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Vapor−Liquid Equilibrium Data for Methanol, Ethanol, Methyl Acetate, Ethyl Acetate, and *o*-Xylene at 101.3 kPa

José Costa-López,* Alfonso Garvín, and Francisco J. España

Chemical Engineering Department, Barcelona University, Barcelona 08028, Spain

Vapor−liquid equilibrium was measured for the binary systems methanol + *o*-xylene, ethanol + *o*-xylene, methyl acetate + *o*-xylene and ethyl acetate + *o*-xylene, and for the multicomponent mixtures methanol + methyl acetate + *o*-xylene, ethanol + ethyl acetate + *o*-xylene, and methanol + ethanol + methyl acetate + ethyl acetate + *o*-xylene at 101.3 kPa. The Wilson and Van Laar models were compared with the UNIFAC method. Results show that the correlation was satisfactory.

Introduction

One of the effluents of the industrial poly(vinyl alcohol) synthesis is a mixture of methyl alcohol and methyl acetate. In order to develop a new process to produce ethyl acetate by means of a transesterification with ethyl alcohol, this process incorporates extractive distillation, using *o*-xylene as the extraction solvent. Vapor−liquid equilibrium (VLE) data are needed for the correct calculation and design of the distillation columns.

In the present work, we report vapor−liquid equilibrium (VLE) data for mixtures containing methyl alcohol, ethyl alcohol, methyl acetate, ethyl acetate, and *o*-xylene. Due to our interest in predicting the multicomponent equilibrium, those binary systems that were not found in the literature (methyl alcohol + *o*-xylene, ethyl alcohol + *o*-xylene, methyl acetate + *o*-xylene, and ethyl acetate + *o*-xylene) as well as the multicomponent systems (methyl alcohol + methyl acetate + *o*-xylene, ethyl alcohol + ethyl acetate + *o*-xylene, and methyl alcohol + ethyl alcohol + methyl acetate + ethyl alcohol + *o*-xylene) have been studied.

Experimental Section

Chemicals. Methanol, ethanol, and ethyl acetate were Merck chromatography grade (purity >99.8 mass %). Methyl acetate was Merck high-purity grade (>99.0 mass %), and its impurity was methanol. *o*-Xylene was also Merck high-purity grade (>98.0%), and it was rectificated twice in a packed column. The purity of *o*-xylene achieved by the rectification procedure was checked by GC to be 99.5%. All the substances were dried with Union Carbide 3 Å molecular sieves, provided by Fluka. After the rectification and the drying process, the purities checked by GC were for methanol, ethanol, and ethyl acetate 99.9 mass %, for methyl acetate 99.8 mass %, *o*-xylene 99.6 mass %. See the properties in Table 1.

Apparatus and Procedure. The apparatus used was an all-glass, dynamic vapor phase recirculating still based on the Othmer apparatus, with a magnetic stirrer. The equilibrium temperature was measured with a digital Crison thermometer with an accuracy of ±0.1 K, and the pressure was measured using a mercury tube manometer with an accuracy of ±0.07 kPa. The pressure was kept constant using a cartesian manostat, manufactured by Gilmont. Measurements were made at 101.33 kPa for all the systems. Some researchers report that this kind of ebulliometer may present problems of poor mixing, overheating, or partial condensation. In order to avoid these problems, a small amount of extra heating was applied in the upper zone of the apparatus and its coating was improved. The extra heater was designed to keep the upper zone at the same temperature as in the boiler. The operation of the apparatus was checked with methanol + methyl acetate, and the results agree with those of Nagata (*12*) as can be seen in Figures 1 and 2. The consistency test was made as described below, and the results were satisfactory. In each experiment, the pressure control system was set at 101.3 kPa, the heater and the agitator

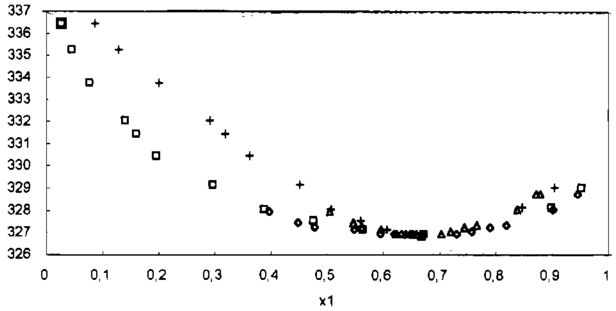

Figure 1. Boiling point diagram of the mixture methyl acetate (1) + methanol (2). Experimental data are compared with those obtained by Nagata: +, Nagata (*12*); □, this work.

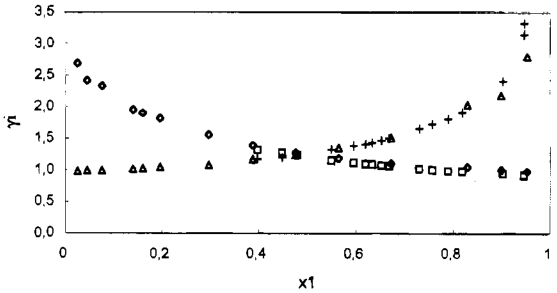

Figure 2. Activity coefficient diagram of the mixture methyl acetate (1) + methanol (2): +, Nagata (*12*); □, this work.

Table 1. Densities *d*, Refractive Indexes *n*, and Boiling Points T_b of the Chemicals Used in This Study

	d(293.15 K)/(g·cm^{-3})		n(D,293.15 K)		T_b/K	
compound	exptl	lit. (*18*)	exptl	lit. (*4*)	exptl	lit. (*4*)
methanol	0.7914	0.79129	1.3290	1.3288	337.85	337.85
ethanol	0.7894	0.78937	1.3612	1.3611	351.55	351.65
methyl acetate	0.9338	0.9342	1.3599	1.3595	329.85	330.05
ethyl acetate	0.9002	0.9003	1.3726	1.3723	350.25	350.21
o-xylene	0.8800	0.8801	1.5058	1.5055	417.45	417.55

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Table 2. Experimental VLE for the System Methanol (1) + *o*-Xylene (2) at a Constant Pressure (101.3 kPa): Liquid Mole Fraction (*x*), Vapor Mole Fraction (*y*), Temperature (*T*), Vapor Fugacity Coefficient (ϕ), Activity Coefficient (γ)

x_1	y_1	ϕ_1	ϕ_2	γ_1	γ_2	T/K
0.9878	0.9910	0.9548	0.9753	0.9518	10.894	337.85
0.9833	0.9881	0.9549	0.9746	0.9498	10.413	337.95
0.9767	0.9845	0.9550	0.9738	0.9526	9.7604	337.95
0.9670	0.9796	0.9551	0.9727	0.9538	9.0097	338.05
0.9334	0.9682	0.9555	0.9702	0.9618	6.8145	338.45
0.8684	0.9568	0.9559	0.9677	1.0063	4.5934	338.85
0.8424	0.9531	0.9565	0.9669	1.0101	4.0504	339.45
0.8330	0.9565	0.9568	0.9676	1.0097	3.4837	339.85
0.7674	0.9497	0.9574	0.9662	1.0639	2.8157	340.45
0.4933	0.9452	0.9584	0.9654	1.5806	1.3417	341.55
0.2176	0.9384	0.9609	0.9643	3.1715	0.8564	344.65
0.0249	0.8000	0.9795	0.9541	8.4648	0.6974	375.25

Table 3. Experimental VLE for the System Ethanol (1) + *o*-xylene (2) at a Constant Pressure (101.3 kPa): Liquid Mole Fraction (*x*), Vapor Mole Fraction (*y*), Temperature (*T*), Vapor Fugacity Coefficient (ϕ), Activity Coefficient (γ)

x_1	y_1	ϕ_1	ϕ_2	γ_1	γ_2	T/K
0.9952	0.9966	0.9622	0.9541	0.9630	5.7426	351.45
0.9859	0.9903	0.9624	0.9534	0.9510	5.5401	351.85
0.9773	0.9852	0.9624	0.9527	0.9544	5.2430	351.85
0.9578	0.9740	0.9626	0.9513	0.9517	4.8795	352.15
0.9059	0.9509	0.9629	0.9484	0.9712	4.0674	352.45
0.8679	0.9416	0.9632	0.9474	0.9884	3.3913	352.85
0.8501	0.9370	0.9634	0.9470	0.9927	3.1837	353.15
0.8091	0.9291	0.9636	0.9461	1.0264	2.7889	353.35
0.7677	0.9236	0.9637	0.9455	1.0712	2.4593	353.45
0.6769	0.9121	0.9647	0.9450	1.1246	1.9028	355.15
0.4866	0.8925	0.9658	0.9436	1.4305	1.3642	356.95
0.2511	0.8732	0.9682	0.9438	2.3149	0.9373	361.25
0.1094	0.8149	0.9729	0.9434	3.5847	0.8245	370.45
0.0522	0.6591	0.9813	0.9417	3.6719	0.8484	385.95
0.0065	0.2290	1.0011	0.9424	5.0920	0.8867	410.45

were connected, and the mixture reached the boiling point and was kept there for 120 min, to ensure that a steady state was attained. Once equilibrium was established, a sample of the boiling liquid and the condensed vapor was taken through a septum using a syringe, to avoid evaporation and to minimize the quantity of sample removed.

Analysis was carried out with a Shimadzu gas chromatography GC-9A equipped with a flame ionization detector. The GC response was integrated using a Shimadzu Chromatopac C-R3A. The GC column was a Supelco packed with 3% SP-1500 in Carbopack B 80/120 (3 m × 0.0032 m). Analysis conditions were as follows: temperature, 353 K for 5 min, ramped for 12 min at 10 K min^{-1} and 473 K for 20 min), nitrogen as the carrier gas.

The calibration was made with gravimetrically prepared standard solutions, and the standard deviation of the analysis was less than 0.001 mole fraction. At least two analyses were done of each sample.

Results and Discussion

Measurements were made at 101.3 kPa for methanol + *o*-xylene, ethanol + *o*-xylene, methyl acetate + *o*-xylene, and ethyl acetate + *o*-xylene and are presented in Tables 2–5. The results were regressed to obtain the Wilson (*21*), Van Laar (*19*), and NRTL (*16*) parameters of the respective equation of the activity coefficient (γ_i). The experimental activity coefficient was calculated as follows:

$$\gamma_i = y_i P \phi_i / x_i P_i^\circ \tag{1}$$

Vapor phase nonidealities were calculated from the second virial coefficients obtained by the method of Hayden and O'Connell (*8*). The values used for the critical constants, the acentric factors, dipole moments, and solvation parameters were taken from Reid et al. (*15*). Vapor pressures were calculated by use of the Antoine equation (Table 6) with the constants from the TRC Tables (*18*). Data regression was done using the ASPEN Plus data regression system based on the Britt–Luecke algorithm to obtain the model parameters (*3*).

The thermodynamic consistency of the experimental data was checked by means of the Herrington test (*9*), and L–W (*22*) area test. The systems present L–W area deviations below 3 except for the system ethyl acetate + *o*-xylene, which was 3.1. Furthermore, a consistency test based on the method of Van Ness et al. (*20*) has been done. The test employed has been developed by Gess et al. (*7*). In this test, vapor fugacities are taken into account. A variation of Barker's method (*2*) is used to obtain parameter estimates. Results of the medium average deviation in

Table 4. Experimental VLE for the System Methyl Acetate (1) + *o*-Xylene (2) at a Constant Pressure (101.3 kPa): Liquid Mole Fraction (*x*), Vapor Mole Fraction (*y*), Temperature (*T*), Vapor Fugacity Coefficient (ϕ), Activity Coefficient (γ)

x_1	y_1	ϕ_1	ϕ_2	γ_1	γ_2	T/K
0.9333	0.9848	0.9483	0.9142	0.9222	4.0129	332.45
0.8682	0.9851	0.9494	0.9159	0.9371	1.8363	334.15
0.7619	0.9777	0.9511	0.9179	0.9635	1.3443	337.05
0.6437	0.9655	0.9534	0.9202	0.9939	1.1751	340.95
0.5526	0.9552	0.9553	0.9223	1.0299	1.0559	344.35
0.4760	0.9421	0.9573	0.9243	1.0502	0.9977	348.15
0.3996	0.9271	0.9591	0.9261	1.1058	0.9505	351.75
0.3321	0.9017	0.9618	0.9286	1.1009	0.9293	357.35
0.2219	0.8469	0.9662	0.9323	1.1822	0.8676	367.15
0.1762	0.7981	0.9690	0.9341	1.1849	0.8614	373.65
0.1197	0.7121	0.9738	0.9380	1.1637	0.7809	385.45
0.0799	0.6032	0.9776	0.9386	1.2532	0.8252	392.55
0.0480	0.4384	0.9833	0.9399	1.2429	0.8621	401.65
0.0332	0.3372	0.9869	0.9414	1.2316	0.8577	407.15
0.0144	0.1410	0.9941	0.9434	1.0316	0.8987	414.25

Table 5. Experimental VLE for the System Ethyl Acetate (1) + *o*-Xylene (2) at a Constant Pressure (101.3 kPa): Liquid Mole Fraction (*x*), Vapor Mole Fraction (*y*), Temperature (*T*), Vapor Fugacity Coefficient (ϕ), Activity Coefficient (γ)

x_1	y_1	ϕ_1	ϕ_2	γ_1	γ_2	T/K
0.9761	0.9988	0.9463	0.9153	0.9267	0.3826	351.55
0.9080	0.9886	0.9473	0.9165	0.9313	0.9003	353.35
0.7762	0.9650	0.9494	0.9188	0.9477	0.9867	357.05
0.6054	0.9285	0.9526	0.9225	0.9756	0.9170	363.05
0.5724	0.9204	0.9534	0.9235	0.9759	0.8897	364.65
0.4843	0.8931	0.9547	0.9245	1.0409	0.9059	367.15
0.4712	0.8889	0.9549	0.9248	1.0495	0.9025	367.65
0.4024	0.8571	0.9562	0.9256	1.0715	0.9081	371.15
0.3412	0.8245	0.9587	0.9287	1.0809	0.8755	375.45
0.2397	0.7318	0.9625	0.9317	1.1128	0.9009	383.15
0.1116	0.5305	0.9699	0.9375	1.1950	0.8534	398.15
0.0139	0.1261	0.9814	0.9433	1.5848	0.9113	414.35

Table 6. Parameters of the Antoine Equation (*18*)

parameter	methanol	ethanol	methyl acetate	ethyl acetate	*o*-xylene
A	5.15043	4.92365	4.18621	4.13361	4.13072
B	1549.48	1410.46	1156.43	1195.13	1479.82
C	236.642	208.514	2193.69	212.47	214.315

Table 7. Results of the Consistency Test

system	MAD(y_i)	system	MAD(y_i)
methanol + *o*-xylene	0.0099	methyl acetate + *o*-xylene	0.0098
ethanol + *o*-xylene	0.0077	ethyl acetate + *o*-xylene	0.0101

Table 8. Results of the Regression of the Binary Systems

	Van Laar		Wilson		NRTL		
system	A	B	Λ_{12}	Λ_{21}	Δg_{12}/(kJ/mol)	Δg_{12}/(kJ/mol)	α
methanol + *o*-xylene	2.1593	2.2558	0.2154	0.2208	4.7070	4.9230	0.47
ethanol + *o*-xylene	1.5399	1.7534	0.4023	0.2923	3.3763	3.0622	0.47
methyl acetate + *o*-xylene	0.2807	1.1083	1.7715	0.1538	4.4732	−1.4616	0.47
ethyl acetate + *o*-xylene	0.2781	0.2979	0.9247	0.8000	−1.5765	3.2014	0.47

Table 9. Estimation Deviation Values

system	prediction method	Δy	RMSD/%	ΔT/K
methanol + *o*-xylene	Van Laar	0.013	2.31	0.82
	Wilson	0.011	2.14	0.25
	NRTL	0.010	2.04	0.60
	UNIFAC	0.018	2.74	0.89
ethanol + *o*-xylene	Van Laar	0.0023	0.87	0.43
	Wilson	0.0026	0.93	0.32
	NRTL	0.0020	0.82	0.35
	UNIFAC	0.0032	1.03	0.35
methyl acetate + *o*-xylene	Van Laar	0.015	2.27	1.24
	Wilson	0.016	2.28	1.23
	NRTL	0.015	2.25	1.21
	UNIFAC	0.0031	1.01	2.29
ethyl acetate + *o*-xylene	Van Laar	0.019	2.85	0.56
	Wilson	0.019	2.85	0.56
	NRTL	0.024	3.88	1.17
	UNIFAC	0.010	2.05	1.51

composition MAD(y_i) has to be less than 0.01 to be consistent. See the results in Table 7.

The objective function that was found that gave the better results for the regressions was

$$Q = \sum(\gamma_{\text{measd}} - \gamma_{\text{calcd}})^2 \qquad (2)$$

The Wilson equation, which did not consider the influence of the temperature on the parameter, was employed. The results of the regression are showed in Table 8. The results of the deviation parameters are presented in Table 9.

From the VLE results of the binary systems, we predicted the multicomponent equilibrium, obtaining the additional binary parameters by regressing data in the literature. These parameters are reported in Table 10. Isobaric VLE measurements were made on the following mixtures: methanol + methyl acetate + *o*-xylene, ethanol + ethyl acetate + *o*-xylene, and methanol + ethanol + methyl acetate + ethyl acetate + *o*-xylene. The results are listed in Tables 11−13.

After the experimental work, the same data generation process that was followed with the binary systems was

Table 10. Wilson, Van Laar, and NRTL Parameters Regressed from the Literature

		Van Laar		Wilson		NRTL		
system	ref	A	B	Λ_{12}	Λ_{21}	Δg_{12}/(kJ/mol)	Δg_{21}/(kJ/mol)	α_{12}
methanol + ethanol	*1*	−0.1846	0.2273	2.5073	0.1470	5.1504	−2.8590	0.3
methanol + methyl acetate	*11*	0.8736	1.0272	0.6977	0.4733	3.8543	−0.9756	0.1
methanol + ethyl acetate	*14*	0.9472	0.9680	0.5868	0.5630	1.5324	1.5535	0.47
ethanol + methyl acetate	*13*	0.3024	0.4130	0.7987	0.8737	1.6802	−0.4768	0.4
ethanol + ethyl acetate	*11*	0.7349	0.8213	0.7253	0.5755	2.9386	−0.5422	0.1
methyl acetate + ethyl acetate	*10*	0.0845	0.9680	1.0242	0.8916	0.2510	0.0002	0.47

Table 11. Experimental VLE Data for the System Methanol (1) + Methyl Acetate (2) + *o*-Xylene (3) at a Constant Pressure (101.3 kPa): Liquid Mole Fraction (x), Vapor Mole Fraction (y), Temperature (T), Vapor Coefficient Fugacity (ϕ_i), Activity Coefficient (γ_i)

x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3	T/K
0.7825	0.0993	0.7728	0.1993	1.0279	1.6048	3.8692	0.9563	0.9635	0.9820	335.55
0.6899	0.2114	0.6376	0.3438	1.0698	1.4222	3.4552	0.9541	0.9617	0.9736	332.85
0.7096	0.1867	0.6641	0.3155	1.0621	1.4533	3.5351	0.9545	0.9620	0.9753	333.35
0.6503	0.2533	0.6030	0.3816	1.1039	1.3480	3.0292	0.9536	0.9611	0.9710	332.15
0.5966	0.3122	0.5559	0.4309	1.1552	1.2778	2.8434	0.9531	0.9605	0.9676	331.15
0.5378	0.3738	0.5197	0.4700	1.2374	1.1958	2.3893	0.9527	0.9599	0.9644	330.35
0.4973	0.4208	0.4745	0.5167	1.2419	1.1838	2.2149	0.9524	0.9595	0.9621	329.95
0.4340	0.4821	0.4436	0.5489	1.3584	1.1164	1.8809	0.9525	0.9591	0.9591	329.45
0.0294	0.2600	0.3076	0.6049	5.6584	1.0637	0.9254	0.9761	0.9675	0.9505	353.45
0.4365	0.0760	0.8296	0.1234	1.6825	1.1311	1.3204	0.9597	0.9645	0.9837	339.75
0.5390	0.0512	0.8635	0.0878	1.4235	1.1978	1.6351	0.9594	0.9647	0.9856	339.65

Table 12. Experimental VLE Data for the System Ethanol (1) + Ethyl Acetate (2) + *o*-Xylene (3) at a Constant Pressure (101.3 kPa): Liquid Mole Fraction (x), Vapor Mole Fraction (y), Temperature (T), Vapor Coefficient Fugacity (ϕ_i), Activity Coefficient (γ_i)

x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3	T/K
0.2933	0.0286	0.8492	0.0402	2.3498	1.1304	1.1248	0.9717	0.9552	0.9662	358.55
0.2365	0.0577	0.8028	0.0795	2.6466	1.0712	1.1008	0.9728	0.9562	0.9643	359.65
0.1843	0.0881	0.7413	0.1363	2.8732	1.1202	1.0124	0.9742	0.9575	0.9620	362.05
0.1284	0.1390	0.6230	0.2344	3.1958	1.1419	1.0723	0.9764	0.9596	0.9583	364.35
0.1035	0.2444	0.4682	0.3988	3.0028	1.1133	1.1266	0.9767	0.9610	0.9536	364.15
0.2052	0.1846	0.6514	0.2424	2.5234	1.0392	1.1639	0.9732	0.9579	0.9592	359.15
0.3075	0.1084	0.7600	0.1449	2.1066	1.1205	1.1754	0.9715	0.9559	0.9637	357.25
0.3801	0.0610	0.8198	0.0789	1.8936	1.1100	1.3534	0.9707	0.9549	0.9662	356.45
0.4952	0.0499	0.8442	0.0653	1.5594	1.1620	1.5529	0.9698	0.9543	0.9675	355.35
0.4350	0.1066	0.7799	0.1367	1.6595	1.1509	1.4328	0.9700	0.9550	0.9653	355.05
0.2894	0.2121	0.6565	0.2592	2.0390	1.0712	1.2839	0.9711	0.9568	0.9600	355.85
0.2109	0.2727	0.5702	0.3445	2.3230	1.0677	1.1938	0.9722	0.9582	0.9564	357.05

Table 13. Experimental VLE Data for the System Methanol (1) + Ethanol (2) + Methyl Acetate (3) + Ethyl Acetate (4) + *o*-Xylene (5) at a Constant Pressure (101 kPa): Liquid Mole Fraction (x), Vapor Mole Fraction (y), Temperature (T), Vapor Coefficient Fugacity (ϕ_i), Activity Coefficient (γ_i)

x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	γ_1	γ_2	γ_3	γ_4	γ_5	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	T/K
0.5619	0.2300	0.0712	0.0861	0.6023	0.1303	0.1550	0.0964	1.0092	0.9394	1.5995	1.6186	4.5916	0.9588	0.9567	0.9645	0.9564	0.9793	338.15
0.3731	0.2058	0.0379	0.0714	0.6353	0.1743	0.0752	0.0671	1.3377	1.1493	1.2485	1.1471	1.8306	0.9629	0.9609	0.9647	0.9563	0.9793	342.95
0.0360	0.0453	0.0486	0.0341	0.4709	0.2472	0.1357	0.0529	6.2931	4.3026	1.1572	1.2053	0.7451	0.9775	0.9725	0.9683	0.9600	0.9648	356.85
0.0259	0.0458	0.1441	0.1473	0.2864	0.2080	0.4086	0.0192	6.1983	4.2190	1.3333	0.1160	0.9534	0.9782	0.9710	0.9690	0.9608	0.9528	352.55
0.4035	0.1700	0.0382	0.0694	0.6701	0.1438	0.0716	0.0635	1.2941	1.1377	1.1707	1.1091	1.8860	0.9623	0.9603	0.9648	0.9564	0.9803	343.15
0.0264	0.2706	0.1146	0.1117	0.1070	0.4721	0.2450	0.1133	2.4521	1.7701	1.0738	0.9694	1.1310	0.9730	0.9681	0.9656	0.9569	0.9604	350.25
0.3408	0.2455	0.0318	0.0996	0.5772	0.2137	0.0634	0.0974	1.2582	1.1100	1.1979	1.1340	1.9015	0.9637	0.9614	0.9648	0.9562	0.9775	344.45
0.0642	0.2008	0.2607	0.0864	0.1783	0.2695	0.4405	0.0691	2.1227	1.7578	1.0325	0.9469	1.2257	0.9688	0.9629	0.9642	0.9571	0.9562	343.85
0.2966	0.3060	0.0277	0.1224	0.5042	0.2681	0.0573	0.1265	1.2500	1.1048	1.2286	1.1865	1.9405	0.9646	0.9621	0.9649	0.9560	0.9753	344.75
0.0913	0.1674	0.3475	0.0713	0.2326	0.2001	0.4906	0.0449	2.2185	1.8084	0.9633	0.8429	1.2739	0.9657	0.9593	0.9630	0.9566	0.9539	340.35
0.0705	0.2931	0.2604	0.1211	0.1432	0.2965	0.4327	0.0958	1.6603	1.4271	1.0743	0.9972	1.4977	0.9673	0.9616	0.9637	0.9563	0.9561	342.05

Table 14. Estimation Deviation Values for the Multicomponent Mixtures

system	estimation model	Δy	RMSD/%	ΔT/K
methanol + methyl acetate + *o*-Xylene	Van Laar	0.0227	2.62	2.4
	Wilson	0.0053	1.26	0.5
	NRTL	0.0095	1.68	0.4
	UNIFAC	0.0084	1.59	0.4
ethanol + ethyl acetate + *o*-xylene	Van Laar	0.0241	2.58	2.1
	Wilson	0.0094	1.61	1.6
	NRTL	0.0114	1.78	1.0
	UNIFAC	0.0117	1.80	1.3
methanol + ethanol + methyl acetate + ethyl acetate + *o*-xylene	Van Laar	0.0223	1.93	4.4
	Wilson	0.0206	1.85	1.7
	NRTL	0.0235	1.97	2.3
	UNIFAC	0.0199	1.82	1.7

carried out. Consequently, it was possible to evaluate the deviation parameters shown in Table 14. This deviation is obtaining by calculating the activity coeficient only with parameters from binary data regression.

Conclusions

The Wilson equation correlates the results for binary systems better than the UNIFAC (*6*) method. This fact is highly remarkable for those systems containing compounds with a very different boiling point (methanol + *o*-xylene, ethanol + *o*-xylene).

For the ternary mixtures the best estimation method is the Wilson equation. The root mean square deviation values of 0.91% and 0.55% are of the same level or better than those found by Davies et al. (*5*) for mixtures containing alcohols and esters (~2%).

For the five-compound mixtures, the Wilson equation provides the same accuracy as the UNIFAC method. The Wilson calculations are much easier than UNIFAC. An RMSD value of 3.3% is good for a five-compound system, especially if we take into account the results found by Suzuky et al. (*17*) for quaternary mixtures of alcohols and esters, for which they found an RMSD value of 4.2% for the vapor phase composition and concluded the agreement was adequate.

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