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Isothermal Vapor−Liquid Equilibria in the Two Binary and the Ternary Systems Composed of *tert*-Amyl Methyl Ether, *tert*-Butanol, and Isooctane

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ABSTRACT: Vapor−liquid equilibrium (VLE) data in the two binary methyl 2-methyl-2-butyl ether (*tert*-amyl methyl ether, TAME) + 2-methyl-2-propanol (*tert*-butanol) and TAME + 2,2,4-trimethylpentane (isooctane) systems and in the ternary TAME + *tert*-butanol + isooctane system are reported. The data were measured isothermally at (318.13, 328.20, and 338.28) K covering the pressure range from (15 to 51) kPa. The binary VLE data were correlated using the Wilson and nonrandom two-liquid (NRTL) equations by means of a new algorithm; resulting parameters were then used for the calculation of phase behavior in the ternary system and for subsequent comparison with experimental data.

INTRODUCTION

New results of a continuing project dealing with phase equilibria in mixtures belonging to distinct families of organic compounds are reported in this paper. Vapor−liquid equilibria are determined for two binary and one ternary systems containing an ether, alcohol, and hydrocarbon. Within the series of papers, the systems of components having a common alkyl group (isopropyl or *tert*-butyl), namely, 2-propanol + diisopropyl ether + 2,2,4-trimethylpentane,[1] *tert*-butanol + 2,2,4-trimethylpentane + 1-tert-butoxy-2-propanol,[2] *tert*-butyl methyl ether + *tert*-butanol + 2,2,4-trimethylpentane,[3] 2-propanol + diisopropyl ether + 1-methoxy-*tert*-butyl methyl ether,[4] 2-propanol + diisopropyl ether + 4-methyl-2-pentanone,[5] 2-methylpentane + 3-methyl-2-butanone + 3-methyl-2-butanol,[6] 2-propanol + 3-methyl-2-butanone + 2,2,4-trimethylpentane,[7] and *tert*-butyl methyl ether + 3,3-dimethyl-2-butanone + 2,2-dimethyl-1-propanol,[8] have already been investigated. Compounds used in this paper contain the −OH, −O−, and *tert*-butyl groups, namely, *tert*-amyl methyl ether (TAME), 2-methyl-2-propanol (*tert*-butanol), and 2,2,4-trimethylpentane (isooctane). The new data were measured at the three constant temperature levels, particularly at (318.13, 328.20, and 338.28) K, to be consistent with the previous papers.

EXPERIMENTAL SECTION

Apparatus and Procedure. Experimental vapor−liquid equilibrium (VLE) data were measured in an all-glass circulation still chargeable with 150 mL of liquid phase; essentially, it was the Dvorák−Boublík type which is quoted in our previous experimental papers (e.g., ref 6). The pressure was measured indirectly via the boiling point of water in an ebulliometer connected in parallel to the still; the uncertainty was ± 0.1 % of the measured value. The equilibrium temperature was determined with the digital thermometer F250 (ASL, UK) calibrated against a Pt-resistance thermometer traceable to the National Bureau of Standards (NBS, Washington, DC, USA) certificate (1962); however, the basic resistance was regularly rechecked by the triple point of water, and the absolute uncertainty of temperature measurement (on ITS-90 scale) was estimated as ± 0.02 K. Samples withdrawn for GC analysis (even though in small grounded flasks) were kept in a desiccator filled with silica gel because of their hygroscopicity. Liquid-phase and vapor-phase compositions in all systems were determined using a gas chromatograph HP6850 (Hewlett-Packard) with thermal conductivity detection. The estimated uncertainty of the composition measurement was better than ± 0.001 mol fraction. Density was measured with a vibrating tube densimeter DMA 58 (A. Paar, Austria); the refractive index was determined using the precise Abbe type refractometer (Bellingham & Stanley, UK).

Materials. TAME (Fluka AG, Buchs, Switzerland), purum grade, declared purity ≥ 97 %, was dried with metallic Na and then rectified in presence of Na, and 40 % of middle fraction was collected and stabilized with trace of pyrogallol. Purity determined by GC was 99.64 %. The density was $d_4^{298.15} = 0.76585$ g·cm^{-3} and refractive index $n_D^{293.15} = 1.38614$; literature values are $d_4^{298.15} = 0.7656$ g·cm^{-3} and $n_D^{293.15} = 1.3859$.[9]

tert-Butanol (Fluka, Buchs, Switzerland), puriss p.a. grade, material of declared purity of ≥ 99.7 %, was fractionated on 30-plate packed column and used without further purification. The product was kept over molecular sieve 4A. Purity determined by GC was 99.59 %, and the density $d_4^{298.15} = 0.78044$ g·cm^{-3}; literature value is $d_4^{298.15} = 0.7812$ g·cm^{-3}.[9] The temperature of 298.15 K is slightly below the melting temperature; however, we succeeded to measure the density of the subcooled liquid.

Isooctane (Fluka AG, Buchs, Switzerland), puriss p.a. grade (> 99 %) was used as received and stored over molecular sieve 4A to

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Table 1. VLE Experimental Data and Calculated (NRTL) Activity Coefficients in Binary Systems

x_1	y_1	P kPa	γ_1	γ_2	ΔG^E J·mol^{-1}
TAME (1) + *tert*-Butanol (2)					
T = 318.13 K					
0.0000	0.0000	17.95	1.866	1.000	0.0
0.1459	0.2653	21.34	1.648	1.010	219.1
0.1977	0.3304	22.23	1.581	1.019	281.9
0.2475	0.3871	23.02	1.517	1.031	337.6
0.3132	0.4495	23.86	1.441	1.053	398.0
0.3817	0.5060	24.56	1.368	1.083	447.1
0.4566	0.5595	25.22	1.294	1.128	484.3
0.4966	0.5855	25.52	1.257	1.158	496.0
0.5665	0.6288	25.87	1.199	1.223	501.8
0.6213	0.6629	26.09	1.156	1.289	492.5
0.6893	0.7044	26.16	1.111	1.392	463.0
0.7664	0.7527	26.19	1.067	1.551	403.0
0.8562	0.8214	25.90	1.028	1.821	292.4
0.9458	0.9161	25.07	1.005	2.242	131.6
0.9816	0.9685	24.48	1.001	2.478	51.0
1.0000	1.0000	23.96	1.000	2.638	0.0
T = 328.20 K					
0.0000	0.0000	30.35	1.846	1.000	0.0
0.1524	0.2461	34.66	1.628	1.011	225.6
0.1998	0.3058	35.68	1.566	1.019	285.1
0.2559	0.3610	36.74	1.499	1.032	345.2
0.3223	0.4222	37.74	1.424	1.054	406.1
0.3893	0.4761	38.52	1.354	1.083	453.8
0.4655	0.5312	39.28	1.280	1.130	490.8
0.5050	0.5577	39.52	1.245	1.159	501.3
0.5727	0.6022	39.78	1.189	1.223	505.6
0.6285	0.6387	39.95	1.147	1.291	494.4
0.6961	0.6829	39.94	1.103	1.396	461.5
0.7710	0.7354	39.60	1.061	1.554	397.7
0.8548	0.8042	38.95	1.026	1.800	291.3
0.9481	0.9142	37.30	1.004	2.217	122.6
0.9812	0.9670	36.22	1.001	2.426	46.3
1.0000	1.0000	35.45	1.000	2.562	0.0
T = 338.28 K					
0.0000	0.0000	48.93	1.826	1.000	0.0
0.1586	0.2269	54.33	1.608	1.011	233.2
0.2089	0.2833	55.53	1.546	1.020	294.3
0.2642	0.3397	56.70	1.480	1.033	355.0
0.3300	0.3984	57.78	1.407	1.055	414.9
0.3970	0.4501	58.61	1.339	1.085	461.6
0.4735	0.5062	59.29	1.267	1.132	497.1
0.5126	0.5330	59.43	1.233	1.162	506.6
0.5788	0.5781	59.52	1.179	1.225	508.8
0.6350	0.6168	59.47	1.138	1.294	495.3
0.7018	0.6639	59.10	1.095	1.400	459.0
0.8574	0.7957	56.82	1.023	1.801	280.4
0.9481	0.9105	53.85	1.003	2.190	114.5
0.9821	0.9648	52.11	1.000	2.379	41.3
1.0000	1.0000	51.05	1.000	2.491	0.0

Table 1. Continued

x_1	y_1	P kPa	γ_1	γ_2	ΔG^E J·mol^{-1}
TAME (1) + Isooctane (2)					
T = 318.13 K					
0.0000	0.0000	15.85	1.159	1.000	0.0
0.0213	0.0354	16.13	1.147	1.000	8.3
0.0570	0.0905	16.48	1.131	1.001	19.9
0.1314	0.1983	17.31	1.102	1.003	41.5
0.2018	0.2897	18.02	1.081	1.007	57.1
0.2918	0.3942	18.87	1.062	1.013	71.2
0.4823	0.5840	20.43	1.038	1.028	85.0
0.5622	0.6542	21.02	1.032	1.034	85.9
0.6328	0.7121	21.64	1.028	1.041	84.5
0.6934	0.7603	22.11	1.025	1.047	81.8
0.7633	0.8178	22.69	1.021	1.056	76.6
0.8162	0.8590	23.00	1.019	1.066	71.3
0.8864	0.9124	23.49	1.014	1.092	60.5
0.9129	0.9329	23.66	1.012	1.114	54.4
1.0000	1.0000	23.96	1.000	1.912	0.0
T = 328.20 K					
0.0000	0.0000	23.68	1.157	1.000	0.0
0.0214	0.0352	24.05	1.146	1.000	8.2
0.0573	0.0906	24.58	1.130	1.001	20.3
0.1337	0.1971	25.76	1.102	1.003	42.5
0.2032	0.2896	26.79	1.082	1.007	58.7
0.2937	0.3938	28.05	1.063	1.013	73.6
0.4922	0.5911	30.49	1.039	1.028	89.0
0.5635	0.6539	31.27	1.033	1.034	89.9
0.6356	0.7151	32.22	1.029	1.041	88.7
0.6946	0.7610	32.81	1.026	1.047	86.2
0.7639	0.8179	33.58	1.022	1.057	81.1
0.8168	0.8577	34.13	1.019	1.067	75.5
0.8561	0.8889	34.51	1.017	1.080	69.8
0.8862	0.9122	34.78	1.015	1.096	64.1
0.9126	0.9327	35.11	1.012	1.121	57.2
0.9345	0.9495	35.27	1.010	1.157	50.1
1.0000	1.0000	35.45	1.000	1.877	0.0
T = 338.28 K					
0.0000	0.0000	34.40	1.155	1.000	0.0
0.0215	0.0344	34.90	1.144	1.000	8.2
0.0577	0.0908	35.70	1.129	1.001	20.9
0.1335	0.1976	37.31	1.102	1.003	43.5
0.2049	0.2868	38.73	1.083	1.007	60.0
0.2956	0.3922	40.46	1.065	1.012	75.8
0.4977	0.5936	44.11	1.040	1.028	92.9
0.5675	0.6545	45.22	1.034	1.034	94.0
0.6376	0.7152	46.45	1.030	1.041	93.1
0.6964	0.7627	47.39	1.026	1.047	90.6
0.7646	0.8177	48.51	1.023	1.057	85.4
0.8165	0.8580	49.39	1.020	1.069	79.5
0.8560	0.8886	49.78	1.017	1.083	73.7
0.8870	0.9128	50.24	1.015	1.101	67.2
0.8871	0.9130	50.35	1.015	1.102	66.9
0.9127	0.9327	50.63	1.012	1.128	60.1
0.9341	0.9492	50.78	1.010	1.163	52.7
1.0000	1.0000	51.05	1.000	1.844	0.0

Table 2. Parameters of the Wilson Equation Valid between (318 and 338) K and Evaluated Standard Deviations

$(\lambda_{12} - \lambda_{11})$ J·mol^{-1}	$(\lambda_{21} - \lambda_{22})$ J·mol^{-1}	V_1 mL·mol^{-1}	V_2 mL·mol^{-1}	no. of points	Δx	Δy	ΔP kPa	ΔT K
			TAME (1) + *tert*-Butanol (2)					
−891.556	3470.32	136.8−140.3	97.6−100.3	41	0.0028	0.0029	0.069	0.06
			TAME (1) + Isooctane (2)					
−721.074	1732.96	136.8−140.3	170.2−174.5	44	0.0036	0.0021	0.056	0.05
			tert-Butanol (1) + Isooctane (2)					
5804.479	−8.9111	97.6−100.3	170.2−174.5	37	0.0068	0.0093	0.090	0.09

Table 3. Parameters of the NRTL Equation Valid between (318 and 338) K and Evaluated Standard Deviations

$(g_{12} - g_{22})$ J·mol^{-1}	$(g_{21} - g_{11})$ J·mol^{-1}	α_{ij}	no. of points	Δx	Δy	ΔP kPa	ΔT K
			TAME (1) + *tert*-Butanol (2)				
2263.88	326.387	0.6266	41	0.0026	0.0031	0.061	0.06
			TAME (1) + isooctane (2)				
1548.47	328.101	5.4712	44	0.0019	0.0022	0.020	0.02
			tert-Butanol (1) + isooctane (2)				
1634.92	1167.13	−1.7903	37	0.0040	0.0054	0.022	0.02

remove water. Purity determined by GC was 99.97 %. The density was $d_4^{298.15}$ = 0.68780 g·cm^{-3} and $n_D^{293.15}$ = 1.38894; literature value are $d_4^{298.15}$ = 0.68784 g·cm^{-3} and $n_D^{293.15}$ = 1.38898.[9]

RESULTS

The direct experimental (x, y, P) values together with the activity coefficients, γ_1, γ_2, and ΔG^E (evaluated from the nonrandom two-liquid, NRTL, correlation), for the binary TAME + *tert*-butanol and the TAME + isooctane systems are given in Table 1. The data for the third system (i.e., *tert*-butanol + isooctane) were published in ref 3 (erratum: there are misprints in ref 3 where denotations of the isotherm at 339.28 K should be replaced by the value of 338.28 K); however, they were recorrelated here with use of the same procedure described below. The data were correlated using the Wilson and NRTL equations in the forms as follows (expressions for ln γ_2 can be easily obtained after interchanging indices 1 and 2):

(1) The Wilson equation

$$\ln \gamma_1 = 1 - \ln(x_1 + x_2 A_{12}) - \frac{x_1}{x_1 + x_2 A_{12}} - \frac{x_2 A_{21}}{x_2 + x_1 A_{21}} \quad (1)$$

where $A_{12} = (V_1/V_2)\exp[-(\lambda_{12} - \lambda_{11})/RT]$, $A_{21} = (V_2/V_1)\exp[-(\lambda_{21} - \lambda_{22})/RT]$, and V_i is liquid molar volume of pure component i. The concentration dependence of the activity coefficient contains two adjustable parameters, $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$.

(2) The NRTL equation

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_1 + x_2 G_{12})^2} \right] \quad (2)$$

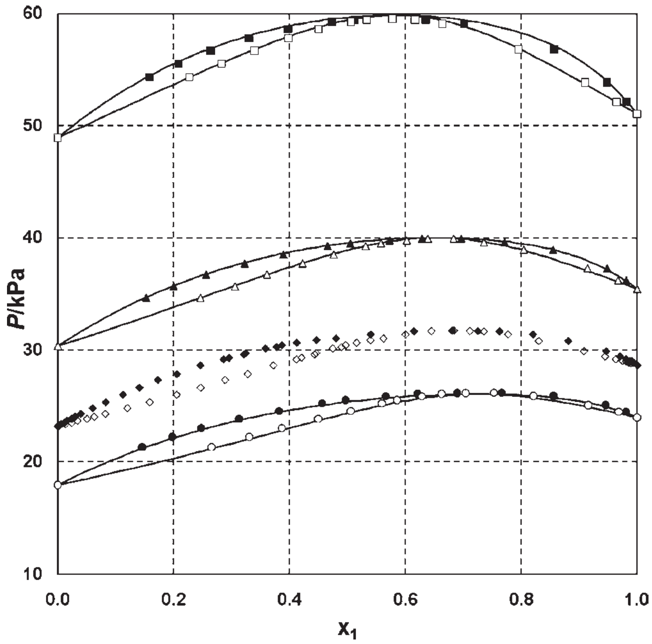

Figure 1. Isothermal VLE in TAME (1) + *tert*-butanol (2). Open points, vapor phase; solid points, liquid phase; solid lines, NRTL correlation; ○, ●, 318.13 K; △, ▲, 328.20 K; □, ■, 338.28 K; ◇, ◆, 322.70 K.[15]

where $G_{12} = \exp[-\alpha_{12}\tau_{12}]$, $G_{21} = \exp[-\alpha_{21}\tau_{21}]$, $\tau_{12} = (g_{12} - g_{22})/RT$, and $\tau_{21} = (g_{21} - g_{11})/RT$. The equation contains three adjustable parameters, namely, $(g_{12} - g_{22})$, $(g_{21} - g_{11})$, and $\alpha_{12} = \alpha_{21}$.

Vapor-phase imperfection and variation of the Gibbs energy of the pure liquid components with pressure were accounted for in terms of the second virial coefficients and the molar volumes under saturation pressure estimated, respectively, by the method of Hayden and O'Connell[10] and of Hougen and Watson.[11] The adjustable parameters for the binary systems were evaluated with use of the program based on the maximum likelihood procedure[12] which was recently modified by Pavlíček and Wichterle.[13] This new robust algorithm makes it possible to correlate VLE isotherms or isobars together resulting in one set of universal parameters valid in the experimental pressure and temperature range. It can be applied to any correlation equation with temperature-independent parameters such as, for example, the Wilson or NRTL equations.

Within the correlation procedure,[12] the experimental vapor pressures of the pure components were used as a rule instead of a

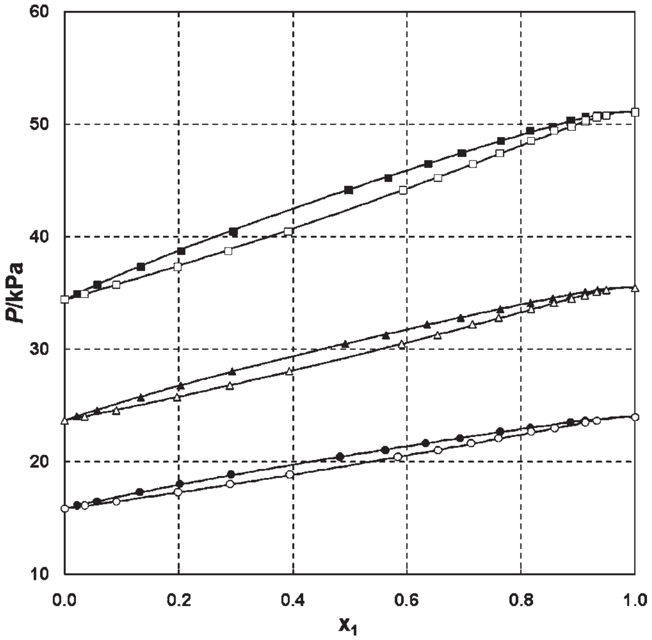

Figure 2. Isothermal VLE in TAME (1) + isooctane (2). Open points, vapor phase; solid points, liquid phase; solid lines, NRTL correlation; ○, ●, 318.13 K; △, ▲, 328.20 K; □, ■, 338.28 K.

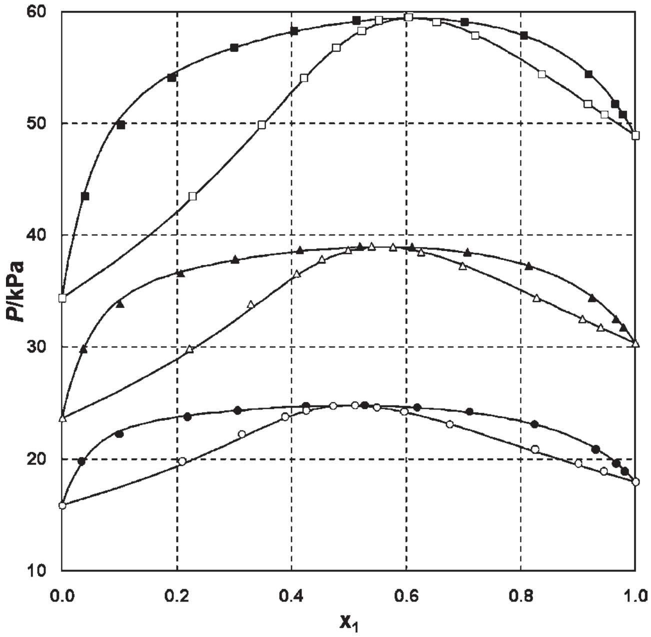

Figure 3. Isothermal VLE in *tert*-butanol (1) + isooctane (2). Open points, vapor phase; solid points, liquid phase; solid lines, NRTL correlation, this work; ○, ●, 318.13 K; △, ▲, 328.20 K; □, ■, 338.28 K. Experimental data are taken from ref 3.

Table 4. Experimental Azeotropic Data

	T_{az}		P_{az}
system	K	x_{az}	kPa
TAME (1) + *tert*-butanol (2)	318.13	0.7386	26.20
	328.20	0.6549	39.98
	338.28	0.5770	59.52
TAME (1) + isooctane (2)	318.13	0.5062	24.84
	328.20	0.5517	39.00
	338.28	0.5963	59.49
tert-butanol (1) + isooctane (2)	nonazeotrope		

vapor pressure equation for calculation, which is a procedure generally recognized and recommended for isothermal data. It can be realized by the adjustment of the parameter A in the Antoine equation to the experimental value of vapor pressure at the particular isotherm. Naturally, this is not applicable to the new procedure,[13] and to keep the experimental pressures unchanged for pure components, the measured vapor pressures of pure component were used for a functional correlation of Antoine parameters for this purpose only. Such a correlation was carried out for all three components.

The standard deviations necessary for computation input were estimated as 0.0030 for mole fraction of phases, 0.03 K for temperature, and 0.1 % of the pressure value for pressure. Parameters for the Wilson and NRTL equations are presented in Tables 2 and 3, respectively, together with resulting standard deviations for all variables (x, y, P, T). The approximate values of molar volumes of pure components required for the Wilson equation are given in Table 2; however, they have always been evaluated at given temperature. The experimental data are illustrated in Figures 1 to 3 as x, y, P plots. Solid lines represent the smoothed values based on optimized NRTL equation parameters. Two binary systems exhibit azeotropic behavior. Experimental data for azeotropes were obtained by plotting x versus $x-y$ and x versus P; numerically smoothed curves in these simple plots provide values which are summarized in Table 4.

The experimental data for the ternary system were determined at the same isothermal conditions as for the binary systems and are presented in Table 5. Overall compositions of mixtures in the equilibrium still were formed approximately by subsequent addition of TAME to five (regularly distributed) initial *tert*-butanol + isooctane mixtures. In this way, the region of ternary compositions was regularly covered; altogether 127 experimental points were measured. Azeotropic behavior in the ternary system was observed. However, it is impossible to evaluate azeotropes from experimental data using some interpolation procedure; it could be only calculated from a correlation equation.

The parameters obtained from the correlation of the three binary VLE data were exploited for the prediction of ternary data using both the Wilson and the NRTL equations expressing the activity coefficient, γ_i (i = 1, 2, 3), as

$$\ln \gamma_i = -\ln\left(\sum_{s=1}^{3} x_s A_{is}\right) + 1 - \sum_{r=1}^{3} \frac{x_r A_{ri}}{\sum_{s=1}^{3} x_s A_{rs}} \tag{3}$$

where $A_{ij} = (V_j/V_i)\exp[-(\lambda_{ij} - \lambda_{ii})/RT]$ and

$$\ln \gamma_i = \frac{\sum_{r=1}^{3} \tau_{ri} G_{ri} x_r}{\sum_{s=1}^{3} G_{si} x_s} + \sum_{r=1}^{3} \frac{x_r G_{ir}}{\sum_{s=1}^{3} G_{sr} x_s}\left(\tau_{ir} - \frac{\sum_{t=1}^{3} \tau_{tr} G_{tr} x_t}{\sum_{s=1}^{3} G_{sr} x_s}\right) \tag{4}$$

Table 5. VLE Experimental Data in the Ternary TAME (1) + *tert*-Butanol (2) + Isooctane (3) System

x_1	x_2	y_1	y_2	P/kPa	x_1	x_2	y_1	y_2	P/kPa
T = 318.13 K									
0.0381	0.6486	0.0461	0.5550	24.78	0.0388	0.1561	0.0412	0.3511	23.43
0.2190	0.5243	0.2475	0.4609	25.42	0.0299	0.1152	0.0327	0.3229	22.63
0.2921	0.4725	0.3197	0.4260	25.61	0.4930	0.4188	0.5337	0.3694	25.71
0.3848	0.4063	0.4045	0.3854	25.72	0.4497	0.3728	0.4652	0.3603	25.78
0.4643	0.3523	0.4752	0.3488	25.88	0.4028	0.3235	0.4072	0.3432	25.57
0.3323	0.5477	0.3929	0.4543	25.07	0.3599	0.2793	0.3576	0.3368	24.98
0.3058	0.4945	0.3413	0.4324	25.67	0.3181	0.2299	0.3150	0.3227	24.52
0.2804	0.4424	0.2997	0.4173	25.74	0.2767	0.1634	0.2786	0.2974	23.89
0.2482	0.3755	0.2565	0.3953	25.46	0.2281	0.1092	0.2385	0.2665	22.92
0.2134	0.3153	0.2164	0.3800	25.10	0.8455	0.0975	0.8135	0.1409	24.98
0.1821	0.2091	0.1847	0.3486	24.23	0.7814	0.0875	0.7586	0.1389	24.70
0.1376	0.1253	0.1460	0.3002	23.30	0.6963	0.0751	0.6887	0.1363	24.04
0.0912	0.0514	0.1087	0.2331	21.20	0.5982	0.0627	0.6090	0.1337	23.37
0.1287	0.8413	0.2230	0.7049	21.97	0.5120	0.0499	0.5412	0.1274	22.65
0.1266	0.7778	0.1882	0.6325	23.30	0.4171	0.0396	0.4615	0.1226	21.70
0.1187	0.6964	0.1553	0.5682	24.40	0.3118	0.0279	0.3688	0.1115	20.64
0.1080	0.6113	0.1288	0.5222	24.97	0.2254	0.0190	0.2898	0.1032	19.87
0.0971	0.5221	0.1079	0.4876	24.85	0.6385	0.3174	0.6498	0.3069	25.67
0.0856	0.4468	0.0917	0.4587	25.29	0.5956	0.2901	0.5938	0.3006	25.84
0.0723	0.3523	0.0751	0.4316	25.13	0.5334	0.2518	0.5232	0.2920	25.42
0.0605	0.2878	0.0626	0.4038	24.75	0.4681	0.2123	0.4570	0.2839	25.33
T = 328.20 K									
0.0388	0.6420	0.0432	0.5839	39.03	0.0391	0.1459	0.0399	0.3655	35.96
0.2244	0.5126	0.2360	0.4877	39.56	0.0295	0.0974	0.0320	0.3413	34.52
0.2961	0.4645	0.3034	0.4565	39.70	0.4995	0.4108	0.5097	0.3987	39.50
0.3913	0.3962	0.3893	0.4097	39.70	0.4593	0.3566	0.4479	0.3849	39.31
0.4724	0.3405	0.4591	0.3718	39.66	0.4068	0.3178	0.3926	0.3683	39.22
0.3394	0.5381	0.3735	0.4828	39.56	0.3654	0.2588	0.3458	0.3593	38.40
0.3124	0.4834	0.3258	0.4606	39.85	0.3212	0.2210	0.3059	0.3411	37.70
0.2847	0.4327	0.2853	0.4458	39.80	0.2803	0.1657	0.2721	0.3151	36.66
0.2523	0.3686	0.2458	0.4250	39.40	0.2295	0.1075	0.2343	0.2796	34.73
0.2161	0.2991	0.2094	0.3920	38.52	0.8476	0.0954	0.8067	0.1485	37.47
0.1861	0.2108	0.1819	0.3513	37.49	0.7829	0.0853	0.7529	0.1457	36.96
0.1386	0.1129	0.1429	0.3266	35.55	0.6976	0.0739	0.6840	0.1427	35.78
0.0941	0.0563	0.1079	0.2376	31.96	0.5986	0.0601	0.6063	0.1366	34.91
0.1335	0.8348	0.2057	0.7282	35.59	0.5131	0.0496	0.5385	0.1317	33.88
0.1304	0.7699	0.1751	0.6588	37.30	0.4101	0.0360	0.4594	0.1253	32.60
0.1214	0.6887	0.1452	0.5976	38.66	0.3133	0.0285	0.3672	0.1142	30.89
0.1107	0.5996	0.1212	0.5518	39.31	0.2143	0.0147	0.2883	0.1010	29.46
0.0987	0.5143	0.1019	0.5155	39.22	0.6486	0.3066	0.6294	0.3289	39.36
0.0870	0.4413	0.0870	0.4873	39.39	0.6008	0.2837	0.5762	0.3216	39.46
0.0735	0.3400	0.0716	0.4578	38.86	0.5375	0.2464	0.5090	0.3120	38.89
0.0615	0.2800	0.0599	0.4283	38.21	0.4714	0.2072	0.4460	0.3014	38.42
T = 338.28 K									
0.0396	0.6347	0.0407	0.6103	59.80	0.0395	0.1422	0.0390	0.3774	52.85
0.2283	0.5042	0.2237	0.5175	59.75	0.0305	0.1103	0.0314	0.3523	50.99
0.3000	0.4566	0.2896	0.4823	59.78	0.5044	0.4039	0.4889	0.4243	58.93
0.3963	0.3883	0.3740	0.4347	59.33	0.4647	0.3481	0.4331	0.4057	58.42
0.4754	0.3370	0.4440	0.3940	59.03	0.4101	0.3127	0.3786	0.3933	58.35
0.3471	0.5266	0.3555	0.5092	59.77	0.3675	0.2584	0.3366	0.3767	57.24
0.3168	0.4759	0.3099	0.4869	60.02	0.3235	0.2134	0.2986	0.3582	55.83
0.2874	0.4270	0.2728	0.4711	59.87	0.2819	0.1603	0.2668	0.3285	53.92
0.2556	0.3596	0.2365	0.4478	58.96	0.2271	0.0941	0.2317	0.2830	50.97
0.2183	0.2935	0.2006	0.4235	57.81	0.8489	0.0939	0.8005	0.1553	54.52
0.1884	0.2179	0.1758	0.3824	55.58	0.7842	0.0844	0.7483	0.1515	53.70
0.1407	0.1170	0.1410	0.3330	52.03	0.6985	0.0729	0.6802	0.1479	52.42
0.0919	0.0523	0.1072	0.2511	46.87	0.5992	0.0593	0.6038	0.1403	50.79
0.1378	0.8290	0.1922	0.7460	55.60	0.5143	0.0496	0.5364	0.1347	49.24
0.1327	0.7654	0.1632	0.6834	57.66	0.4181	0.0389	0.4578	0.1267	47.32
0.1241	0.6803	0.1363	0.6240	59.24	0.3114	0.0283	0.3660	0.1161	45.43
0.1125	0.5931	0.1145	0.5779	59.88	0.2285	0.0201	0.2869	0.1012	42.89
0.1003	0.5057	0.0967	0.5405	59.82	0.6503	0.3046	0.6116	0.3484	58.69
0.0882	0.4342	0.0827	0.5131	59.39	0.6052	0.2783	0.5613	0.3403	58.68
0.0743	0.3484	0.0686	0.4796	58.44	0.5412	0.2413	0.4969	0.3297	57.59
0.0623	0.2778	0.0576	0.4522	57.16	0.4742	0.2042	0.4366	0.3179	56.61
0.0459	0.1783	0.0441	0.4070	54.83					

where $G_{ij} = \exp[-\alpha_{ij}\tau_{ij}]$, $\tau_{ij} = (g_{ij} - g_{jj})/RT$, $\tau_{ii} = 0$, $\alpha_{ij} = \alpha_{ji}$, and $G_{ii} = 1$, respectively. The necessary molar volumes were estimated with the use of the method of Hougen and Watson.[11]

The computation was carried out by means of the method published in ref 12 enabling the calculation of the "closest" solution by minimization of the standard deviations of all involved variables (temperature, pressure, and vapor and liquid compositions). Resulting absolute deviations are averaged and summarized in Table 6.

DISCUSSION AND CONCLUSIONS

In the bibliography covering the period from 1888 to 2008,[14] the only published VLE data concerning the presented systems were found for TAME + *tert*-butanol.[15] Those data were determined at 322.73 K from total pressure measurements, and this isotherm is plotted together with our data in Figure 1. The qualitative agreement is obviously good.

Nevertheless, the reliability of both the data and the correlation procedure is verified by the fact that the resulting standard deviations are approximately proportional to the magnitudes of input uncertainties. Generally, the inspection of deviation distribution from smoothed data confirms that there are only expectable, random, and nonsystematic errors. A thermodynamic test of consistency has been carried out with the use of the procedure proposed by Van Ness.[16] According to this test, for the presented data, the "consistency indices" are equal largely to 3 (ranging from 2 to 5 for all nine isothermal data sets) within the ten-degree scale: 1, excellent; 10, nonacceptable. The evaluated deviations from correlations together with experimental data shown in Figures 1 to 3 (where solid lines represent the NRTL correlation) prove that measurement of the experimental data and numerical procedures were carried out in a proper way.

The experimental ternary data were compared with the data predicted using binary parameters. The absolute average deviations presented in Table 6 indicate surprisingly that the Wilson correlation yields approximately 40 % better results than the NRTL equation in prediction of ternary data. In any case, both results are very good. It should be pointed out that results need

Table 6. Prediction of VLE in the Ternary TAME (1) + *tert*-Butanol (2) + Isooctane (3) System at Temperatures from (318 to 338) K Using the Binary Parameters of the Wilson and NRTL Equations[a]

T/K	Δx_1	Δx_2	Δx_3	Δx (all)	Δy_1	Δy_2	Δy_3	Δy (all)	ΔP/kPa	ΔT/K
					Wilson Equation					
318.13	0.0016	0.0036	0.0041	0.0031	0.0028	0.0051	0.0041	0.0040	0.009	0.16
328.20	0.0015	0.0046	0.0048	0.0036	0.0025	0.0055	0.0042	0.0040	0.011	0.12
338.28	0.0020	0.0070	0.0056	0.0049	0.0024	0.0055	0.0036	0.0038	0.022	0.15
					NRTL Equation					
318.13	0.0032	0.0096	0.0087	0.0072	0.0045	0.0089	0.0054	0.0063	0.014	0.24
328.20	0.0034	0.0097	0.0085	0.0072	0.0054	0.0101	0.0061	0.0072	0.023	0.25
338.28	0.0033	0.0105	0.0087	0.0075	0.0065	0.0118	0.0061	0.0081	0.038	0.25

[a] Δ is an absolute average deviation of calculated and experimental data (127 experimental points).

not necessarily reflect the quality of data. The experimental data are certainly better, because the imperfections of models also contribute to a certain worsening of calculated values.

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