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Liquid-liquid Equilibria in the Ternary Systems H_2O – Phenol – 2-Butanone and H_2O – Phenol – 2-Propanol

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Liquid-liquid phase equilibria (LLE) in the systems H_2O – phenol – 2-butanone at 25 °C and H_2O – phenol – 2-propanol at 25 °C were experimentally determined with a combination of turbidimetric titration and refractometry methods. UNIFAC model was found qualitatively suitable for prediction of LLE in both systems. NRTL and UNIQUAC model parameters were determined as well. The correlation was found qualitative for the system with 2-butanone and larger deviations from experimental data were found in the system with 2-propanol.

Key words:
Liquid-liquid equilibria, phenol, 2-butanone, 2-propanol, NRTL, UNIQUAC

Introduction

Extraction as a separation process, although a mature technology, remains in the focus of interest due to its efficiency, rapid equilibration, low energy requirements and in many cases acceptability from the environmental standpoint. The methods for designing extraction process are all well known, and they are based on available liquid-liquid phase equilibria (LLE) data.

Phenol is a common organic chemical, found as product, by-product or reactant in many industrial chemical processes. It is solid at room temperature (melting point at 40.9 °C), sparingly soluble in water (8.3 g/100 mL at 20 °C). Multicomponent systems involving water and phenol may be found in extraction of phenol from water solutions in preparative or wastewater purification units, or in some industrial syntheses, such as the preparation of modified formaldehyde resins.[1]

Many systems involving phenol, water, and an organic solvent as a third component have been studied with respect to LLE. For reasons of brevity we shall list only a few of the available references on systems involving esters;[2–4] ketones:[5–8] and alcohols:[5,7,9,10]

According to our best knowledge, there is only one study regarding the system with 2-butanone, presenting binodal data at 20 and 45 °C and tie-lines at 45 °C, all at atmospheric pressure.[11] For the system with 2-propanol, three-phase vapor-liquid-liquid equilibria (VLLE) has been studied in the temperature range 15–72.5 °C, with particular emphasis on 25 °C.[10,12] Thus, we present tie-line data LLE for the two systems at 25 °C and at atmospheric pressure together with elaborate thermodynamic treatment.

Experimental part

In this contribution we experimentally determined the equilibrium compositions for the systems $H_2O(1)$ – phenol(2) – 2-butanone(3) and $H_2O(1)$ – phenol(2) – 2-propanol(3) at atmospheric pressure, and at temperature of 25 °C. All the composition determinations were done gravimetrically according to the procedure described below.

Chemicals

Phenol (p.a., M = 94.11 g mol^{-1}, melting point 40.5–41.5 °C) and 2-butanone (p.a., M = 72.11 g mol^{-1}, boiling point 79–80 °C) were obtained from Fluka and propanol (p.a., M = 60.10 g mol^{-1}, ρ = 0.785–0.787 g cm^{-3}, boiling point 81.5–82.5 °C) was obtained from Kemika, Zagreb, Croatia. The chemicals were used with no further treatment. Milli-Q water (18 MΩ cm^{-1} water, Millipore, Bedford, MA, USA) was used in all experiments.

Binodal curve and refractive index measurements

Binodal curve measurements were done as follows. The system with 2-butanone contained two partially miscible component binaries (water – phenol, water – 2-butanone), with two separate branches of binodal curves. To cover the whole composition range of interest, the following procedure was ap-

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plied. Solid phenol was dissolved in water at appropriate concentration; the exact concentration was determined by weighing. The binary solution was then mixed with 2-butanone in various proportions to create a set of ternary solutions in the homogeneous region. Again, the exact concentrations were determined by weighing. The weighed amounts of solutions were then titrated (in vials equipped with silicone rubber septa to prevent evaporation) by dropwise addition of pure water until incipient turbidity at the organic-rich binodal branch is observed. Due to the previously checked fact that miscibility in the investigated system slightly increases with the temperature, the solutions were allowed to rest for 60 minutes in an air bath thermostated at 25 °C. In case of disappearance of turbidity, an additional drop of titrant is added. The stable turbidity was an indication of reaching the binodal curve. The final composition was then determined by weighing. The points on the water-rich binodal branch were determined by a similar procedure, either by titrating pure water with ternary homogeneous solutions of phenol, water and 2-butanone (previous compositions determined by weighing, as pointed out before) or by titrating binary homogeneous solutions of 2-butanone and water with a homogeneous solution of phenol and water of appropriate concentration (again previously determined by weighing). The selection of the appropriate solution compositions for the titration procedures was done according to preliminary experiments. Again, incipient turbidity was looked for and checked in a thermostated air bath at 25 °C, as described before.

The procedure for the 2-propanol system was somewhat simpler, since there was only one partially miscible binary (water – phenol) and a closed binodal curve with two branches merging in a plait point. Again, solid phenol was dissolved in water at appropriate concentration; the binary solution was then mixed with 2-propanol in various proportions to create ternary solutions. Exact concentrations were determined by weighing. The solutions were titrated by dropwise addition of pure water until incipient turbidity at the organic-rich binodal branch is observed. The water-rich branch was determined by titrating the solutions of 2-propanol in water with a solution of phenol in water of appropriate concentration. Incipient turbidity was checked by resting the solution in a thermostated air bath at 25 °C for 60 min. In case of disappearance of turbidity, an additional drop of titrant was added.

After observing the incipient turbidity, solutions were heated to 35 °C to merge the major phase (representing the overall composition) with the minor phase turning the turbidity into a clear so-

lution (the immiscibility region was found to decrease with increasing temperature by preliminary measurements). Refractive indices of the clear solutions were determined by an Abbe refractometer (RL3 type, PZO Warszawa, Poland), thermostated at 35 °C. Triplicate measurements were performed.

Preliminary measurements revealed that there was a phase inversion phenomenon in both systems, i.e. in one portion of the composition range the water-rich phase was heavier, while in another it was lighter than the organic-rich phase.

Tie lines

Two-phase three-component solutions (approx. 4 mL) were prepared by weighing the components. The solutions were shaken well (4 hrs of shaking) in a thermostated air bath equipped with a shaker and then left overnight, all at 25 °C for a day to settle and reach equilibrium separation. After physically separating the phases and heating to 35 °C, the refractive indices of the two coexisting phases were determined (in triplicate) using the above mentioned instrument.

Results

Binodal curve

Binodal curve data are presented in Table 1. The equations in the work of Hlavatý[13] used for empirical description of binodal curve were found unsuitable for the two studied systems. Thus, binodal curves were reconstructed by nonlinear interpolation.

Tie lines

Refractive indices (triplicate averages) of equilibrium phases are given in Table 2. The refractive indices enabled determination of corresponding equilibrium phase compositions, via w_i vs. n_D diagrams and previously constructed binodal curves. The results are added into Table 2.

Modeling and discussion

Comparison with literature data

The experimental results for the system H₂O(1) – phenol(2) – 2-butanone(3) at 25 °C and atmospheric pressure are compared with literature data at 20 and 45 °C.[11] The results are shown in Fig. 1. Data show a decrease in the immiscibility region with increased temperature, particularly at low 2-butanone content. This is consistent with experimental findings for upper critical solution temperatures, UCST, of immiscible binaries. Namely, H₂O

T a b l e   1 – *Experimentally determined binodal curve compositions (mass fractions, w_i) and corresponding refractive indices (n_D, triplicate averages)*

phase[a]	H$_2$O(1) – phenol(2) – 2-buta-none(3), 25 °C			H$_2$O(1) – phenol(2) – 2-propanol(3), 25 °C		
	w_2	w_3	n_D (35 °C)	w_2	w_3	n_D (35 °C)
org	0.0000	0.8716	1.3736	0.7108	0.0000	1.4781
org	0.1748	0.7191	1.4011	0.6856	0.0482	1.4750
org	0.2536	0.6406	1.4133	0.6439	0.1127	1.4684
org	0.3521	0.5484	1.4290	0.6095	0.1540	1.4633
org	0.4278	0.4602	1.4418	0.5695	0.1888	1.4560
org	0.5162	0.3755	1.4561	0.5219	0.2374	1.4486
org	0.5998	0.2817	1.4689	0.4908	0.2637	1.4436
org	0.6599	0.1964	1.4772	0.4393	0.2882	1.4341
org	0.7132	0.1073	1.4848	0.3943	0.3013	1.4261
org	0.7206	0.0511	1.4831	0.3325	0.3146	1.4154
org	0.6968	0.0000	1.4754	0.2854	0.3094	1.4061
aq	0.0000	0.2598	1.3500	0.2656	0.3022	1.4021
aq	0.0062	0.2352	1.3478	0.2310	0.2876	1.3950
aq	0.0136	0.1572	1.3441	0.2024	0.2684	1.3891
aq	0.0131	0.0777	1.3409	0.1706	0.2491	1.3822
aq	0.0177	0.0494	1.3397	0.1436	0.2312	1.3761
aq	0.0241	0.0367	1.3397	0.1158	0.2153	1.3701
aq	0.0300	0.0244	1.3399	0.0877	0.1851	1.3634
aq	0.0388	0.0208	1.3409	0.0698	0.1530	1.3580
aq	0.0462	0.0106	1.3422	0.0613	0.1119	1.3532
aq	0.0595	0.0044	1.3445	0.0560	0.0747	1.3496
aq	0.0817	0.0000	1.3497	0.0638	0.0382	1.3480
				0.0742	0.0000	1.3469

[a]For the H$_2$O(1) – phenol(2) – 2-butanone(3) system two separate binodal branches (organic-rich, org) and water-rich, aq) are clearly identified.

T a b l e   2 – *Refractive index values (n_D, triplicate averages) and compositions (mass fractions, w_i) of equilibrium phases*

H$_2$O(1) – phenol(2) – 2-butanone(3), 25 °C

Water phase			Organic phase		
n_D (35 °C)	$w_{2,aq}$	$w_{3,aq}$	n_D (35 °C)	$w_{2,org}$	$w_{3,org}$
1.3482	0.002	0.235	1.3801	0.063	0.828
1.3458	0.003	0.190	1.3944	0.150	0.746
1.3440	0.003	0.163	1.4085	0.232	0.665
1.3431	0.005	0.133	1.4162	0.278	0.619
1.3423	0.006	0.115	1.4290	0.357	0.542
1.3405	0.012	0.071	1.4367	0.406	0.494
1.3401	0.015	0.060	1.4471	0.471	0.428
1.3399	0.018	0.052	1.4554	0.521	0.373
1.3403	0.034	0.021	1.4682	0.601	0.281
1.3439	0.056	0.006	1.4841	0.700	0.133
1.3462	0.067	0.003	1.4849	0.719	0.063

H$_2$O(1) – phenol(2) – 2-propanol(3), 25 °C

Water phase			Organic phase		
n_D (35 °C)	$w_{2,aq}$	$w_{3,aq}$	n_D (35 °C)	$w_{2,org}$	$w_{3,org}$
1.3485	0.063	0.046	1.4717	0.666	0.078
1.3490	0.060	0.056	1.4700	0.655	0.094
1.3495	0.056	0.069	1.4605	0.593	0.170
1.3500	0.059	0.098	1.4554	0.562	0.203
1.3504	0.061	0.103	1.4523	0.544	0.219
1.3520	0.061	0.120	1.4407	0.475	0.273
1.3535	0.065	0.131	1.4304	0.416	0.296
1.3583	0.071	0.157	1.4211	0.362	0.310
1.3622	0.087	0.181	1.4120	0.312	0.317

– 2-butanone system has an UCST at approximately 140 °C, and temperature variation of equilibrium solubilities between 20 and 45 °C is rather low;[14] H$_2$O – phenol binary has an UCST at around 67 °C and mutual solubility of components decreases between 20 and 45 °C.[15] Experimental results for the system H$_2$O(1) – phenol(2) – 2-propanol(3) at 25 °C are compared in Fig. 2 with selected literature data at various temperatures.[12] Good match is found with experimental and literature binodal data; tie lines are inclined towards the water vertex, pointing to a better solubility of 2-propanol in phenol than in water (on the mass basis).

UNIFAC model

UNIFAC model as a group contribution model allows for the prediction of LLE data if a suitable parameter data set is used. Here, we used the ChemCAD 6.3.1. software with built-in thermodynamic data tables (UNIFAC LLE – corresponding to dataset from,[16] including the 2-propanol exception) to calculate the phase diagrams of the investigated systems. The results for the systems H$_2$O(1) – phenol(2) – 2-butanone(3) and H$_2$O(1) – phenol(2) – 2-propanol(3) are shown in Figs. 3 and 4, respectively. Here, UNIFAC was able to describe the phase diagram qualitatively, but the region of immiscibility was predicted too large.
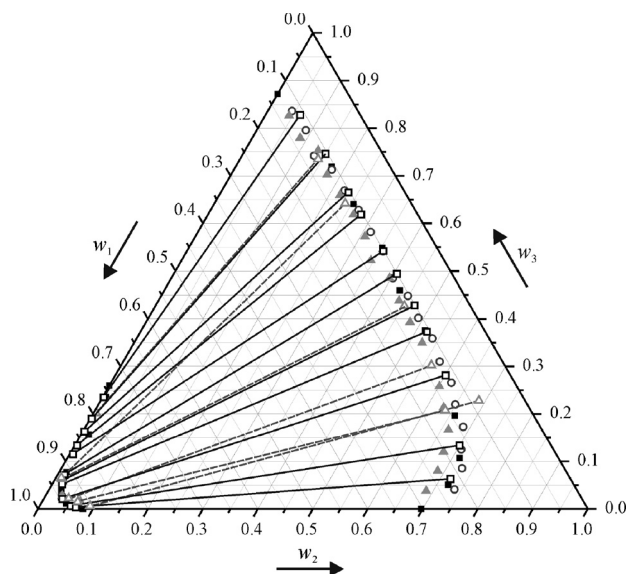
F i g . 1 – *Comparison of experimentally determined binodal curve and tie lines with literature binodal[11] and tie line data for the system* $H_2O(1)$ *– phenol(2) – 2-butanone(3):* ■ *this work binodal at 25 °C,* □ —— *this work tie line at 25 °C,* ○ *literature binodal at 20 °C,* ▲ *literature binodal at 45 °C,* △ - - - *literature tie line at 45 °C*
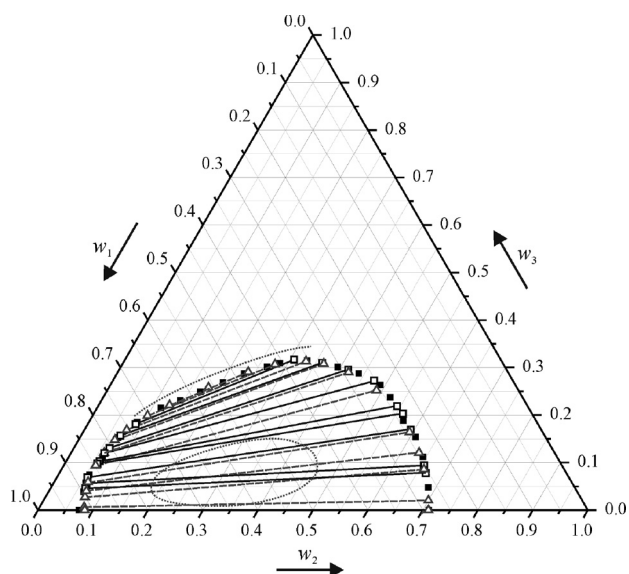

F i g . 3 – *Comparison of experimentally determined binodal curve and tie lines with UNIFAC LLE prediction for the system* $H_2O(1)$ *– phenol(2) – 2-butanone(3):* □ —— *this work experimental,* ○ ········ *UNIFAC LLE prediction*

F i g . 2 – *Comparison of experimentally determined binodal curve and tie lines with literature binodal and tie line data[12] for the system* $H_2O(1)$ *– phenol(2) – 2-propanol(3):* ■ *this work binodal at 25 °C,* □ —— *this work tie line at 25 °C,* △ - - - *literature VLLE tie line at 25 °C,* ········ *literature VLLE binodals at 15 and 70 °C*

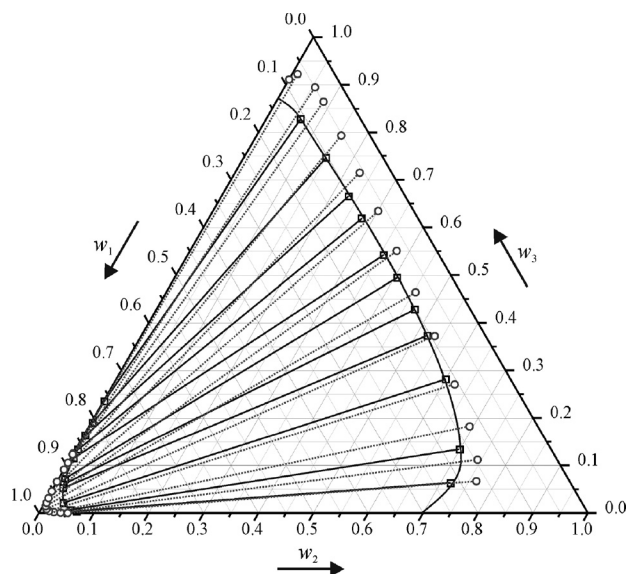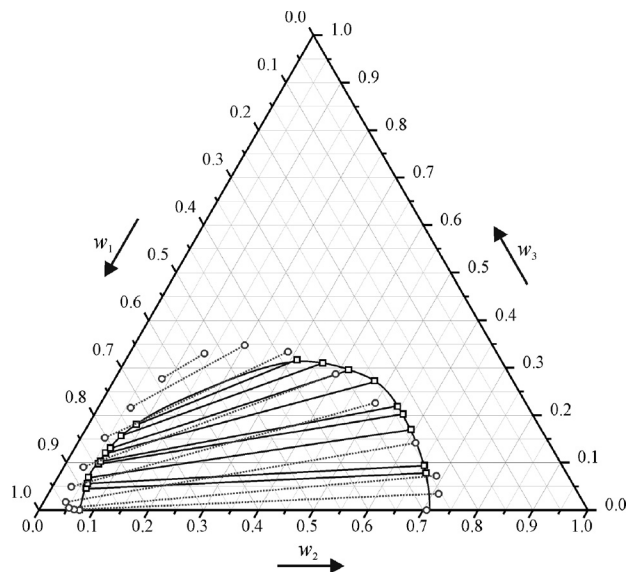F i g . 4 – *Comparison of experimentally determined binodal curve and tie lines with UNIFAC LLE prediction for the system* $H_2O(1)$ *– phenol(2) – 2-propanol(3):* □ —— *this work experimental,* ○ ········ *UNIFAC LLE prediction*

NRTL and UNIQUAC models

NRTL model[17] takes into account local concentration variations as induced by differences between Gibbs interaction energies of the same and unalike species. Interaction energy parameters for pairs of species are τ_{ij} and τ_{ji}. An additional nonrandomness parameter $\alpha_{ij} = \alpha_{ji}$ is introduced in the model, giving a set of three parameters per pair of components. The excess Gibbs function, g^{ex}, is:

$$\frac{g^{ex}}{RT} = \sum_{i=1}^{n_c} x_i \left[\frac{\sum_{j=1}^{n_c} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n_c} G_{ki} x_k} \right], \qquad (1)$$

with:

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}). \qquad (2)$$

n_c is the number of components. Commonly, α-parameters are fixed.[18] 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[19] gives excess Gibbs function as a sum of two contributions: combinatorial, $g^{ex,C}$, based on the lattice theory that accounts for the size and shape differences of the species:

$$\frac{g^{ex,C}}{RT} = \sum_{i=1}^{n_c} x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_{i=1}^{n_c} q_i x_i \ln \frac{\Theta_i}{\Phi_i}, \quad (3)$$

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

$$\frac{g^{ex,R}}{RT} = -\sum_{i=1}^{n_c} q_i x_i \ln \left(\sum_{j=1}^{n_c} \Theta_j \tau_{ji} \right). \qquad (4)$$

The model includes a set of two adjustable parameters τ_{ij} and τ_{ji} per pair of components. $z = 10$ is the lattice coordination number. Φ_i, Θ_i and x_i are volume, area and molar fractions of component i, respectively; the formulas for calculating Φ_i, Θ_i from volume and surface parameters, r_i and q_i of the components, respectively, are:

$$\Phi_i = \frac{x_i r_i}{\sum\limits_{j=1}^{nk} x_j r_j} \qquad (5)$$

$$\Theta_i = \frac{x_i q_i}{\sum\limits_{j=1}^{nk} x_j q_j} \qquad (6)$$

r_i and q_i of the components are calculated using the group contribution approach and group parameters as given in,[16] not accounting for the "propanol problem". Both models have six adjustable parameters to be determined from experimental data. In this paper, we have chosen the two-step Sorensen-Arlt method.[18] In the first step, function:

$$OF_1 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \left(\frac{x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II}}{x_i^I \gamma_i^I + x_i^{II} \gamma_i^{II}} \right)_j^2 +$$
$$+ Q(\tau_{12}^2 + \tau_{21}^2 + \tau_{13}^2 + \tau_{31}^2 + \tau_{23}^2 + \tau_{32}^2) \qquad (7)$$

is minimized with respect to parameters. In the denominator of the first term on the right-hand side of the equation (double sum with respect to number of

components, $n_c = 3$, and number of tie-lines, n_d), one can recognize the liquid-liquid equilibrium equation, $a_i^I = a_i^{II}$ or $(x_i\gamma_i)^I = (x_i\gamma_i)^{II}$, written in terms of component activities, a_i, or activity coefficients, γ_i. The second term is the so-called penalty function, used to penalize for the unrealistically large values of τ producing minima in OF_1 in NRTL. Therefore, we used the empirical value of the penalization factor $Q = 0.001$ for NRTL and $Q = 0$ for UNIQUAC.

The optimal set of τ-parameters describes the equilibrium fairly well, but it 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:

$$OF_2 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \sum_{p=I}^{II} [(x_i^p)_{exptl} - (x_i^p)_{calc}]_j^2 +$$
$$+ Q(\tau_{12}^2 + \tau_{21}^2 + \tau_{13}^2 + \tau_{31}^2 + \tau_{23}^2 + \tau_{32}^2) \qquad (8)$$

where the number of components $n_c = 3$, n_d is again the number of tie lines, and p takes string 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.

The described procedure apparently worked well for the system H₂O(1) – phenol(2) – 2-butanone(3) with both models considered. However, for the system H₂O(1) – phenol(2) – 2-propanol(3) it worked only with UNIQUAC. Therefore, we modified the procedure by fixing NRTL τ-parameters for the water – phenol binary to the values calculated from the mutual solubility data of phenol and water at 25 °C, using α-values set at either 0.2 or 0.3. Now, the procedure was able to find optimal τ-parameters for the water – 2-propanol and phenol – 2-propanol binaries.

Model parameters are summarized in Table 3, together with average absolute prediction errors in mole fractions as calculated by:

$$A = \sqrt{\frac{\sum\limits_{j=1}^{n_d} \sum\limits_{i=1}^{n_c} \sum\limits_{p=I}^{II} [(x_i^p)_{exptl} - (x_i^p)]_j^2}{n_d \cdot n_c \cdot 2}} \qquad (9)$$

Experimental and calculated compositions are compared in Table 4 and Figs. 5 and 6. For the system H₂O(1) – phenol(2) – 2-butanone(3), Fig. 5, the agreement seems to be reasonably good. Equilibrium phase compositions of the organic-rich phase are well predicted, and NRTL gives much better description of the water-rich phase than UNIQUAC.

T a b l e 3 – *Optimal NRTL and UNIQUAC model parameters and prediction errors*

	$H_2O(1)$ – phenol(2) – 2-butanone(3), 25 °C		$H_2O(1)$ – phenol(2) – 2-propanol(3), 25 °C	
	NRTL	UNIQUAC	NRTL	UNIQUAC
A	0.01106	0.01153	0.01923	0.01915
α_{12}	0.2		0.3	
α_{13}	0.3		0.3	
α_{23}	0.2		0.2	
τ_{12}	2.6995	1.0008	0.6362	0.9131
τ_{13}	3.6004	1.0694	4.8511	0.2635
τ_{21}	0.1838	0.3277	0.9474	0.2877
τ_{23}	–2.4498	1.5527	–1.8055	0.2180
τ_{31}	–0.5493	0.8142	–0.9032	1.8348
τ_{32}	–2.1180	1.5053	–2.1517	1.5293

T a b l e 4 – *Calculated compositions (mass fractions, w_i) of equilibrium liquid phases*

$H_2O(1)$ – phenol(2) – 2-butanone(3), 25 °C							
NRTL				UNIQUAC			
$w_{2,aq}$	$w_{3,aq}$	$w_{2,org}$	$w_{3,org}$	$w_{2,aq}$	$w_{3,aq}$	$w_{2,org}$	$w_{3,org}$
0.0010	0.2604	0.0647	0.8294	0.0038	0.2198	0.0615	0.8263
0.0027	0.1964	0.1514	0.7485	0.0103	0.1800	0.1471	0.7488
0.0048	0.1443	0.2306	0.6700	0.0179	0.1462	0.2270	0.6720
0.0065	0.1177	0.2767	0.6229	0.0234	0.1280	0.2743	0.6261
0.0103	0.0816	0.3504	0.5462	0.0344	0.1015	0.3500	0.5501
0.0140	0.0613	0.4010	0.4924	0.0439	0.0851	0.4020	0.4967
0.0206	0.0416	0.4614	0.4270	0.0580	0.0675	0.4639	0.4315
0.0282	0.0294	0.5093	0.3741	0.0720	0.0551	0.5128	0.3785
0.0498	0.0146	0.5910	0.2806	0.1040	0.0368	0.5951	0.2842
0.1189	0.0038	0.6999	0.1389	0.1787	0.0166	0.6997	0.1394
0.1802	0.0016	0.7334	0.0709	0.2324	0.0092	0.7258	0.0693

$H_2O(1)$ – phenol(2) – 2-propanol(3), 25 °C							
NRTL				UNIQUAC			
$w_{2,aq}$	$w_{3,aq}$	$w_{2,org}$	$w_{3,org}$	$w_{2,aq}$	$w_{3,aq}$	$w_{2,org}$	$w_{3,org}$
0.0523	0.0088	0.6451	0.0909	0.0841	0.0451	0.6955	0.0807
0.0490	0.0122	0.6292	0.1083	0.0854	0.0538	0.6729	0.0971
0.0407	0.0329	0.5614	0.1755	0.0898	0.0873	0.5823	0.1626
0.0390	0.0494	0.5237	0.2095	0.0916	0.1046	0.5342	0.1973
0.0388	0.0577	0.5075	0.2234	0.0922	0.1117	0.5145	0.2114
0.0406	0.0932	0.4493	0.2707	0.0935	0.1364	0.4465	0.2605
0.0435	0.1186	0.4146	0.2964	0.0937	0.1507	0.4080	0.2887
0.0478	0.1461	0.3811	0.3192	0.0931	0.1653	0.3703	0.3168
0.0523	0.1694	0.3548	0.3356	0.0923	0.1772	0.3341	0.3363
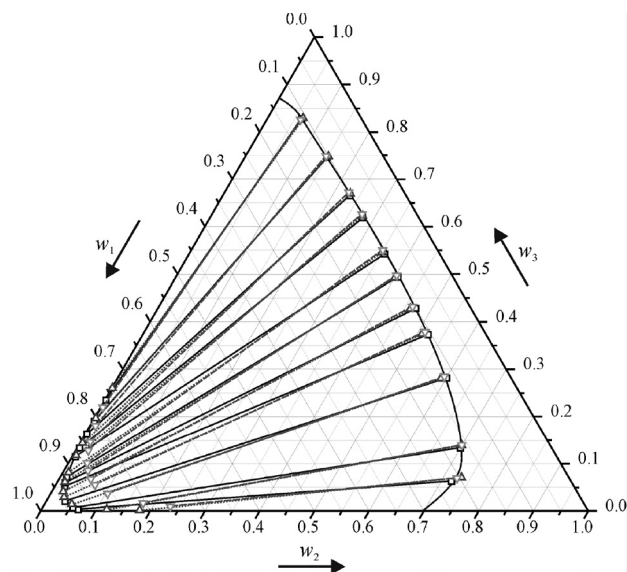
F i g . 5 – *Comparison of experimentally determined binodal curve and tie lines with NRTL and UNIQUAC LLE correlation for the system $H_2O(1)$ – phenol(2) – 2-butanone(3):* □ —— *this work experimental,* △ ········ *NRTL,* ▽ - - - *UNIQUAC*
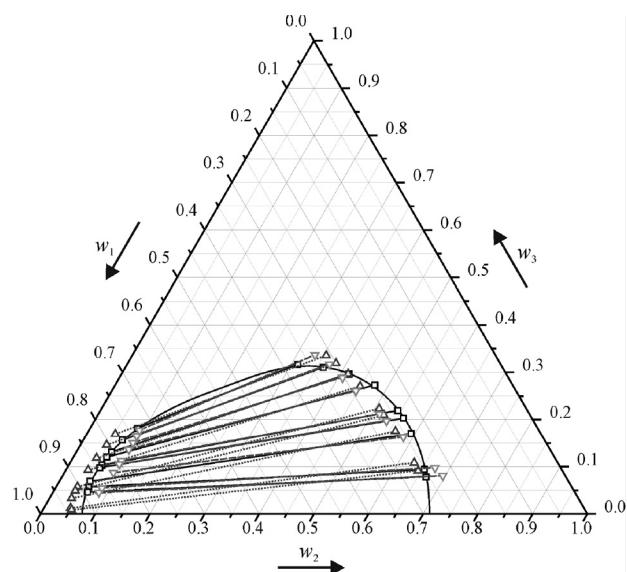
F i g . 6 – *Comparison of experimentally determined binodal curve and tie lines with NRTL and UNIQUAC LLE correlation for the system $H_2O(1)$ – phenol(2) – 2-propanol(3):* □ —— *this work experimental,* △ ········ *NRTL,* ▽ - - - *UNIQUAC*

However, both models seriously underestimate the solubility of phenol in water in the binary system.

The description of $H_2O(1)$ – phenol(2) – 2-propanol(3) system, Fig. 6, is much worse, with both of the tested models. We repeated the calculations with the literature data of Rusanov[12] to test whether our experimental data produced the discrepancy; however, little changed.

There are few ways to improve the description of both systems with NRTL. One has to keep in mind that we used preset α-parameter values, as sug-

gested by.[19] It is indeed possible to allow for the variation of NRTL α-parameters to obtain hopefully better description of experimental data, but there is no generally accepted way to do this (nine-parameter optimization is generally much more difficult than six-parameter optimization). The variation of the penalizing factor Q might help as well, but this would be pure trial and error procedure. However, nothing of the mentioned would help with UNIQUAC. This leads us to the conclusion that the investigated systems might be too complex to be described accurately with the models (NRTL and UNIQUAC) of the mean-field type. There are a few possible facts that might contribute to this conclusion. At first, both systems seem to be extremely dependent on temperature. Temperature variation of the shape of phase diagram for the system with 2-propanol was proved by literature data.[12] One possible cause may be the relative vicinity of the phenol – water UCST (67 °C[15]). As we pointed out before, empirical binodal line correlations of Hlavaty[13] that are routinely applied for many systems failed in the case of system with 2-propanol. In addition, 2-propanol LLE systems are known to exhibit complex behavior and the reasons for this is not yet clear.[16]

Conclusion

In this work, we studied liquid-liquid phase equilibria in the systems H$_2$O – phenol – 2-butanone and H$_2$O – phenol – 2-propanol, both at 25 °C and atmospheric pressure. Binodal curves and tie lines were determined with a combination of turbidimetric titration and refractive index measurements to show good agreement with rather rare literature data. Parameters of NRTL and UNIQUAC activity coefficient models were regressed from the experimental results. However, the description of the systems with common mean-field thermodynamic models was met with difficulties. The system H$_2$O – phenol – 2-butanone was described with predictive UNIFAC and correlative NRTL and UNIQUAC models. The agreement with experiment was qualitative and the errors were largest in the region of low 2-butanone content. In the case of H$_2$O – phenol – 2-propanol system, UNIFAC gave the qualitatively correct description of LLE ternary phase diagram. NRTL and UNIQUAC models were found to give qualitatively fair correlation as well; UNIQUAC worked somewhat better in predicting the tie-line slopes.

Nomenclature

A – average absolute deviation of experimental and calculated molar fractions

aq – subscript denoting aqueous (or lower) phase

calc – subscript denoting model or calculated value

exptl – subscript denoting experimental value

g^{ex} – molar excess Gibbs energy, J mol^{-1}

$g^{ex,C}$ – combinatorial part of molar excess Gibbs energy in UNIQUAC activity coefficient model, J mol^{-1}

$g^{ex,R}$ – residual part of molar excess Gibbs energy in UNIQUAC activity, coefficient model, J mol^{-1}

G_{ij} – symbol appearing in NRTL model, exponential function of model parameters

I – superscript denoting equilibrium liquid phase I

II – superscript denoting equilibrium liquid phase II

n_b – number of binodal curve experimental data points

n_c – number of components

n_D – refractive index

n_d – number of tie line experimental data points

OF_{1-2} – objective function to be minimized

org – subscript denoting organic (or upper) phase

Q – penalization factor

q_i – surface parameter of component i in UNIQUAC activity coefficient model

R – gas constant, J K^{-1} mol^{-1}

r_i – volume parameter of component i in UNIQUAC activity coefficient model

T – temperature, K

w_i – mass fraction of component i

x_i – molar fraction of component i

z – lattice coordination number

α_{ij} – nonrandomness parameter of NRTL activity coefficient model

γ_i – activity coefficient of component i

Θ_i – area fraction of component i

τ_{ij} – interaction parameter of NRTL or UNIQUAC activity coefficient models

Φ_i – volume fraction of component i

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