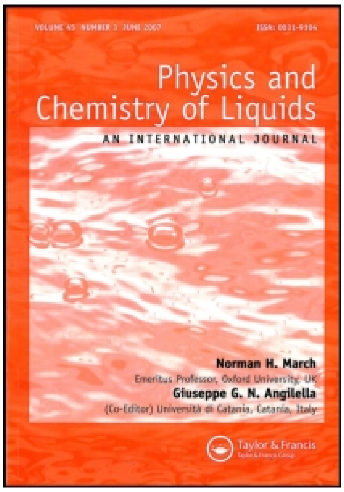

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Phase equilibria of binary mixtures containing methyl acetate, water, methanol or ethanol at 101.3 kPa

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Phase equilibria of binary mixtures containing methyl acetate, water, methanol or ethanol at 101.3 kPa

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Isobaric vapor–liquid equilibria data at 101.3 kPa were reported for the binary mixtures (methyl acetate + (water or methanol or ethanol), methanol + (water or ethanol) and (ethanol + water)). The experimental data were tested for thermodynamic consistency by means of the Wisniak method and were demonstrated to be consistent. The experimental data were correlated using Wilson, NRTL and UNIQUAC models for the activity coefficients and predicted using the UNIFAC and PSRK equation of state for testing theirs capability. The results show that the obtained data for the studied binary systems are more reliable than other published data.

Keywords: phase equilibria; associating binary mixture; correlation, modelling errors

1. Introduction

Thermodynamic measurements and phase equilibria of ethanol, water and the different flavour components (alcohols, aldehydes and acetates, so-called congeners) in distillated alcoholic beverages are of practical interest to the food industry since industrial procedures applied are closely related to their temperature and pressure dependence in order to obtain a high quality final product. In the last few years, published studies have highlighted a clear need for accurate information about these types of mixtures, in order to develop and optimise industrial techniques. Despite the considerable effort invested in the field of thermodynamic properties, a great scarcity of data is observed in the available literature for mixtures of components present in commercial distillated alcoholic beverages. Such properties are strongly dependent on hydrogen bond potency of hydroxyl or polar groups, chain length, isomeric structures and molecular package. After decades of study, there is still much room for improvement in our ability to understand the behavior of these systems and add accurate data to the available literature. Simulation and optimisation are not used in

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the right manner in this matter, with an overestimation of equipment size or high energy-consuming conditions being usually applied due to inaccurate calculations. The difficulties of simulation in these types of processes, as well as possible errors derived from that, have been commented upon previously [1]. As a continuation of previous work related to alcoholic beverages [2–4], this work is part of a research project whose objective is to measure thermodynamic properties and vapour–liquid equilibrium (VLE) data for different systems involved in most distillation processes to benefit subsequent studies of modelling and simulation.

In this work, the VLE at 101.3 kPa was determined for binary systems: methyl acetate + water, methyl acetate + methanol, methyl acetate + ethanol, methanol + water, methanol + ethanol and ethanol + water. These mixtures also have some special characteristics. The concentration of the solute in the vapor phase is small and shows molecular association. Thermodynamic consistency was achieved to validate the new experimental data. In this way, data obtained have lower deviations when compared with previously published data; thereby, the information of available literature was improvement. The $\gamma-\varphi$ approximation was used to fit the experimental data and obtain the UNIFAC Dortmund model [5], which was used for VLE prediction. Also, the predictive Soave–Redlich–Kwong (PSRK) model proposed by Holderbaum and Gmehling [6] was used in the $\varphi-\varphi$ approximation.

2. Experimental section

All chemicals were Lichrosolv quality (Merck Farma y Química S.A.). The pure components were recently acquired and kept in an inert argon atmosphere after the bottles were opened. The materials were degassed ultrasonically and dried over molecular sieves Type 4A or 3A, 1/16 in. Chromatographic (GLC) analysis gave purities of 0.998 for methyl acetate, methanol and ethanol, with maximum water contents of 6.8×10^{-3}, 1.5×10^{-2} and 2.2×10^{-2} mass% (Metrohm 737 KF coulometer), respectively. Water was millipore quality with organic total mass <5 ppb and resistivity of 18.2 MΩcm. The densities and refractive indices at 298.15 K, as well as normal boiling points, were within recommended values and are shown in Table 1.

Table 1. Observed physical properties of pure compounds and literature data (densities (ρ), refractive indices (n_D) at 298.15 K, and normal boiling points (T_b)).

	Mw (kg kmol^{-1})	ρ (kg m^{-3})		n_D		T_b (K)	
		Obs.	Lit.	Obs.	Lit.	Obs.	Lit.
Methyl acetate	74.080^a	0.92674	0.9273^b 0.9279^c	1.35850	1.3589^b 1.3614^c	329.82	330.4^a 330.09^d
Water	18.015^a	0.9970	0.99705^c	1.33250	1.33250^c	373.15	373.15^a
Methanol	32.042^a	0.78665	0.78664^b 0.78664^c	1.32645	1.32652^b 1.32652^c	337.86	337.7^a 337.85^d
Ethanol	46.069^a	0.78502	0.78509^b 0.78504^c	1.35922	1.35941^b 1.35941^c	352.07	351.4^a 351.44^d

Note: [a]See [7]; [b]See [8]; [c]See [9]; [d]See [10].

The system used to measure VLE data was a dynamic recirculating apparatus described previously [11,12]. The equilibrium temperature was measured with a digital platinum 100 resistance thermometer with an accuracy of ±0.1 K. For the pressure measurement, a digital manometer regulator (Divatronic DT1 model), manufactured by Leybold with an accuracy of ±0.1 kPa, was used. Both vapour and liquid phase compositions for the systems were determined by measurements of physical properties (density and refractive index) and application of mathematical correlations, published earlier by the authors [13–16]. The accuracy of the composition measurements on each phase was estimated as better than ±0.001 in molar fraction for each mixture. The VLE experimental data at 101.3 kPa of the studied binary systems are compiled in Table 2.

Table 2. Observed vapour-liquid equilibrium data for different binary systems.

x_1	y_1	T (K)	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
Methyl acetate (1) + water (2)								
0.002	0.140	95.64	23.732	1.009	0.979	0.991	0.935	0.993
0.005	0.295	90.39	23.206	1.226	0.978	0.992	0.941	0.994
0.014	0.577	77.81	21.348	2.015	0.977	0.995	0.955	0.996
0.022	0.682	71.27	19.808	2.656	0.977	0.997	0.961	0.997
0.029	0.739	66.90	18.413	3.216	0.977	0.999	0.965	0.997
0.042	0.794	61.90	16.207	4.032	0.977	1.001	0.969	0.998
0.712	0.835	57.45	1.158	4.964	0.978	1.003	0.972	0.998
0.800	0.861	56.99	1.080	5.079	0.978	1.004	0.973	0.998
0.873	0.894	56.67	1.041	5.164	0.979	1.006	0.973	0.998
0.873	0.895	56.67	1.041	5.164	0.979	1.006	0.973	0.998
0.930	0.933	56.54	1.024	5.207	0.981	1.008	0.973	0.998
0.991	0.989	56.62	1.020	5.203	0.983	1.011	0.973	0.998
Methyl acetate (1) + methanol (2)								
0.009	0.027	64.00	2.417	1.009	0.975	0.983	0.967	0.983
0.054	0.145	61.90	2.259	1.096	0.975	0.983	0.969	0.984
0.074	0.186	61.14	2.194	1.130	0.975	0.983	0.969	0.984
0.103	0.240	60.12	2.101	1.177	0.974	0.983	0.970	0.985
0.104	0.242	60.09	2.097	1.178	0.974	0.983	0.970	0.985
0.121	0.269	59.58	2.048	1.203	0.974	0.983	0.971	0.985
0.123	0.272	59.52	2.042	1.206	0.974	0.983	0.971	0.985
0.145	0.306	58.88	1.978	1.238	0.974	0.984	0.971	0.986
0.148	0.309	58.82	1.971	1.241	0.974	0.984	0.971	0.986
0.165	0.332	58.39	1.924	1.263	0.975	0.984	0.972	0.986
0.199	0.373	57.63	1.834	1.304	0.975	0.985	0.972	0.986
0.216	0.391	57.30	1.794	1.322	0.975	0.985	0.972	0.986
0.266	0.438	56.45	1.680	1.370	0.975	0.986	0.973	0.987
0.295	0.462	56.05	1.621	1.393	0.976	0.986	0.973	0.987
0.327	0.486	55.65	1.558	1.417	0.976	0.987	0.973	0.987
0.354	0.505	55.36	1.509	1.435	0.976	0.988	0.974	0.987
0.371	0.516	55.19	1.480	1.446	0.976	0.988	0.974	0.987
0.419	0.545	54.80	1.406	1.471	0.977	0.989	0.974	0.987
0.440	0.557	54.65	1.375	1.480	0.977	0.989	0.974	0.987
0.485	0.582	54.37	1.315	1.499	0.978	0.990	0.974	0.988

(*Continued*)

Table 2. Continued.

x_1	y_1	T (K)	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
0.519	0.599	54.21	1.274	1.510	0.978	0.990	0.974	0.988
0.537	0.609	54.13	1.254	1.516	0.978	0.991	0.975	0.988
0.632	0.658	53.87	1.164	1.535	0.979	0.993	0.975	0.988
0.636	0.660	53.86	1.160	1.536	0.979	0.993	0.975	0.988
0.673	0.680	53.83	1.132	1.539	0.980	0.993	0.975	0.988
0.696	0.693	53.83	1.116	1.540	0.980	0.994	0.975	0.988
0.719	0.707	53.84	1.102	1.540	0.981	0.995	0.975	0.988
0.742	0.721	53.87	1.089	1.539	0.981	0.995	0.975	0.988
0.795	0.757	54.02	1.063	1.532	0.983	0.997	0.975	0.988
0.885	0.837	54.65	1.035	1.498	0.986	1.001	0.974	0.987
0.924	0.881	55.12	1.030	1.473	0.988	1.003	0.974	0.987
0.981	0.965	56.19	1.029	1.416	0.992	1.008	0.973	0.987
Methyl acetate (1) + ethanol (2)								
0.011	0.050	76.97	2.541	1.011	0.979	0.979	0.956	0.980
0.039	0.165	74.47	2.420	1.116	0.978	0.978	0.958	0.981
0.089	0.310	70.97	2.231	1.287	0.979	0.979	0.961	0.983
0.121	0.378	69.19	2.121	1.385	0.979	0.980	0.963	0.984
0.174	0.465	66.77	1.955	1.535	0.980	0.981	0.965	0.985
0.257	0.558	64.02	1.734	1.729	0.982	0.983	0.967	0.987
0.267	0.566	63.75	1.711	1.749	0.982	0.983	0.967	0.987
0.292	0.587	63.11	1.653	1.799	0.982	0.984	0.968	0.987
0.316	0.605	62.58	1.604	1.842	0.983	0.984	0.968	0.987
0.325	0.611	62.39	1.585	1.858	0.983	0.984	0.968	0.987
0.336	0.619	62.17	1.563	1.876	0.983	0.985	0.969	0.987
0.369	0.639	61.55	1.502	1.928	0.984	0.985	0.969	0.988
0.374	0.642	61.46	1.493	1.936	0.984	0.985	0.969	0.988
0.437	0.676	60.48	1.392	2.024	0.985	0.987	0.970	0.988
0.534	0.722	59.28	1.266	2.138	0.986	0.988	0.971	0.989
0.551	0.730	59.10	1.248	2.156	0.986	0.989	0.971	0.989
0.576	0.740	58.85	1.223	2.181	0.987	0.989	0.971	0.989
0.636	0.767	58.30	1.169	2.238	0.988	0.990	0.972	0.989
0.637	0.767	58.29	1.168	2.239	0.988	0.990	0.972	0.989
0.661	0.778	58.09	1.150	2.260	0.988	0.991	0.972	0.989
0.692	0.792	57.84	1.128	2.287	0.989	0.991	0.972	0.989
0.699	0.796	57.79	1.124	2.292	0.989	0.992	0.972	0.989
0.752	0.821	57.42	1.094	2.334	0.990	0.993	0.972	0.989
0.760	0.825	57.37	1.089	2.340	0.990	0.993	0.972	0.989
0.765	0.828	57.34	1.087	2.343	0.991	0.993	0.972	0.989
0.768	0.830	57.32	1.085	2.345	0.991	0.993	0.972	0.989
0.808	0.851	57.09	1.069	2.373	0.992	0.994	0.972	0.990
0.816	0.856	57.04	1.066	2.379	0.992	0.995	0.973	0.990
0.861	0.884	56.84	1.052	2.404	0.993	0.996	0.973	0.990
0.862	0.884	56.83	1.052	2.405	0.993	0.996	0.973	0.990
0.882	0.898	56.75	1.047	2.416	0.994	0.997	0.973	0.990
0.924	0.930	56.64	1.040	2.433	0.996	0.999	0.973	0.990
Methanol (1) + water (2)								
0.0001	0.001	99.65	2.425	1.013	0.986	0.992	0.956	0.992
0.001	0.009	99.46	2.384	1.019	0.986	0.992	0.956	0.992
0.010	0.075	97.79	2.313	1.082	0.985	0.992	0.958	0.992
0.064	0.321	90.81	2.017	1.400	0.985	0.993	0.964	0.994

(*Continued*)

Table 2. Continued.

x_1	y_1	T (K)	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
0.103	0.425	87.38	1.851	1.596	0.985	0.994	0.967	0.994
0.217	0.596	81.04	1.516	2.052	0.986	0.996	0.972	0.995
0.306	0.672	77.93	1.355	2.331	0.987	0.997	0.974	0.996
0.316	0.679	77.62	1.340	2.361	0.987	0.998	0.975	0.996
0.383	0.722	75.80	1.256	2.547	0.988	0.999	0.976	0.996
0.443	0.757	74.35	1.198	2.708	0.988	1.000	0.977	0.996
0.444	0.757	74.32	1.197	2.712	0.988	1.000	0.977	0.996
0.532	0.802	72.44	1.133	2.939	0.989	1.001	0.978	0.997
0.632	0.847	70.52	1.084	3.195	0.990	1.002	0.979	0.997
0.676	0.867	69.73	1.068	3.307	0.991	1.003	0.980	0.997
0.689	0.872	69.49	1.064	3.343	0.991	1.003	0.980	0.997
0.696	0.875	69.37	1.062	3.360	0.991	1.003	0.980	0.997
0.768	0.906	68.12	1.044	3.552	0.992	1.004	0.981	0.997
0.770	0.906	68.11	1.043	3.553	0.992	1.004	0.981	0.997
0.827	0.930	67.16	1.034	3.708	0.992	1.005	0.981	0.997
0.896	0.958	66.05	1.026	3.898	0.993	1.006	0.982	0.997
0.914	0.966	65.75	1.025	3.952	0.993	1.007	0.982	0.997
0.933	0.973	65.46	1.024	4.004	0.993	1.007	0.982	0.997
0.937	0.975	65.40	1.024	4.015	0.993	1.007	0.982	0.997
0.972	0.989	64.86	1.023	4.115	0.994	1.008	0.983	0.997
0.977	0.991	64.78	1.023	4.130	0.994	1.008	0.983	0.997
0.977	0.991	64.77	1.023	4.132	0.994	1.008	0.983	0.997
Methanol (1) + ethanol (2)								
0.018	0.034	77.71	1.152	1.006	0.985	0.979	0.975	0.979
0.096	0.167	76.08	1.139	1.073	0.986	0.979	0.976	0.980
0.171	0.277	74.65	1.127	1.136	0.987	0.979	0.977	0.981
0.179	0.289	74.49	1.126	1.143	0.987	0.979	0.977	0.981
0.182	0.293	74.44	1.125	1.145	0.987	0.979	0.977	0.981
0.246	0.376	73.31	1.115	1.199	0.988	0.980	0.978	0.982
0.275	0.411	72.83	1.110	1.223	0.989	0.980	0.978	0.982
0.287	0.426	72.62	1.108	1.234	0.989	0.980	0.978	0.982
0.294	0.434	72.51	1.107	1.239	0.989	0.980	0.978	0.982
0.312	0.455	72.22	1.104	1.254	0.990	0.981	0.978	0.982
0.326	0.469	72.01	1.102	1.265	0.990	0.981	0.978	0.983
0.400	0.547	70.90	1.090	1.325	0.991	0.982	0.979	0.983
0.423	0.569	70.57	1.087	1.344	0.992	0.982	0.979	0.983
0.442	0.587	70.31	1.084	1.359	0.992	0.983	0.979	0.983
0.459	0.602	70.09	1.081	1.371	0.993	0.983	0.980	0.984
0.534	0.667	69.12	1.070	1.429	0.995	0.984	0.980	0.984
0.569	0.696	68.69	1.065	1.456	0.995	0.985	0.980	0.984
0.580	0.705	68.56	1.063	1.464	0.996	0.985	0.980	0.984
0.598	0.719	68.35	1.061	1.478	0.996	0.985	0.981	0.985
0.599	0.720	68.34	1.060	1.478	0.996	0.985	0.981	0.985
0.682	0.782	67.42	1.050	1.539	0.998	0.987	0.981	0.985
0.726	0.813	66.98	1.044	1.569	0.999	0.988	0.981	0.985
0.761	0.838	66.63	1.041	1.593	1.000	0.989	0.982	0.985
0.763	0.839	66.61	1.041	1.595	1.000	0.989	0.982	0.985
0.876	0.916	65.57	1.032	1.671	1.004	0.991	0.982	0.986
0.941	0.959	65.04	1.030	1.712	1.006	0.993	0.982	0.986
Ethanol (1) + water (2)								
0.015	0.170	95.99	5.838	0.974	0.981	0.991	0.965	0.993
0.032	0.276	92.69	5.133	1.099	0.980	0.992	0.968	0.993

(*Continued*)

Table 2. Continued.

x_1	y_1	T (K)	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
0.046	0.336	90.68	4.624	1.186	0.980	0.992	0.969	0.994
0.068	0.398	88.50	3.978	1.288	0.980	0.992	0.971	0.994
0.079	0.420	87.72	3.717	1.328	0.980	0.992	0.972	0.994
0.119	0.473	85.80	2.991	1.430	0.979	0.993	0.973	0.995
0.163	0.508	84.54	2.454	1.503	0.979	0.993	0.974	0.995
0.190	0.524	83.99	2.215	1.536	0.979	0.994	0.975	0.995
0.206	0.532	83.72	2.094	1.553	0.979	0.994	0.975	0.995
0.232	0.544	83.33	1.933	1.577	0.979	0.994	0.975	0.995
0.236	0.546	83.27	1.908	1.581	0.979	0.994	0.975	0.995
0.239	0.547	83.23	1.896	1.584	0.979	0.994	0.975	0.995
0.281	0.565	82.70	1.698	1.618	0.979	0.994	0.976	0.995
0.286	0.567	82.64	1.675	1.622	0.979	0.994	0.976	0.995
0.291	0.569	82.59	1.658	1.625	0.979	0.994	0.976	0.995
0.303	0.574	82.45	1.614	1.634	0.979	0.995	0.976	0.995
0.344	0.590	82.01	1.486	1.663	0.979	0.995	0.976	0.995
0.367	0.599	81.79	1.427	1.678	0.979	0.995	0.976	0.995
0.380	0.605	81.66	1.396	1.687	0.979	0.995	0.976	0.995
0.392	0.610	81.55	1.371	1.695	0.979	0.995	0.976	0.995
0.397	0.612	81.50	1.360	1.698	0.979	0.995	0.977	0.995
0.410	0.617	81.38	1.336	1.707	0.979	0.995	0.977	0.995
0.412	0.618	81.36	1.332	1.708	0.979	0.995	0.977	0.995
0.481	0.648	80.76	1.224	1.751	0.980	0.996	0.977	0.995
0.527	0.669	80.40	1.171	1.777	0.980	0.996	0.977	0.995
0.617	0.715	79.77	1.094	1.825	0.980	0.998	0.978	0.996
0.688	0.754	79.36	1.053	1.857	0.981	0.999	0.978	0.996
0.722	0.775	79.19	1.037	1.871	0.981	0.999	0.978	0.996
0.757	0.797	79.04	1.023	1.884	0.982	1.000	0.978	0.996
0.851	0.862	78.77	0.997	1.909	0.983	1.002	0.978	0.996
0.898	0.899	78.72	0.988	1.915	0.984	1.003	0.978	0.996
0.908	0.908	78.72	0.987	1.916	0.984	1.004	0.978	0.996
0.931	0.928	78.73	0.984	1.916	0.984	1.004	0.978	0.996
0.944	0.941	78.75	0.983	1.916	0.985	1.005	0.978	0.996
0.947	0.943	78.75	0.983	1.916	0.985	1.005	0.978	0.996
0.967	0.963	78.79	0.982	1.914	0.985	1.006	0.978	0.996

x_1, Liquid-phase mole fraction; y_1, vapour-phase mole fraction; T, boiling temperature; γ_1 and γ_2, activity coefficients; ϕ_1 and ϕ_2, fugacity coefficients; ϕ_1^s and ϕ_2^s, fugacity coefficients at saturation at 101.3 kPa

3. Data treatment

3.1. *VLE consistency data*

Phase equilibrium data should be tested in order to assure and guarantee an acceptable quality and reliability of VLE data. Available literature offers different procedures to test the thermodynamic consistency of a set of data for isothermal or isobaric condition. The thermodynamic consistency of the measured VLE data have been tested with the Wisniak method [17] to reject possible inconsistent equilibrium points from the experimental determined collection. According to this test, two experimental points (a) and (b) are thermodynamically consistent when:

$$D < D_{\max} \tag{1}$$

Table 3. Coefficients for heat of vapourisation and density liquid, Equations (3) and (4).

Compound	ΔT (K)	A	B	C	D
Ethanol	159–514[a]	55789000	0.31245	0	0
	159–514[b]	1.6288	0.27469	514	0.23178
Methanol	175–512[a]	50451000	0.33594	0	0
	175–512[b]	2.3267	0.27073	512.5	0.24713
Methyl acetate	175–506[a]	44920000	0.3685	0	0
	175–506[b]	1.13	0.2593	506.55	0.2764
Water	273–647[a]	52053000	0.31990	−0.212	0.25795
	300–380[b,c]	5.7783	0.3124	462.2545	0.05977

[a]Interval for heat vapourisation, [b]interval for liquid density, [c]calculated from [14].

Table 4. Results of the thermodynamic consistency test; L, W and D are variables defined in Equation (2).

System (1) + (2)	L	W	D
Methyl acetate + water	19.84	20.30	1.15
Methyl acetate + methanol	5.10	5.00	1.05
Methyl acetate + ethanol	6.59	6.81	1.61
Methanol + water	7.52	7.56	0.30
Methanol + ethanol	1.48	1.47	0.18
Ethanol + water	7.21	7.26	0.37

where $D_{\max}$ is the maximum deviation with a value of 3, D is the local deviation, which is expressed as:

$$D = 100\left|\frac{L - W}{L + W}\right|, \tag{2}$$

where L and W are each side temperature function integrals on liquid composition for the Wisniak test [13]. The correlations for heat of vapourisation (J kmol^{-1}) and density liquid (kmol m^{-3}) used are:

$$\Delta_{\text{vap}}H = A(1 - T_r)(B + CT_r + DT_r^2) \tag{3}$$

$$\rho = \frac{A}{B^{\left(1+(1-T/C)^D\right)}}, \tag{4}$$

where, T is the temperature in K, T_r is the reduced temperature and the constants A, B, C and D are shown in Table 3. The physical properties used were taken from Diadem Public v1.2 [10], and the activity coefficients were calculated as shown in the next section.

Table 4 shows the values for the integrals L and W calculated for the thermodynamic consistent test and the values for the deviation D. Also, this table shows that the condition $D < D_{\max}$ satisfies all systems. Therefore, the thermodynamic consistency of the binary VLE data reported in this work is confirmed.

Table 5. Antoine and Mathias and Copeman Coefficients.

Compound	A_i^a	B_i^a	C_i^a	ΔT (K)[b]	C_1^c	c_2^c	C_3^c
Ethanol	8.322	1718.10	237.52	296.9–463.2	1.412530	0.287222	−1.496099
Methanol	7.898	1474.08	229.13	292.0–461.3	1.433991	−0.768115	0.226212
Methyl acetate	7.065	1157.622	219.724	277.1–462.7	1.069537	−0.759819	1.492479
Water	8.012	1695.167	230.41	276.6–590.9	1.093544	−0.673056	0.699288

[a]See [19]; [b]see [18]; [c]calculated in this work.

3.2. *Equilibrium equation and activity coefficients*

The activity coefficients (γ_i) of the components were calculated from the following equation:

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^o}, \tag{5}$$

were x_i and y_i are the liquid and vapor mole fractions in equilibrium, Φ_i is the vapor phase correction factor, P is the total pressure and P_i^o is the vapour pressure of pure component i.

These vapour pressures were calculated from the Antoine equation:

$$\log P = A_i - \frac{B_i}{T(^\circ\mathrm{C}) + C_i}, \tag{6}$$

where, P is the vapor pressure in mmHg, T is temperature in °C and the constants $A_{i.}$, B_i and C_i are reported in Table 5. The value constants for the pure compounds were obtained in literature by Riddick *et al.* [9].

The vapour phase correction factor is given by:

$$\Phi_i = \frac{\phi_i}{\phi_i^{\mathrm{sat}}} \exp\left[-\frac{V_i(P - P_i^o)}{RT}\right], \tag{7}$$

where ϕ_i is the fugacity coefficient of component i in the mixture, ϕ_i^{sat} is the fugacity coefficient at saturation condition and V_i is the molar volume of component i in the liquid phase calculated using the correlation of the liquid density. Fugacity coefficients were calculated with PSRK model, where the expression proposed by Mathias and Copeman [18] is used to evaluate $\alpha(T)$ in the PSRK model:

$$\alpha(T) = \left[1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3\right]^2 \quad \text{for } T_r < 1, \tag{8}$$

where, T_r is the reduced temperature and T_c is the critical temperature, while c_1, c_2 and c_3 are empirical parameters. These parameters for the pure compounds were calculated in this work and are shown in Table 5. The physical properties for the pure components used in the PSRK model were taken from [10] and shown in Table 6.

The calculated fugacity and activity coefficients are shown in Table 2 for all data points.

Table 6. Physical properties for components: *T*c, critical temperature; *P*c, critical pressure; ω, acentric factor; and uniquac parameters *r* and *q*.

Compound	*T*c (K)	*P*c (bar)	ω	*r*	*q*
Ethanol	514.0	61.5	0.644	2.11	1.97
Methanol	512.5	81.0	0.566	1.43	1.43
Methyl acetate	506.6	47.5	0.331	2.80	2.58
Water	647.1	221.2	0.345	0.92	1.4

3.3. *Modelling – Correlation model*

The VLE data were correlated in the $\gamma - \varphi$ approximation, where the PSRK equation of state was used to evaluate the fugacity coefficients, as the thermodynamic model in a bubble-point calculation. The description of the models applied here (Wilson, NRTL, and UNIQUAC) is freely available in the literature [7] and hence it is not discussed here. In the φ approximation, the Wilson, NRTL and UNIQUAC models were used instead of the UNIFAC model to calculate the excess Gibbs energy in the PSRK model. Theoretically, the range for the parameters A_{ij} (Wilson, NRTL and UNIQUAC) is defined as $(-10^4,\ 10^4)$ J mol^{-1}. Since this is a very wide range based on physical considerations, it is extremely likely that it will contain the globally optimal parameter values. Renon and Prausnitz [18] explain that the range for α_{ij} with theoretical bases can have values from 0.2 to 0.55. To evaluate these parameters, the regression was performed using a genetic algorithm code, implemented and fully explained in the study by Alvarez *et al.* [19], with the minimisation of the overall objective function (*Q*).

$$Q = \sum_{j=1}^{N} \left([y_{1j}^{\mathrm{exp}} - y_{1j}^{\mathrm{cal}}]/\sigma_y \right)^2 + \sum_{j=1}^{N} \left([T^{\mathrm{cal}} - T^{\mathrm{exp}}]/\sigma_T \right)^2, \tag{9}$$

where σ_y is the accuracy in the vapour mole fraction (10^{-3}), σ_T is the accuracy in the temperature (10^{-1}), *N* is the number of data sets, y_i is the molar fraction of the component *i* and the superscript 'exp' and 'cal' are the experimental and calculated values, respectively. The fitting parameters of these models and deviations are shown Table 7, the relative percent deviations in temperature and vapour phase compositions are calculated by Valderrama and Alvarez [20]:

$$|\Delta T|\% = \frac{100}{N} \sum_{i=1}^{N} \frac{|T_i^{\mathrm{cal}} - T_i^{\mathrm{exp}}|}{T_i^{\mathrm{exp}}} \tag{10}$$

$$|\Delta y|\% = \frac{100}{N} \sum_{i=1}^{N} \frac{|y_i^{\mathrm{cal}} - y_i^{\mathrm{exp}}|}{y_i^{\mathrm{exp}}}, \tag{11}$$

where *N* is the number of data sets, *T* is the temperature, y_i is the vapour molar fraction of the component *i* and the superscript 'exp' and 'cal' are the experimental and calculated values, respectively. Also, this table shows that all models present similar deviations in temperature and concentration in vapour phase, with a slightly better performance of the UNIQUAC model. The modelling of VLE data are

Table 7. Correlation parameters for activity coefficients and average deviation for the studied systems.

Model	A_{12} (KJ mol^{-1})	A_{21} (KJ mol^{-1})	$\lvert\Delta T\rvert$ % (K)	$\lvert\Delta y_1\rvert$ %	$\lvert\Delta y_2\rvert$ %
Methyl acetate (1) + water (2)					
Wilson	3249.187	8660.565	0.27	2.95	12.96
NRTL ($\alpha_{12}=0.415$)	3276.966	7494.240	0.05	0.73	2.36
UNIQUAC^{c}	2216.998	959.094	0.10	0.42	1.46
UNIFAC	–	–	0.06	0.75	2.08
PSRK	–	–	0.39	3.25	6.52
Methyl acetate (1) + methanol (2)					
Wilson	−75.011	3815.635	0.02	0.19	0.47
NRTL ($\alpha_{12}=0.534$)	1927.705	1181.491	0.02	0.19	0.50
UNIQUAC^{c}	2922.085	−594.613	0.02	0.22	0.43
UNIFAC	–	–	0.02	0.31	0.52
PSRK	–	–	0.16	2.63	1.86
Methyl acetate (1) + ethanol (2)					
Wilson	467.457	2721.965	0.02	0.23	0.95
NRTL ($\alpha_{12}=0.550$)	1772.065	1504.565	0.02	0.25	1.00
UNIQUAC^{c}	1667.680	−178.669	0.03	0.36	1.03
UNIFAC	–	–	0.06	0.61	1.30
PSRK	–	–	0.23	1.93	2.24
Methanol (1) + water (2)					
Wilson	173.843	2373.103	0.04	0.54	3.87
NRTL ($\alpha_{12}=0.550$)	75.506	2425.812	0.04	1.01	3.08
UNIQUAC^{c}	−1289.764	2072.282	0.05	0.35	2.12
UNIFAC	–	–	0.08	0.45	1.39
PSRK	–	–	0.07	0.53	0.77
Methanol (1) + ethanol (2)					
Wilson	−309.207	1565.299	0.03	0.23	0.66
NRTL ($\alpha_{12}=0.200$)	4229.869	−2822.070	0.02	0.26	0.60
UNIQUAC^{c}	1412.023	−763.408	0.03	0.23	0.64
UNIFAC	–	–	0.02	0.38	0.97
PSRK	–	–	0.02	0.44	0.71
Ethanol (1) + water (2)					
Wilson	2083.9776	3953.5367	0.25	0.39	1.16
NRTL ($\alpha_{12}=0.550$)	734.70	5007.82	0.18	0.92	1.46
UNIQUAC^{c}	−495.0402	1988.1091	0.21	0.75	1.58
UNIFAC	–	–	0.22	0.33	0.82
PSRK	–	–	0.09	1.84	2.46
Mean					
Wilson			0.10	0.76	3.34
NRTL			0.06	0.56	1.50
UNIQUAC			0.07	0.39	1.21
UNIFAC			0.08	0.47	1.18
PSRK			0.16	1.77	2.43

presented in $T-x_1-y_1$ diagrams shown in Figures 1–6. In Figure 7, comparisons between models desviations using Equation (11) are shown for all binary systems, it is easy to observe that UNIQUAC model has a good agreement between experimental and calculated composition vapor phase.

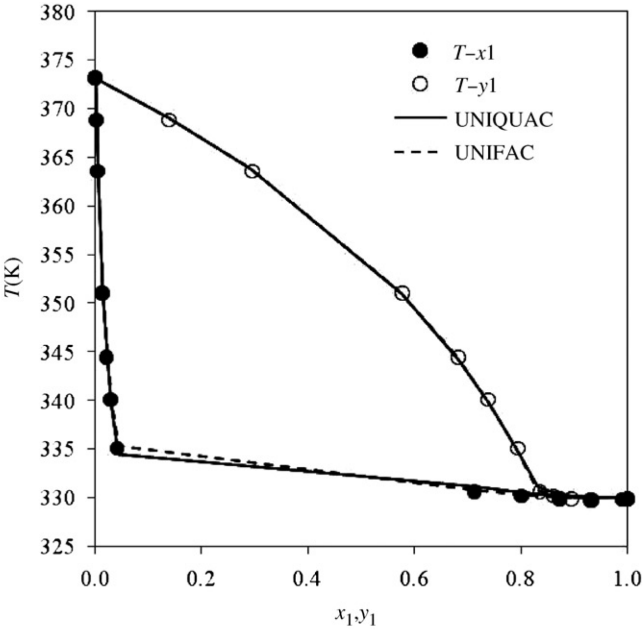

Figure 1. $T - x_1 - y_1$ diagram for methyl acetate (1) + water (2) at 101.3 kPa: (●) experimental liquid phase; (○) experimental vapour phase; (—) UNIQUAC correlation; (- - -) UNIFAC prediction.

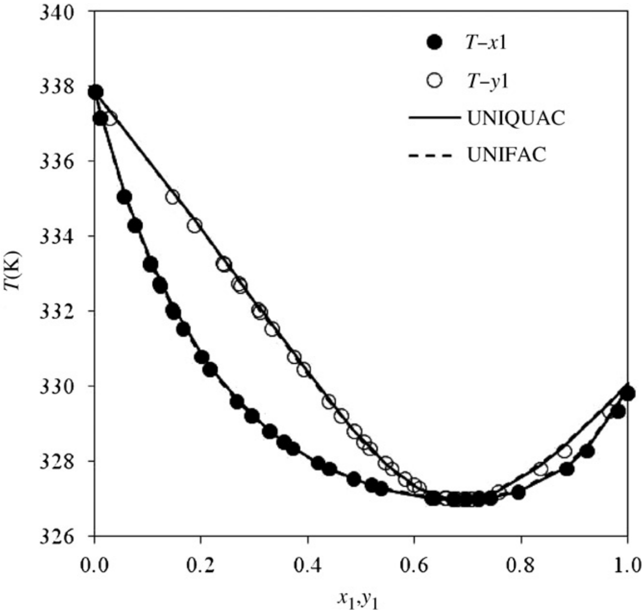

Figure 2. $T - x_1 - y_1$ diagram for methyl acetate (1) + methanol (2) at 101.3 kPa: (●) experimental liquid phase; (○) experimental vapour phase; (—) UNIQUAC correlation; (- - -) UNIFAC prediction.

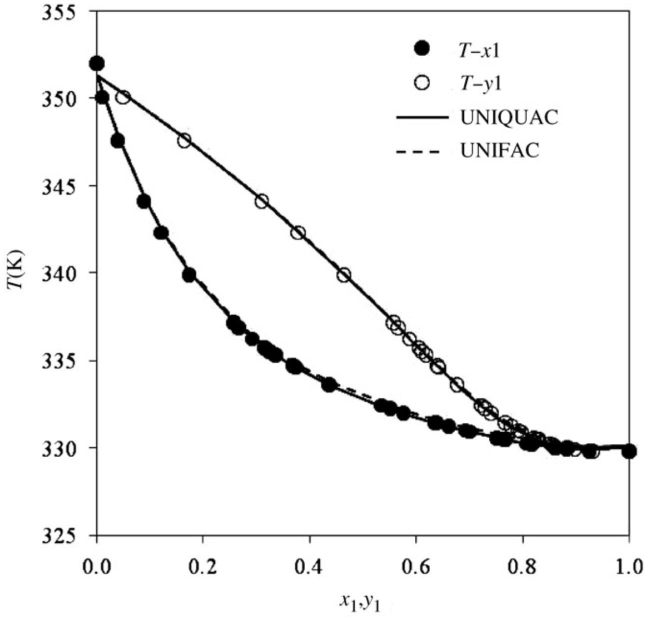

Figure 3. $T-x_1-y_1$ diagram for methyl acetate (1)+ethanol (2) at 101.3 kPa: (•) experimental liquid phase; (○) experimental vapour phase; (—) UNIQUAC correlation; (- - -) UNIFAC prediction.

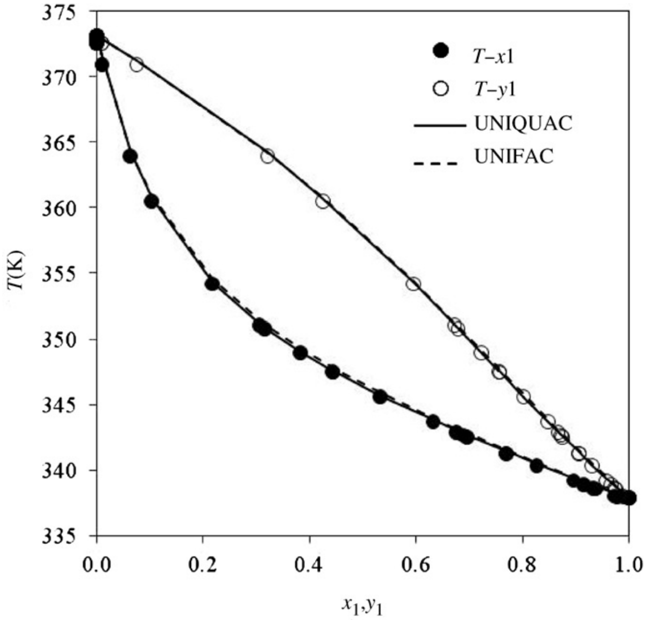

Figure 4. $T-x_1-y_1$ diagram for methanol (1)+water (2) at 101.3 kPa: (•) experimental liquid phase; (○) experimental vapour phase; (—) UNIQUAC correlation; (- - -) UNIFAC prediction.

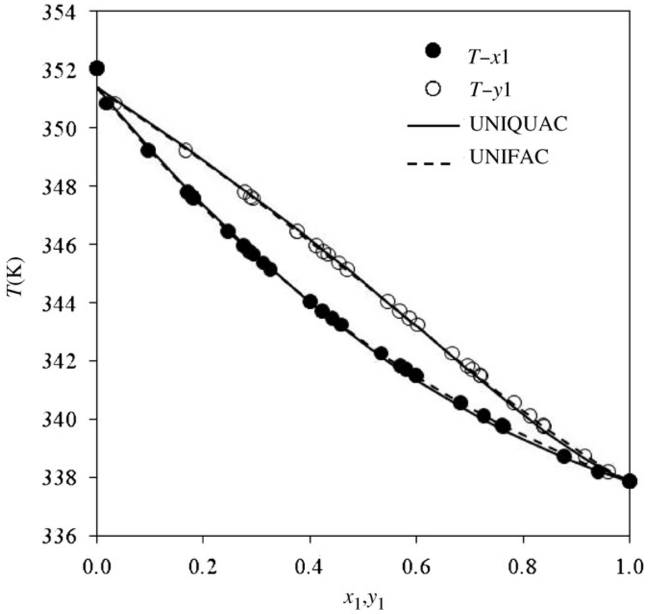

Figure 5. $T - x_1 - y_1$ diagram for methanol (1) + ethanol (2) at 101.3 kPa: (●) experimental liquid phase; (○) experimental vapour phase; (—) UNIQUAC correlation; (- - -) UNIFAC prediction.

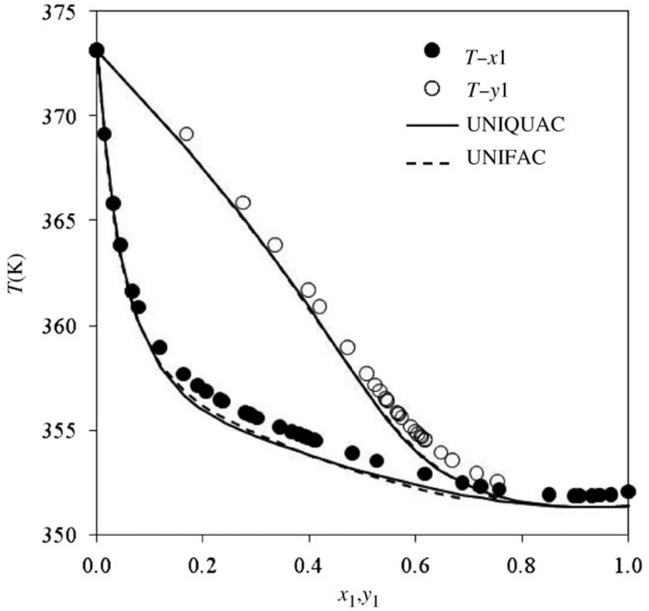

Figure 6. $T - x_1 - y_1$ diagram for ethanol (1) + water (2) at 101.3 kPa: (●) experimental liquid phase; (○) experimental vapour phase; (—) UNIQUAC correlation; (- - -) UNIFAC prediction.

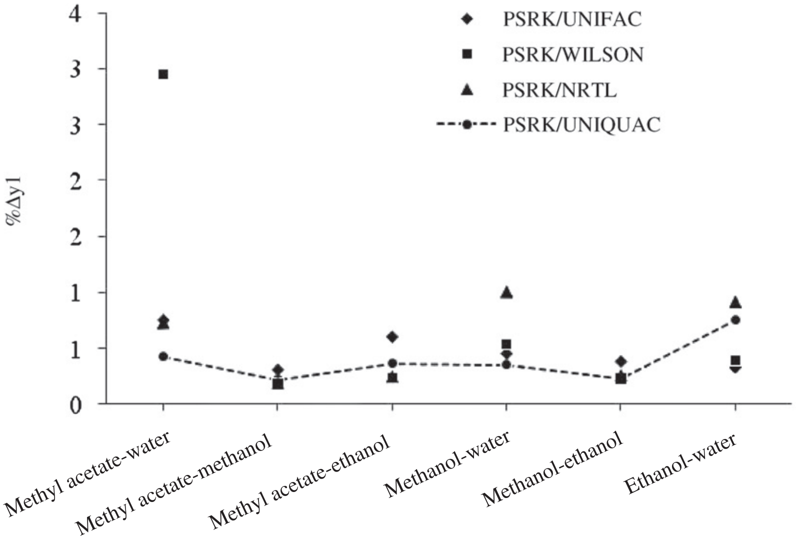

Figure 7. Model deviation for the studied binary systems. $\%\Delta y_1$ calculated with Equation (11).

3.4. *Modelling – Prediction model*

Prediction of VLE for the studied binary mixtures has been carried out by the UNIFAC group contribution method [21] ($\gamma - \varphi$ aproximation) and the PSRK model ($\varphi - \varphi$ aproximation). The group interaction parameters applied were those available from open literature. The results are compared with the experimental values, and the average percent deviation for the temperature ($|\Delta T|\%$) and the composition of the vapour phase ($|\Delta y_i|\%$) are shown in the two last rows of Table 7 for each system, where the PSRK model has greater deviations than UNIFAC model. A qualitative description was obtained with the two predictive methods due to the partially heterogeneous character of the mixture methyl acetate + water and the difference in structure of the enclosed molecules (Figure 1). For the other mixture, the accuracy and description of phase equilibria is better as observed in Figures 2–6.

3.5. *Comparison with previously published data*

In the available literature, different publications [22–41] related to the binary mixtures experimentally studied may be found. Most of them are to be used sparsely, due to the lack of thermodynamic consistency [29,31,32,34,40] or inadequate coverage of the composition range [29,31,39–41] (see point distribution in Figures 8–13 for the different sets of previously published data). In Figures 8–13, a comparison of the boiling temperature deviations corresponding to literature data points from the experimental data correlation obtained in this paper are shown. Different symbols are used to indicate the previous experimental data, the line of zero deviation corresponding to our experimental data, using as abscise the molar fraction of the most volatile compound into each binary system.

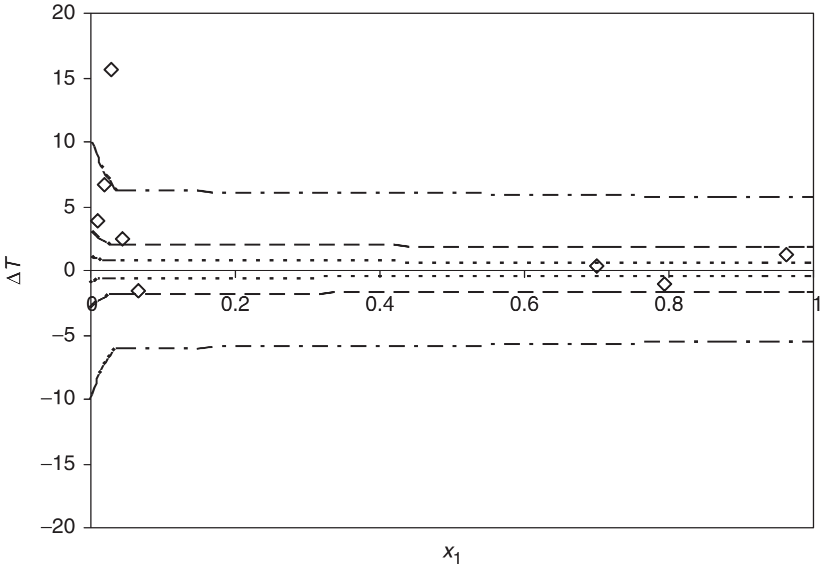

Figure 8. Temperature deviations for the binary mixture methyl acetate (1) + water (2) at 101.3 kPa: (—) experimental data; (◇) Ref. [22]. Semidotted line indicates 10%, dashed line indicates 3% and dotted line indicates 1% deviation from experimental data.

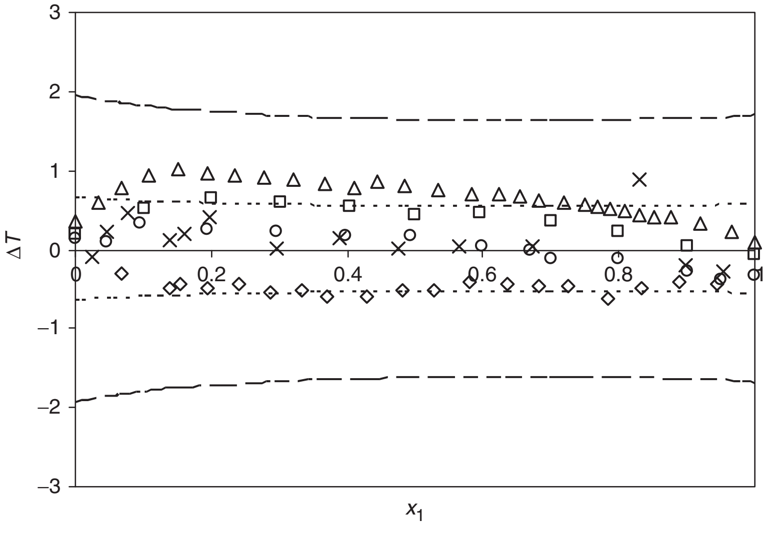

Figure 9. Temperature deviations for the binary mixture methyl acetate (1) + methanol (2) at 101.3 kPa: (—) experimental data; (○) Ref. [23]; (◇) Ref. [24]; (□) Ref. [25]; (Δ) Ref. [26]; (×) Ref. [27]. Dashed line indicates 3% and dotted line indicates 1% deviation from experimental data.

In general terms, a concordance is observed among our experimental data and those reported for each system (better than ±3% in terms of temperature deviation).

Only a collection of data is gathered into open literature for the methyl acetate + water system by Perelygin and Volkov [22]. As observed in Figure 8,

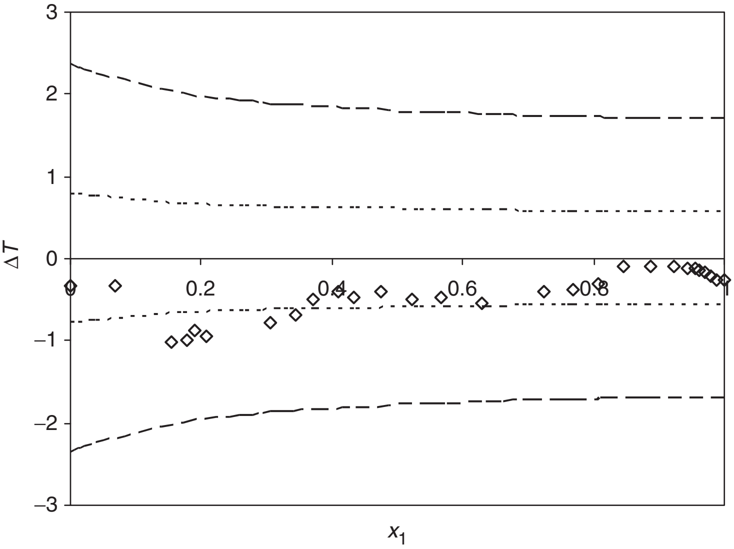

Figure 10. Temperature deviations for the binary mixture methyl acetate (1) + ethanol (2) at 101.3 kPa: (—) experimental data; (◇) Ref. [28]. Dashed line indicates 3% and dotted line indicates 1% deviation from experimental data.

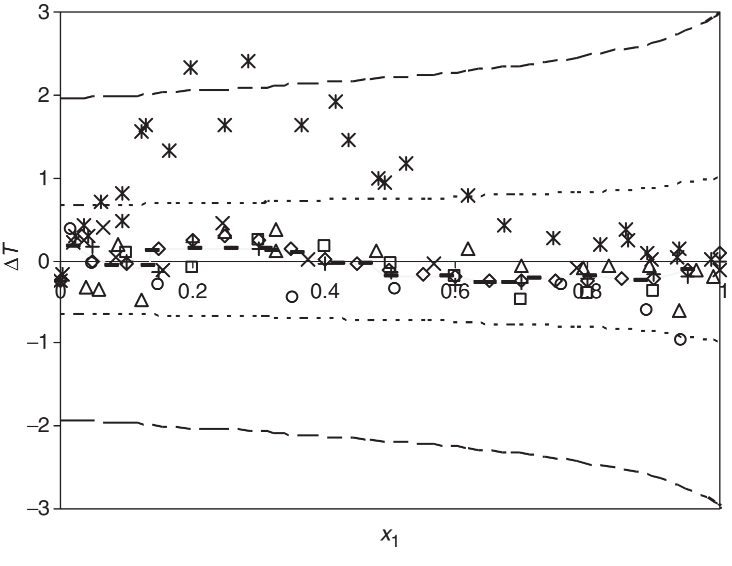

Figure 11. Temperature deviations for the binary mixture methanol (1) + water (2) at 101.3 kPa: (—) experimental data; (○) Ref. [29]; (◇) Ref. [30]; (□) Ref. [31]; (Δ) Ref. [32]; (×) Ref. [33]; (⁎) Ref. [34]; (+) Ref. [35]; (—) Ref. [36]. Dashed line indicates 3% and dotted line indicates 1% deviation from experimental data.

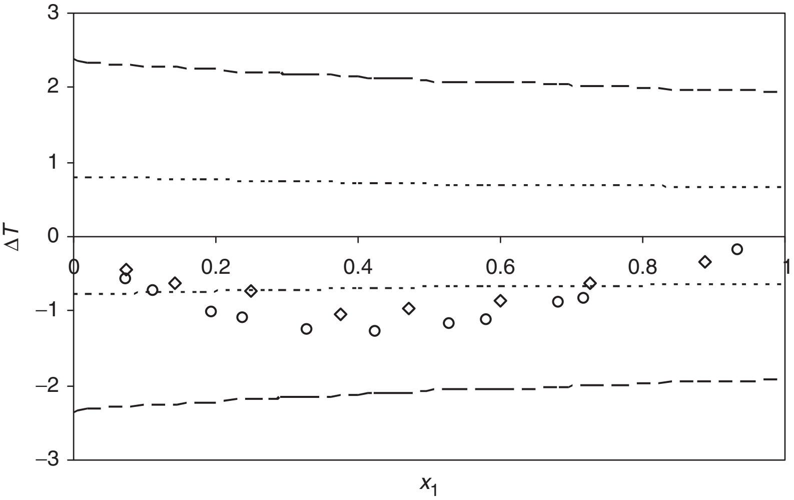

Figure 12. Temperature deviations for the binary mixture methanol (1) + ethanol (2) at 101.3 kPa: (—) experimental data; (○) Ref. [36]; (◇) Ref. [37]. Dashed line indicates 3% and dotted line indicates 1% deviation from experimental data.

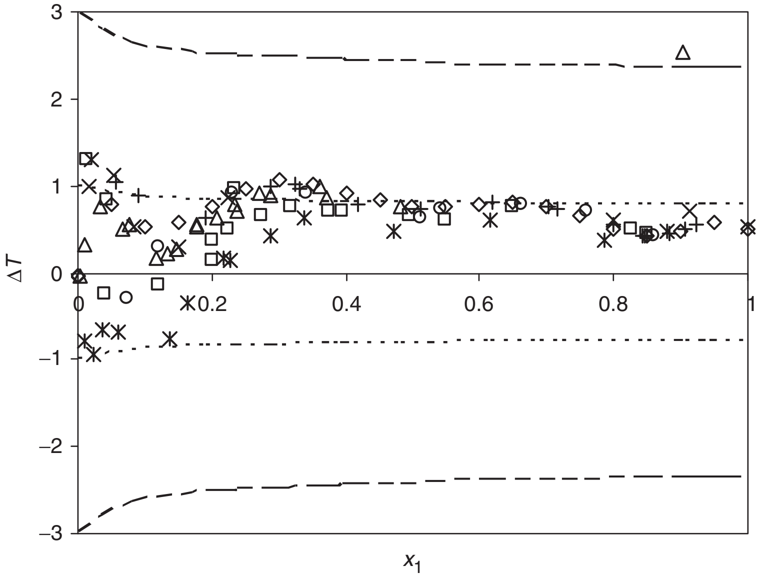

Figure 13. Temperature deviations for the binary mixture ethanol (1) + water (2) at 101.3 kPa: (—) experimental data; (○) Ref. [38]; (◇) Ref. [30]; (□) Ref. [32]; (△) Ref. [39]; (×) Ref. [40]; (⁎) Ref. [41]; (+) Ref. [36]. Dashed line indicates 3% and dotted line indicates 1% deviation from experimental data.

deviations higher than 10% have been computed from the experimental data of this work.

In what is referred as the methyl acetate + methanol mixture, data of Iliuta *et al.* [23] show the lowest deviations (better than 1%), although data shown by Tu *et al.* [24] and Topphoff *et al.* [25] or Nagata [27] are accurate too. For this binary system, the work of Orchilles *et al.* [26] presented the poorest results, showing deviations between 1 and 3% (Figure 9 [23–27]).

For the methyl acetate + ethanol mixture, only one collection of data was found in the available literature [28], showing negative deviations between 1 and 3% with respect to our results (Figure 10).

Literature review related to methanol + water system shows numerous works on VLE at the same condition [29–36]. All of them present acceptable deviations (better than 1%). Only Uchida *et al.*'s [34] study shows important deviations (greater than 3%) for methanol diluted compositions (Figure 11).

Two earlier works [36,37] related to methanol + ethanol system gather results under the same conditions applied in this work. In Figure 12 it should be observed that deviations are between 1 and 3%.

The ethanol + water system shows different collections of VLE studies [30,32, 36,38–41] in the last few years, all of them of acceptable coincidence with our data (≈1%) (Figure 13).

As commented before, the systems are coincident in terms of deviations with our results, around 1% deviations, mainly, methyl acetate + methanol, methyl acetate + ethanol and ethanol + water, and 3% deviations methanol + water and methanol + ethanol mixtures. Only the system methyl acetate + water shows deviations higher than 10%.

4. Conclusions

In this study, the phase equilibrium behaviour of the binary mixtures methyl acetate + (water or methanol or ethanol), methanol + (water or ethanol) and (ethanol + water) were experimentally investigated in order to characterise the interactions of a collection of diferent compounds (so-called congeners) into distillated alcoholic mixtures. The experimental results showed that these mixtures are homogeneous with the exception of the mixture methyl acetate + water that shows the characteristic behaviour of a partially homogeneous system.

Based on the results, the following conclusions can be drawn:

(1) the UNIQUAC model represents the best way for fitting VLE data of this kind of mixtures, despite nonideality and partial miscibility (methyl acetate + water mixture); (2) the high value of the non-randomness parameter in NRTL model shows that the binary systems methyl acetate + water, methyl acetate + methanol, methyl acetate + ethanol, methanol + water and ethanol + water are mixtures with components highly associated; (3) the UNIFAC model shows good predictive description of all mixtures studied; (4) the lack of experimental data in all binary and multicomponent alcoholic distillation mixtures and the qualitative reliability of the group contribution methods when global simulation of distillation alcoholic processes are attempted, suggest a wider study of mixtures and a prudent utilisation of the prediction results into these kind of studies and designs; (5) this data

complements the experimental and thermodynamic information for characterise alcoholic mixtures contained into distillated beverages, which means an improvement of the existing literature until now.

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