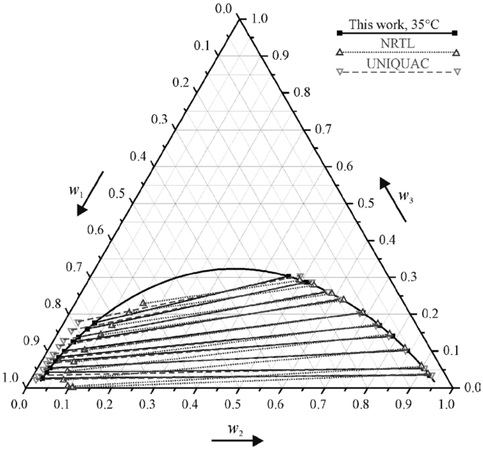

Fig. 10 – Comparison of experimentally determined binodal curve and tie lines with NRTL and UNIQUAC LLE correlation for the system $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3)

and 10. Mass fractions of the water-rich phase are described with less accuracy than for the ester-rich phase for both systems and both models. UNIQUAC was much better in predicting the variation of the slope of tie lines with the increase of propionic acid content, possibly due to better description of the combinatorial part of excess Gibbs energy. However, NRTL may be improved in this respect by allowing a free variation of α-parameters instead of using preset combinations of α-parameter values. But, this would increase the complexity of fitting procedure and jeopardize its convergence properties. Another way to improve the NRTL correlation is the variation of the penalizing factor *Q*, but this would be a pure trial and error procedure.

Conclusions

In this work the liquid-liquid phase equilibria in the two systems comprising water, an ester compound and propionic acid were studied, both experimentally and using available thermodynamic models, in search of suitable solvents for the extraction of propionic acid from water solutions or fermentation broths. The systems investigated were $H_2O(1)$ – *n*-butyl acetate(2) – propionic acid(3) at 35°C (first data at this temperature) and $H_2O(1)$ – dimethyl adipate(2) – propionic acid(3) at 25°C. Binodal curves and tie lines were determined with a combination of turbidimetric titration and refractive index measurements to show fair agreement with literature data. Experimental binodal curves were modeled with the five-parameter Hlavatý equation and tie lines with the two parameter Othmer-Tobias equation to provide

Table 5 – Comparison of experimental and calculated compositions (molar fractions) of equilibrium liquid phases.

Experimental				NRTL				UNIQUAC			
Lower(water) phase		Upper (organic) phase		Lower (water) phase		Upper (organic) phase		Lower (water) phase		Upper (organic) phase	
x_2	x_3	x_2	x_3	x_2	x_3	x_2	x_3	x_2	x_3	x_2	x_3
H_2O(1) – *n*-butyl acetate(2) – propionic acid(3), 35°C											
0.0034	0.0132	**0.8676**	**0.0822**	0.0041	0.0021	0.8777	0.0945	0.0035	0.0154	0.8975	0.0823
0.0029	0.0265	**0.6938**	**0.2351**	0.0049	0.0145	0.6730	0.2407	0.0053	0.0413	0.6776	0.2167
0.0029	0.0308	**0.6572**	**0.2557**	0.0052	0.0180	0.6363	0.2613	0.0056	0.0451	0.6379	0.2364
0.0029	0.0341	**0.5983**	**0.2830**	0.0059	0.0236	0.5827	0.2877	0.0060	0.0497	0.5810	0.2622
0.0031	0.0403	**0.4907**	**0.3185**	0.0076	0.0357	0.4856	0.3228	0.0065	0.0553	0.4810	0.3002
0.0036	0.0493	**0.4205**	**0.3314**	0.0093	0.0458	0.4171	0.3365	0.0067	0.0573	0.4126	0.3203
0.0040	0.0550	**0.3463**	**0.3360**	0.0117	0.0582	0.3475	0.3402	0.0067	0.0582	0.3458	0.3347
0.0052	0.0667	**0.2551**	**0.3269**	0.0166	0.0796	0.2579	0.3287	0.0068	0.0587	0.2617	0.3440
0.0075	0.0819	**0.1833**	**0.3048**	0.0243	0.1064	0.1843	0.3022	0.0069	0.0603	0.1950	0.3431
H_2O(1) – dimethyl adipate(2) – propionic acid(3), 25°C											
0.0027	0.0067	0.6747	0.0601	0.0125	0.0004	0.6598	0.0658	0.0013	0.0057	0.7041	0.0633
0.0029	0.0110	0.6321	0.0877	0.0108	0.0012	0.6122	0.0956	0.0014	0.0082	0.6397	0.0912
0.0032	0.0144	0.5203	0.1478	0.0087	0.0056	0.5027	0.1530	0.0016	0.0133	0.5053	0.1446
0.0037	0.0193	0.4345	0.1830	0.0086	0.0125	0.4212	0.1863	0.0017	0.0172	0.4140	0.1764
0.0040	0.0225	0.3746	0.2017	0.0091	0.0194	0.3671	0.2036	0.0019	0.0202	0.3565	0.1940
0.0046	0.0274	0.3105	0.2160	0.0106	0.0294	0.3094	0.2169	0.0021	0.0244	0.2976	0.2092
0.0058	0.0353	0.2442	0.2228	0.0134	0.0439	0.2494	0.2238	0.0024	0.0308	0.2390	0.2204
0.0066	0.0397	0.2086	0.2221	0.0157	0.0537	0.2182	0.2238	0.0027	0.0356	0.2097	0.2238
0.0080	0.0473	0.1643	0.2157	0.0200	0.0689	0.1789	0.2192	0.0034	0.0443	0.1752	0.2253
0.0093	0.0536	0.1349	0.2071	0.0242	0.0815	0.1529	0.2126	0.0041	0.0521	0.1538	0.2243

excellent correlation of the entire experiment with seven empirical parameters per system. In addition, it was shown that UNIFAC predictive activity coefficient model was not able to describe the data with sufficient accuracy. NRTL and UNIQUAC model parameters were determined from the experimental data using the procedure suggested by Sorensen and Arlt. The correlation was fair, but much worse than that obtained by the purely empirical approach of Hlavatý and Othmer-Tobias.

List of symbols

A	Average absolute deviation of experimental and calculated molar fractions, [1]
$A_{1\text{-}3}$	Parameters of Hlavatý empirical equation for binodal curve, [1]
aq	Subscript denoting aqueous (or lower) phase
$B_{1\text{-}3}$	Parameters of β-empirical equation for binodal curve, [1]
$C_{1\text{-}3}$	Parameters of log γ-empirical equation for binodal curve, [1]
exp	Subscript denoting experimental value
g^{ex}	Molar excess Gibbs energy, [J mol^{-1}]
$g^{\mathrm{ex,C}}$	Combinatorial part of molar excess Gibbs energy in UNIQUAC activity coefficient model, [J mol^{-1}]
$g^{\mathrm{ex,R}}$	Residual part of molar excess Gibbs energy in UNIQUAC activity coefficient model, [J mol^{-1}]
G	Symbol appearing in NRTL model, exponential function of model parameters, [1]
I	Superscript denoting equilibrium liquid phase I
II	Superscript denoting equilibrium liquid phase II
k	Parameter of Othmer-Tobias correlation describing the distribution coefficient, [1]
mod	Subscript denoting model or calculated value
n	Parameter of Othmer-Tobias correlation describing the curvature of the equilibrium line, [1]
n_{b}	Number of binodal curve experimental data points
n_{c}	Number of components
n_{D}	Refractive index, [1]
n_{d}	Number of tie line experimental data points
n_{g}	Number of structural groups in a component
$OF_{1\text{-}4}$	Objective function to be minimized, [1]
org	Subscript denoting organic (or upper) phase
Q	Penalization factor, [1]
q_i	Surface parameter of component i in UNIQUAC activity coefficient model, [1]
Q_k	Surface parameter of structural group k, [1]
R	Gas constant, [J K^{-1} mol^{-1}]
r_i	Volume parameter of component i in UNIQUAC activity coefficient model, [1]
R_k	Volume parameter of structural group k, [1]
T	Temperature, [K]
w_2'	Maximum (equilibrium) solubility of component 2 in component 1 in terms of weight fraction, [1]
w_2''	Weight fraction of component 2 in solution comprising maximum (equilibrium) content of component 1, [1]
w_{A}	Composition variable of the empirical equations for binodal curve, [1]
w_i	Weight fraction of component i, [1]
x_i	Molar fraction of component i, [1]

z	Lattice coordination number
a_{ij}	Nonrandomness parameter of NRTL activity coefficient model, [1]
g_i	Activity coefficient of component *i*, [1]
Q_i	Area fraction of component *i*, [1]
n_{ki}	Number of structural groups *k* in component *i*
t_{ij}	Interaction parameter of NRTL or UNIQUAC activity coefficient models, [1]
F_i	Volume fraction of component *i*, [1]

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