Isobaric (vapour+liquid) equilibria data for the binary systems (toluene+acetic acid) and (toluene+methyl ethyl ketone) at atmospheric pressure

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Isobaric vapour–liquid equilibrium data have been measured for the binary systems toluene (1) + acetic acid (2) and toluene (1) + methyl ethyl ketone (2) at atmospheric pressure. An all-glass Fischer–Labodest-type apparatus, capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K was used. The data were correlated by means of the NRTL, UNIQUAC, WILSON models and the applied UNIFAC model with satisfactory results; the relevant parameters are given and results were tested with regard to thermodynamic consistency using the methods of a modified Redlich–Kister and Herington equations.

Keywords: VLE; binary sytems; UNIFAC; UNIQUAC; Wilson; NRTL

1. Introduction

Toluene is a common solvent, able to dissolve paints, paint thinners, many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners and disinfectants. It can also be used as a fullerene indicator, and is a raw material for toluene diisocyanate (used in the manufacture of polyurethane foam), phenol and TNT. Toluene can be used as an octane booster in gasoline fuels used in internal combustion engines. Inhalation of toluene fumes can be intoxicating, but in larger doses nausea-inducing. Chronic or frequent inhalation of toluene over long time periods leads to irreversible brain damage. Toluene may enter the human system not only through vapour inhalation from the liquid evaporation, but also following soil contamination events, where human contact with soil, ingestion of contaminated groundwater or soil vapour off-gassing can occur [1].

In the literature, some researchers studied (toluene + acetic acid) and (toluene + methyl ethyl ketone) binary systems' vapour–liquid equilibria. Steinhauser and White [2] illustrated the application of the Gibbs–Duhem equation to non-ideal data-determined (toluene + methyl ethyl ketone) binary sytems. Rivenq [3] also studied (vapour + liquid) of the (toluene + methyl ethyl ketone) at several different atmospheric pressures. Haughton [4] and Othmer [5] determined the composition and boiling point of the azeotrope for (acetic acid + toluene) mixtures and they reported binary azeotropes at $T = 377.6$ and 373.8 K, respectively.

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In this study, liquid–vapour equilibrium data that belongs to different binary mixtures is reached at isobaric conditions experimentally. Experiments are treated by Fischer–Labodest liquid–vapour equilibrium equipments; samples belonging to the liquid–vapour phase are analysed by HP-6890 gas chromotographic equipment and acid analyses are determined by the volumetric titration method. The uncertainty in the results was 3%. Experimental data reached in such a way is liquid, and vapour-phase compositions belong to the binary system; experimental activity coefficients are determined by a basic computer program. Experimental and predicted data are compared with each other and the relevant parameters are given. This system was chosen because of its commercial interest in the separation of toluene from other chemicals.

2. Materials and methods

2.1. *Chemical materials*

The organic liquids used were obtained from Merck; toluene, methyl ethyl ketone and acetic acid had nominal purities >99.5, >98.5 and >99.7 mass%, respectively. Propan-1-ol was used as the internal standard for gas chromatography. All chemicals were used as supplied after chromatography failed to show any significant organic impurities. The measured values and the purity of used chemicals are listed in Table 1. Refractive indices and densities were measured with Anton Paar (Model 4500) apparatus. The estimated uncertainties in the measurements were in ±0.0001 units. The physical properties measured are in good agreement with published values [6].

2.2. *Experimental procedure*

All experiments were done with a Fischer–Labodest apparatus, described previously in detail elsewhere [7], with a capability of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. In our previous study, a diagram of the Fischer–Labodest

Table 1. Density (ρ) and refractive index (η_D) of the chemicals used in the experiments ($T = 298.3$ K).

Compound	$\frac{\rho \text{ (exp.)}}{\text{g cm}^{-3}}$	$\frac{\rho \text{ (lit.)}}{\text{g cm}^{-3}}$	η_D (exp.)	η_D (lit.) [6]
Toluene	0.8622	0.8623	1.4953	1.4961
Acetic acid	1.0494	1.0446	1.3713	1.3720
Methyl ethyl ketone	0.7985	0.8000	1.3787	1.3788

Table 2. Pure component properties used in this work.

Pure compounds	Interval (T/K)	A	B	C
Toluene	285–385	16.0137	3096.52	−53.67
Acetic acid	285–385	16.8080	3405.57	−56.34
Methyl ethyl ketone	285–385	16.5986	3150.42	−36.65

Note: A, B, C, are the Antoine constants for pure compounds (temperature in K, pressure in kPa).

Table 3. VLE data for the liquid-phase mole fraction x_1, vapour-phase mole fraction y_1, temperature T, and activity coefficients γ for the toluene (1) + acetic acid (2) binary system at 101.3 kPa.

x_1	y_1	T (K)	γ_1	γ_2
0.9614	0.9347	383.55	0.9785	2.1349
0.9164	0.8576	380.35	1.0326	2.3830
0.8697	0.7863	379.10	1.0346	2.3895
0.7838	0.7117	375.95	1.1403	2.1565
0.6466	0.6271	374.15	1.2855	1.8126
0.5817	0.5917	375.15	1.3083	1.6213
0.4979	0.5478	376.55	1.3983	1.4761
0.4404	0.5331	376.75	1.4844	1.3139
0.3788	0.5046	376.65	1.6384	1.2600
0.3125	0.4536	378.15	1.7079	1.1950
0.2744	0.4375	378.55	1.8541	1.1504
0.2351	0.4173	379.15	2.0281	1.1085
0.1912	0.3872	379.40	2.2971	1.0935
0.1493	0.3538	380.65	2.5921	1.0527
0.1416	0.3216	381.65	2.4136	1.0604
0.0972	0.2477	382.65	2.6315	1.0828
0.0708	0.1639	383.35	2.3432	1.1434

Table 4. VLE data for the liquid-phase mole fraction x_1, vapour-phase mole fraction y_1, temperature T, and activity coefficients γ for the toluene (1) + methyl ethyl ketone (2) binary system at 101.3 kPa.

| x_1	y_1	T (K)	γ_1	γ_2
0.9623	0.9818	352.75	1.0216	1.2747
0.8883	0.9491	354.20	1.0221	1.1486
0.8499	0.9321	355.00	1.0234	1.1074
0.8051	0.9075	355.95	1.0213	1.1254
0.7709	0.8805	356.17	1.0112	1.2062
0.7301	0.8626	357.55	1.0191	1.1438
0.6763	0.8368	358.65	1.0321	1.0920
0.6267	0.7900	360.05	1.0080	1.1629
0.5558	0.7695	351.45	1.0614	1.0248
0.5084	0.7135	362.85	1.0321	1.0996
0.5344	0.7376	362.35	1.0302	1.0806
0.4280	0.6741	366.15	1.0513	0.9673
0.3496	0.6167	368.15	1.1117	0.9393
0.2556	0.4756	371.35	1.0707	1.0168
0.1892	0.4199	373.05	1.2180	0.9804
0.1767	0.3820	374.05	1.1538	0.9980
0.1388	0.3593	375.25	1.3366	0.9540
0.1284	0.2743	377.05	1.0499	1.0120
0.1022	0.2105	378.35	0.9772	1.0287
0.0925	0.2727	378.65	1.3875	0.9292
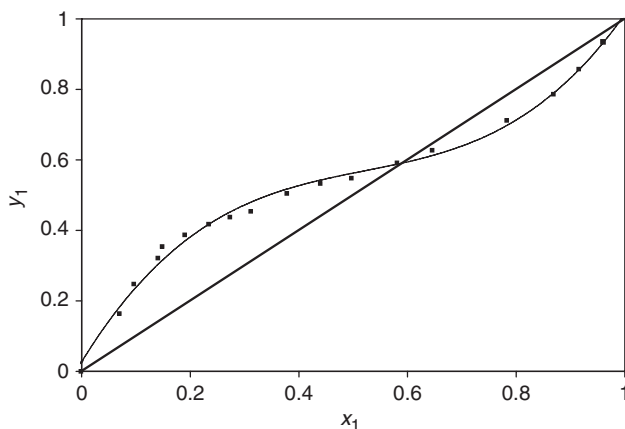
Figure 1. VLE curve for toluene (1) + acetic acid (2) binary system: x_1, liquid-phase mole fraction; y_1, vapour-phase mole fraction.
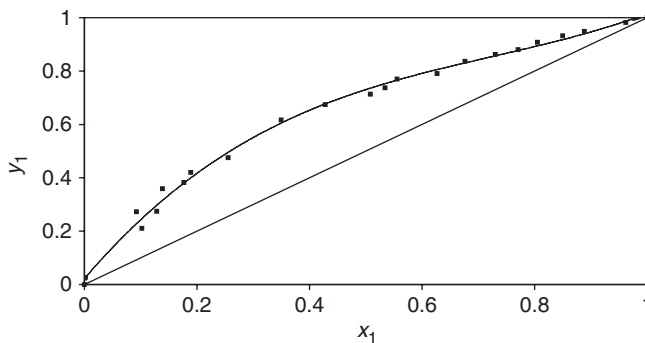

Figure 2. VLE curve for toluene (1) + methyl ethyl ketone (2) binary system: x_1, liquid-phase mole fraction; y_1, vapour-phase mole fraction.

apparatus were presented [8]. Each temperature equilibrium datum achieved was measured with an accuracy of ± 0.05 K using Fischer model-type Beckam thermometers. The apparatus is equipped with a glass temperature probe (PT 100) and a digital thermometer with an accuracy of ± 0.01 K. The total pressure of the system was controlled by an electronic manometer with an accuracy of ± 0.001 kPa. The vapour–liquid equilibrium (VLE) tests were run at 101.3 ± 0.02 kPa. The estimated error in the determination of both liquid and vapour-phase mole fractions is 0.0001.

Isobaric binary VLE for the toluene (1) + methyl ethyl ketone (2) and toluene (1) + acetic acid (2) systems were measured at atmospheric pressure. Approximately 60 mL of the liquid mixture was loaded into the boiling flask and heated by the electric heater. After the liquid in the flask starts to boil, the accumulated liquid in the small cell was sucked out by a syringe at least twice until the steady state. After the steady state, 3 mL toluene was added and then followed by a period of waiting until the steady state returned, which was usually attained within an hour from the start of the boiling. At the steady state, the temperature of the equilibrium chamber was recorded and

Table 5. Comparison of NRTL and WILSON model parameters for VLE data.

	NRTL			WILSON		
x_1	y_1	γ_1	γ_2	y_1	γ_1	γ_2
0.0000	0.0000	7.5950	1.0000	0.0000	5.6430	1.0000
0.0500	0.2514	5.1120	1.0100	0.2329	4.6150	1.0060
0.1000	0.3401	3.7690	1.0360	0.3479	3.8480	1.0210
0.1500	0.3876	2.9950	1.0710	0.4149	3.2700	1.0460
0.2000	0.4212	2.5130	1.1110	0.4583	2.8270	1.0790
0.2500	0.4491	2.1920	1.1560	0.4888	2.4810	1.1220
0.3000	0.4747	1.9650	1.2050	0.5115	2.2050	1.1730
0.3500	0.4992	1.7970	1.2580	0.5294	1.9830	1.2350
0.4000	0.5231	1.6680	1.3150	0.5443	1.8000	1.3090
0.4500	0.5466	1.5640	1.3790	0.5574	1.6490	1.3980
0.5000	0.5698	1.4790	1.4520	0.5694	1.5220	1.5030
0.5500	0.5925	1.4050	1.5360	0.5812	1.4160	1.6280
0.6000	0.6149	1.3400	1.6380	0.5933	1.3260	1.7800
0.6500	0.6367	1.2810	1.7660	0.6065	1.2490	1.9650
0.7000	0.6580	1.2260	1.9340	0.6218	1.1850	2.1940
0.7500	0.6791	1.1750	2.1650	0.6405	1.1300	2.4810
0.8000	0.7005	1.1270	2.5020	0.6649	1.0860	2.8480
0.8500	0.7243	1.0820	3.0270	0.6988	1.0500	3.3280
0.9000	0.7558	1.0430	3.9230	0.7498	1.0230	3.9690
0.9500	0.8144	1.0130	5.6390	0.8348	1.0060	4.8410
1.0000	1.0000	1.0000	9.3700	1.0000	1.0000	6.0190

Note: Liquid-phase mole fraction: x_1, vapour-phase mole fraction: y_1 and activity coefficients γ for: toluene (1) + acetic acid (2) binary systems at 101.3 kPa.

the condensed vapour and liquid samples were taken from each tap to determine their compositions by a gas chromatograph (Hewlett Packard GC, Model 6890 Series) equipped with a thermal conductivity detector (TCD). A 15 m long HP-Plot Q column (320 m diameter with a 20 m film thickness) was used with a temperature-programmed analysis. Three analyses were performed for each sample in order to obtain a mean mass fraction value with repeatability better than 1%.

3. Results and discussion

The activity coefficients of the components in the liquid phase were calculated from Equation (1):

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \exp\left[\frac{(B_{ii} - V_i^0)(P - P_i^0) + (1 - y_i)^2 P \delta_{ij}}{RT}\right], \tag{1}$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}, \tag{2}$$

where T and P are the boiling point and the total pressure, respectively, V_i is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, x_i and y_i are the liquid and vapour-phase compositions, P is the total pressure,

Table 6. Comparison of NRTL and WILSON model parameters for VLE data.

	NRTL			WILSON		
x_1	y_1	γ_1	γ_2	y_1	γ_1	γ_2
0.00000	0.00000	1.104	1.000	0.00000	1.367	1.000
0.05000	0.12589	1.099	1.000	0.14931	1.337	1.001
0.10000	0.23348	1.094	1.000	0.26732	1.308	1.003
0.15000	0.32625	1.089	1.001	0.36277	1.280	1.006
0.20000	0.40687	1.084	1.002	0.44157	1.253	1.011
0.25000	0.47744	1.078	1.003	0.50778	1.227	1.017
0.30000	0.53962	1.073	1.005	0.56432	1.202	1.026
0.35000	0.59477	1.066	1.008	0.61333	1.177	1.036
0.40000	0.64398	1.060	1.011	0.65641	1.154	1.049
0.45000	0.68814	1.054	1.016	0.69479	1.133	1.065
0.50000	0.72802	1.047	1.021	0.72944	1.112	1.083
0.55000	0.76426	1.041	1.028	0.76114	1.093	1.104
0.60000	0.79740	1.034	1.037	0.79052	1.075	1.130
0.65000	0.82793	1.028	1.047	0.81813	1.059	1.159
0.70000	0.85626	1.022	1.060	0.84446	1.045	1.194
0.75000	0.88278	1.016	1.076	0.86994	1.032	1.234
0.80000	0.90783	1.011	1.094	0.89499	1.021	1.281
0.85000	0.93176	1.007	1.117	0.92004	1.012	1.335
0.90000	0.95487	1.003	1.144	0.94554	1.006	1.400
0.95000	0.97751	1.001	1.176	0.97199	1.001	1.475
1.00000	1.00000	1.000	1.215	1.00000	1.000	1.565

Note: Liquid-phase mole fraction: x_1, vapour-phase mole fraction: y_1 and activity coefficients γ for: methyl ethyl ketone (1) + toluene (2) binary systems at 101.3 kPa.

and P_i^0 are the vapour pressures of the pure compounds calculated from Antoine equation. The second virial coefficients for components were obtained from TRC tables [9], and B_{ij} is the cross second virial coefficient calculated using a suitable mixing rule [10].

The vapour pressures of the pure compounds were expressed by the Antoine equation:

$$\log P_i^{\text{sat}}/\text{kPa} = A_i - \frac{B_i}{T/K + C_i}, \tag{3}$$

where the constants A, B and C in Equation (3) were taken from the literature [11]. Values for these pure fluids are shown in Table 2.

The activity coefficients were correlated with the Wilson [12], NRTL [13], UNIQUAC [14] and UNIFAC [15,16] equations. Estimation of the parameters for all the equations was based on minimisation of an objective function [17] in terms of experimental and calculated γ_i values. All the equations correlated with acceptable results for the activity coefficients.

Tables 3 and 4 give experimental values of temperature, activity coefficients and corresponding composition of the liquid- and vapour-phase for the binary systems (toluene + acetic acid) and (toluene + methyl ethyl ketone) at atmospheric pressure, respectively. All the considered binary systems have no immiscibility in the complete composition range.

Table 7. Comparison of UNIFAC and UNIQUAC model parameters for VLE data.

	UNIFAC			UNIQUAC		
x_1	y_1	γ_1	γ_2	y_1	γ_1	γ_2
0.0000	0.0000	3.2900	1.0000	0.0000	5.0640	1.0000
0.0500	0.1637	2.9970	1.0030	0.2225	4.3510	1.0040
0.1000	0.2741	2.7300	1.0110	0.3432	3.7580	1.0170
0.1500	0.3523	2.4910	1.0240	0.4165	3.2690	1.0380
0.2000	0.4101	2.2780	1.0450	0.4643	2.8650	1.0680
0.2500	0.4542	2.0890	1.0720	0.4970	2.5320	1.1080
0.3000	0.4890	1.9230	1.1060	0.5204	2.2550	1.1580
0.3500	0.5172	1.7760	1.1500	0.5377	2.0240	1.2210
0.4000	0.5408	1.6480	1.2030	0.5511	1.8310	1.2970
0.4500	0.5613	1.5350	1.2680	0.5620	1.6690	1.3890
0.5000	0.5797	1.4370	1.3470	0.5715	1.5330	1.5000
0.5500	0.5969	1.3510	1.4420	0.5806	1.4180	1.6350
0.6000	0.6139	1.2760	1.5580	0.5901	1.3220	1.7980
0.6500	0.6316	1.2120	1.6990	0.6012	1.2410	1.9970
0.7000	0.6510	1.1570	1.8710	0.6150	1.1750	2.2390
0.7500	0.6737	1.1100	2.0850	0.6332	1.1200	2.5370
0.8000	0.7017	1.0720	2.3520	0.6585	1.0760	2.9060
0.8500	0.7385	1.0410	2.6890	0.6951	1.0430	3.3630
0.9000	0.7902	1.0190	3.1210	0.7506	1.0190	3.9330
0.9500	0.8687	1.0050	3.6760	0.8403	1.0050	4.6380
1.0000	1.0000	1.0000	4.3850	1.0000	1.0000	5.4880

Note: Liquid-phase mole fraction: x_1, vapour-phase mole fraction: y_1 and activity coefficients γ for: toluene (1) + acetic acid (2) binary systems at 101.3 kPa.

Figures 1 and 2 show VLE curves for the binary systems (toluene + acetic acid) and (toluene + methyl ethyl ketone), respectively. Obviously, it has been seen that azeotropic behaviour was observed for the system toluene (1) + acetic acid (2) at x(toluene) = 0.5817, $T = 375.15$ K, and for the toluene (1) + methyl ethyl ketone (2) binary sytem a binary azeotrope at any composition and temperature was not observed. Haughton [4] and Othmer [5] also observed a binary azeotrope at $T = 377.6$ K, x(toluene) = 0.521 and $T = 373.8$ K, x(toluene) = 0.615. From the figures it can be observed that both systems present a positive deviation from ideality. The activity coefficients of the experimental binary systems were correlated with the most common g^E models (Wilson, NRTL, UNIFAC and UNIQUAC).

NRTL and WILSON model methods have been used to correlate our isobaric VLE data. Tables 5 and 6 demonstrate comparison of the parameters of the WILSON and NRTL activity coefficient models for toluene (1) + acetic acid (2) and toluene (1) + methyl ethyl ketone (2), respectively. Both methods showed similar predictions near the crossover. Between NRTL and WILSON models results observed to increase some deviation between approximately (0.2–0.4) and (0.6–0.8) in mole fractions.

Comparison of the measured data with UNIFAC and UNIQUAC predictions for toluene (1) + acetic acid (2) and toluene (1) + methyl ethyl ketone (2) has been shown in Tables 7 and 8, respectively. The UNIFAC model gave better results than the

Table 8. Comparison of UNIFAC and UNIQUAC model parameters for VLE data.

	UNIFAC			UNIQUAC		
x_1	y_1	γ_1	γ_2	y_1	γ_1	γ_2
0.00000	0.00000	1.181	1.000	0.00000	1.130	1.000
0.05000	0.13243	1.165	1.000	0.12335	1.118	1.000
0.10000	0.24231	1.149	1.002	0.22848	1.107	1.001
0.15000	0.33490	1.134	1.004	0.31907	1.096	1.002
0.20000	0.41402	1.120	1.006	0.39788	1.086	1.004
0.25000	0.48247	1.106	1.010	0.46708	1.076	1.007
0.30000	0.54238	1.093	1.015	0.52835	1.067	1.010
0.35000	0.59536	1.081	1.020	0.58305	1.058	1.014
0.40000	0.64268	1.070	1.027	0.63223	1.050	1.019
0.45000	0.68534	1.059	1.035	0.67677	1.043	1.025
0.50000	0.72413	1.049	1.044	0.71737	1.036	1.031
0.55000	0.75970	1.040	1.054	0.75463	1.029	1.038
0.60000	0.79258	1.032	1.066	0.78903	1.023	1.046
0.65000	0.82321	1.025	1.079	0.82098	1.018	1.055
0.70000	0.85196	1.018	1.094	0.85084	1.013	1.065
0.75000	0.87915	1.013	1.110	0.87889	1.009	1.076
0.80000	0.90505	1.008	1.128	0.90539	1.006	1.089
0.85000	0.92989	1.005	1.148	0.93057	1.004	1.102
0.90000	0.95388	1.002	1.169	0.95462	1.002	1.117
0.95000	0.97719	1.001	1.193	0.97771	1.000	1.133
1.00000	1.00000	1.000	1.219	1.00000	1.000	1.151

Note: Liquid-phase mole fraction: x_1, vapour-phase mole fraction: y_1 and activity coefficients γ for: methyl ethyl ketone (1) + toluene (2) binary systems at 101.3 kPa.

Table 9. The relevant parameters and standard deviations for each model of the binary system. UNIQUAC: $A_{ij} = (u_{ij} - u_{jj}) \, kj \cdot mol^{-1}$. WILSON: $A_{ij} = (a_{ij} - a_{ii}) \, kj \cdot mol^{-1}$. NRTL: $A_{ij} = (g_{ij} - g_{jj}) \, kj \cdot mol^{-1}$.

	Ethyl methyl ketone (1) + toluene (2)							
	$u_{12} - u_{22}$	$u_{21} - u_{11}$	a_{12}	a_{21}	g_{12}	g_{21}	α	$\sigma_y \, (mol \cdot mol^{-1})$
WILSON	–	–	0.208	1.113	–	–	–	0.000185
NRTL	–	–	–	–	1.939	−1.381	0.191	0.000176
UNIQUAC	1.534	−1.048	–	–	–	–	–	0.0002
UNIFAC	–	–	–	–	–	–	–	0.000087
Toluene (1) + acetic acid (2)								
WILSON	–	–	1.426	5.623	–	–	–	0.0036
NRTL	–	–	–	–	2.789	2.512	0.727	0.0027
UNIQUAC	2.781	−0.284	–	–	–	–	–	0.0037
UNIFAC	–	–	–	–	–	–	–	0.0008

Table 10. UNIFAC group volume and surface-area parameters for prediction of vapour–liquid equilibria [16].

Component	Main group	Sub group	R_k	Q_k	Number
Toluene					
ACH	3	10	0.5313	0.4000	5
$ACCH_3$	4	12	1.2663	0.9680	1
Acetic acid					
CH_3	1	1	0.9011	0.8480	1
COOH	20	43	1.3013	1.2240	1
Methyl ethyl ketone					
CH_2	1	2	0.6744	0.5400	1
CH_3	1	1	0.9011	0.8480	1
CH_3CO	9	19	1.6724	1.4880	1
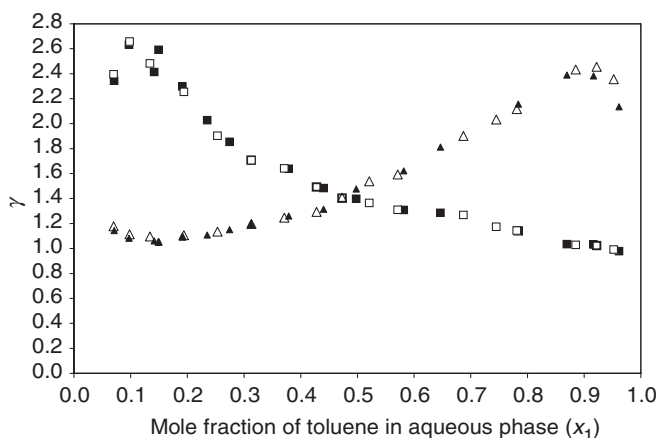
Figure 3. Comparison of the variation of the activity coefficients (γ) in the literature and this study at different compositions. Activity coefficients for toluene: ■, (exp.); □, (lit.) [4]; activity coefficients for acetic acid: ▲, (exp.); △, (lit.) [4].

UNIQUAC model. In addition, the applied UNIFAC and correlated UNIQUAC showed better behaviour of the binary systems than the other two models. Data are accurately correlated using the models' acceptable results. Correlation of the measured data at the lower temperatures work quite well, but the predictions at higher temperatures decrease in accuracy. The relevant parameters are given for each model of the binary system in Table 9 and the UNIFAC group volume and surface-area parameters for prediction of vapour–liquid equilibria are given in Table 10 [16].

Comparison of variation of the boiling points for toluene (1) + acetic acid (2) and toluene (1) + methyl ethyl ketone (2) binary systems and their literature data at different compositions have been presented in Figures 3 and 4, respectively. Experimental results showed a good agreement with the literature data for both systems. Particularly at the same mole fractions, experimental and literature data gave similar results. Big deviations were not observed between the literature and this study.
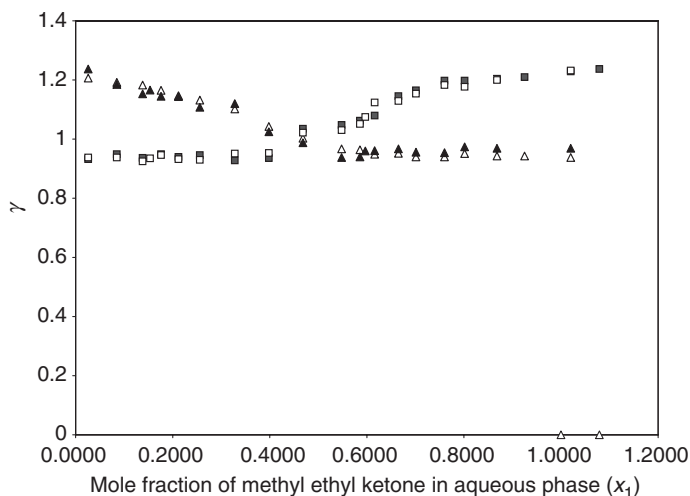
Figure 4. Comparison of the variation of the activity coefficients (γ) in the literature [2] and this study at different compositions. Activity coefficients for methyl ethyl ketone: ■, (exp.); □, (lit.) [2]; activity coefficients for toluene: ▲, (exp.); △, (lit.) [2].
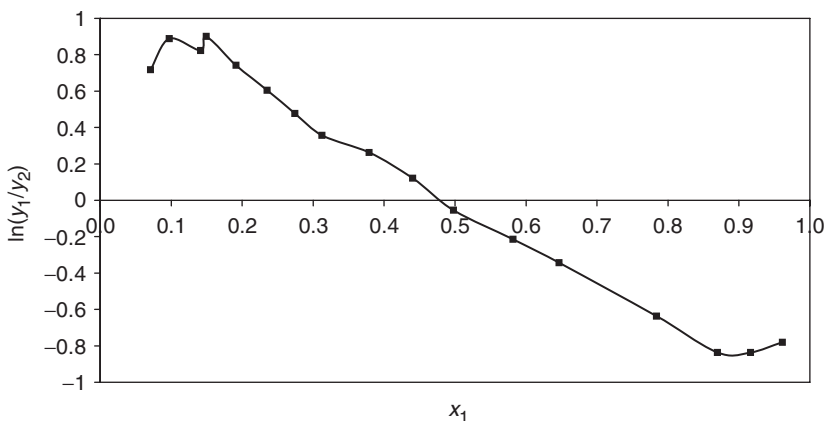

Figure 5. Thermodynamic consistency for toluene (1) + acetic acid (2) binary system.

The root mean square deviations (RMSD) are calculated from the difference between the experimental data and the predictions of each model according to the following equation:

$$RMSD = \sqrt{\frac{1}{N} \sum_{i=1}^{n} \left(y_{i,\text{exp}} - y_{i,\text{calcd}} \right)}, \tag{4}$$

where $Y_{i,\text{exp}}$ is the experimental vapour-phase mole fraction, and $Y_{i,\text{calcd}}$ is the calculated vapour-phase mole fraction. N is the number of experimental data. The RMSD values of toluene (1) + methyl ethyl ketone (2) binary system are found to be 0.000087 for UNIFAC, 0.000176 for NRTL, 0.000185 for WILSON, 0.0002 for UNIQUAC. The RMSD values of
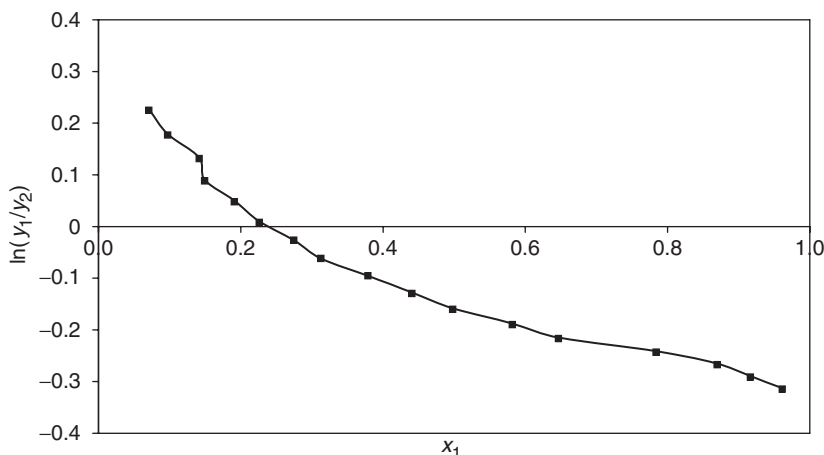
Figure 6. Thermodynamic consistency for toluene (1) + methyl ethyl ketone (2) binary system.

toluene (1) + acetic acid (2) binary system are found to be 0.0008 for UNIFAC, 0.0027 for NRTL, 0.0036 for WILSON, 0.0037 for UNIQUAC (Table 9).

The average deviation in vapour composition is <0.05. These results show that the deviations in vapour-phase compositions are reasonably small, and it is indicated that all four activity coefficient models are suitable to represent the binary experimental data.

Figures 5 and 6 show the thermodynamic consistency of the data using Chao's [18] modified Redlich–Kister [19] equation for both systems. The values of constants in the equation

$$\log \gamma_1/\gamma_2 = a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2), \tag{5}$$

where the coefficients for (toluene + acetic acid) and (toluene + ethyl methyl ketone), a, b, c, d, are determined by fitting the experimental data. The coefficients are found to be $a = 0.032$, $b = 0.710$, $c = 0.076$, $d = 0.124$ and $a = 0.046$, $b = 0.686$, $c = 0.084$, and $d = 0.130$, respectively.

The consistency test of the (toluene + acetic acid) and (toluene + ethyl methyl ketone) data were made by the Herington method [20] using the consistency criterion of $(D - J < 0)$, where D is the percentage deviation described as $(D = 100|I|/\sum)$ and J is a function of the overall range of boiling points described as $(J = 100|\theta|/T_{\min})$. The I is the arithmetic sum and $\sum$ is absolute sum of the areas at x_1 against $\log \gamma_1/\gamma_2$, defined as $I = \int_0^1 [\log(\gamma_1/\gamma_2)]dx_1$. The θ is the total boiling interval of the binary systems, and $T_{\min}$ is the lowest measured temperature value. For these systems, (toluene + acetic acid) and (toluene + ethyl methyl ketone), the consistency criterion was found to be $(D - J) = -3.62$ and -9.74, respectively.

4. Conclusions

Vapour–liquid equilibrium for two binary systems of toluene (1) + acetic acid (2) and toluene (1) + methyl ethyl ketone (2) were measured at 101.3 kPa. The experimental data were correlated using the four main models WILSON, NRTL, UNIQUAC and

UNIFAC equations. According to results, UNIFAC and UNIQUAC models obtain better results than other models. However, for the binary system toluene (1) + acetic acid (2), the UNIFAC method obtains better results than the UNIQUAC method. NRTL and WILSON model methods have been used to predict our isobaric VLE data. For the binary mixtures, both methods obtain similar predictions.

In the other binary system, methyl ethyl ketone (1) + toluene (2) the NRTL, UNIFAC, UNIQUAC and WILSON models, prediction of the measured data at the lower temperature work quite well, but the predictions at higher temperatures decrease in accuracy. The UNIFAC accurately predicts the behaviour of the mixtures measured in this work. The results showed that the calculated parameters are fitted by the models, which satisfied the need for the design and operation of separation processes.

References

[1] F.S. Wagner and M. Grayson, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. (John Wiley & Sons, New York, 1978).
[2] H.H. Steinhauser and R.R. White, Ind. Eng. Chem. **41**, 2912 (1949).
[3] F. Rivenq, Bull. Soc. Chim. Fr. **10**, 3782 (1972).
[4] C.O. Haughton, Chem. Eng. Sci. **16**, 82 (1961).
[5] D.F. Othmer, Ind. Eng. Chem. **35**, 614 (1943).
[6] D.R. Lide, editor. *CRC Handbook of Chemistry and Physics*; Internet Version, 2005; CRC Press: Boca Raton, FL, 2005; http://www.hbcpnetbase.com.
[7] G. Gültekin, J. Chem. Eng. Data **34**, 168 (1989).
[8] İ.M. Hasdemir and H. Uslu, J. Chem. Thermodyn. **39**, 1189 (2007).
[9] TRC-Tables, Selected values of properties of chemical compounds. Thermodynamic Research Center Data Project, Texas A and M University, College Station, TX, 1972.
[10] I. Amdur and E.A. Mason, Phys. Fluids **1**, 370 (1958).
[11] M.S. Richard and M. Stanislaw, *Handbook of the Thermodynamics of Organic Compounds* (Elsevier, Amsterdam, 1987).
[12] G.M. Wilson, Am. Chem. Soc. **86**, 127 (1964).
[13] H. Renon and J.M. Prausnitz, AIChE J. **14**, 135 (1968).
[14] D.S. Abrams and J.M. Prausnitz, AIChE J. **21**, 116 (1975).
[15] B.L. Larsen, P. Rasmussen, and A. Fredenslund, Ind. Eng. Chem. Res. **26**, 2274 (1987).
[16] J. Ghemlimg, P. Rasmussen, and A. Fredensliund, Ind. Eng. Chem. Process Des. Dev. **21**, 118 (1982).
[17] N. Silverman and D.P. Tassios, Ind. Eng. Chem. Process. Des. Dev. **23**, 586 (1984).
[18] K.C. Chao and O.A. Hougen, Chem. Eng. Sci. **7**, 246 (1958).
[19] O. Redlich and A.T. Kister, Znd. Eng. Chem. **40**, 345 (1948).
[20] E.F.G. Herington, J. Inst. Petrol. **37**, 457 (1951).