J. Chem. Eng. Data **2006,** *51,* 2083−2087 **2083**

Vapor−Liquid Equilibrium for Binary Systems of Diacetyl with Methanol and Acetone

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Diacetyl is a byproduct of sugar manufacture and has many food-related uses. Vapor−liquid equilibrium (VLE) data are required in order to design a purification process. A vapor and liquid recirculating still was used to measure data for acetone + diacetyl at 303.15 K, 313.15 K, 323.15 K, and 40 kPa. Data were also measured for methanol + diacetyl at 313.15 K, 323.15 K, 333.15 K, and 40 kPa. The $\gamma-\Phi$ approach to VLE was used to reduce the data to excess Gibbs energy model parameters. The vapor-phase nonideality was accounted for using the truncated (two-term) Virial equation of state. The Wilson, NRTL, and UNIQUAC excess Gibbs energy models were used to account for liquid-phase departure from ideal behavior. The data are shown to be reliable by both point and direct tests for thermodynamic consistency.

Introduction

Diacetyl (2,3-butanedione) is a byproduct of sugar manufacture. Its main use is as a flavor component in beer, wine, and dairy products. Extractive distillation is being considered as a separation technique for purification; therefore, vapor−liquid equilibrium (VLE) data are required for the systems considered. Both isothermal and isobaric VLE measurements for binary mixtures of acetone + diacetyl and methanol + diacetyl were undertaken in this study. A compact and well-tested VLE still[1−3] was used to make the measurements. VLE data were measured for the system acetone + diacetyl at 303.15 K, 313.15 K, 323.15 K, and 40 kPa. Measurements for methanol + diacetyl were made at 313.15 K, 323.15 K, 333.15 K, and 40 kPa. These systems have not been previously measured.

Experimental Section

Chemicals. The specifications and physical properties of the chemicals used in this study are shown in Tables 1 and 2. Gas chromatographic (GC) analysis of all these chemicals showed no significant impurities, and no further purification was attempted. Analysis using a GC fitted with a TCD detector showed no significant water content. Measured vapor pressures compared well with those available in literature as shown by the average absolute deviation of the experimental temperature from the literature values (ΔT), which was found to be at most 0.06 K. Table 1 also shows the weight fraction of the chemicals given by the supplier as well as the fractional GC peak area of each chemical. The critical properties (T_c, P_c, and V_c) of the chemicals are listed in Table 2, as are the R and Q UNIQUAC parameters.

Vapor Pressure Measurements. The vapor pressures were measured in a limited pressure range for acetone, methanol, and diacetyl. The data are presented in Table 3. The data were fitted to the Antoine equation (eq 1), and the regressed parameters are presented in Table 2:

$$\ln P^{\text{sat}} = A - \frac{B}{T + C} \tag{1}$$

Table 1. Purity of the Chemicals Used in This Study

chemical	supplier	100 w	100 $A/(A_{\text{total}})$	ΔT/K
acetone	Rochelle Chemicals	min 99.5	99.968	0.04[a]
diacetyl	Illovo (Pty) Ltd	min 98.82	99.763	0.06[b]
methanol	Rochelle Chemicals	min 99.5	99.875	0.05[a]

[a] Literature data from ref 9. [b] Literature data ref 2.

Table 2. Physical Properties of the Chemicals Used in This Study

	acetone	methanol	diacetyl
P_c/kPa	4700[a]	8090[a]	4590[b]
T_c/K	508.1[a]	512.6[a]	536.1[b]
V_c/cm^3·mol^{-1}	209[a]	118[a]	271.5[b]
R	2.57[c]	1.43[c]	3.34[c]
Q	2.34[c]	1.43[c]	2.98[c]
A (eq 1)	14.209	16.594	14.968
B (eq 1)	2705.12	3644.3	3224.09
C (eq 1)	−50.166	−33.39	−50.939

[a] Literature data from ref 9. [b] Calculated using the Ambrose method.[9] [c] Ref 1.

Table 3. Vapor Pressure Data for Acetone, Methanol, and Diacetyl

acetone			methanol			diacetyl		
P/kPa	T/K	T^a/K	P/kPa	T/K	T^a/K	P/kPa	T/K	T^b/K
30.23	297.66	297.71	30.33	309.79	309.81	33.91	329.85	330.07
35.22	301.25	301.3	35.42	313.06	313.12	39.00	333.64	333.63
45.21	307.33	307.39	40.41	316.02	316.02	43.59	336.76	336.72
50.40	310.08	310.14	45.11	318.43	318.40	48.97	339.99	340.12
55.29	312.52	312.52	50.30	320.90	320.85	53.85	342.80	342.78
60.29	314.76	314.79	55.39	323.14	323.05	58.83	345.41	345.30
65.08	316.80	316.82	59.99	324.96	324.89	63.83	347.62	347.64
70.07	318.77	318.82	65.28	326.95	326.88	68.81	349.90	349.82
						73.79	351.89	351.87

[a] Literature data from ref 9. [b] Literature data from ref 2.

Equipment. A vapor and liquid recirculating still as described by Raal and Muhlbauer[1] and Joseph et al.[2,3] was used to make the VLE measurements. The still features a central vacuum-jacketed Cottrell pump and a packed equilibrium chamber. The disengaged vapor and liquid phases are sampled through septa. VLE measurements for mixtures of various compositions can therefore be made without interruption of the boiling. To improve mixing and to promote smooth boiling, the boiling chamber and condensate receiver were magnetically stirred.

The pressure was maintained as sub-atmospheric using a KNF vacuum pump-controller unit (type NC800). The pressure

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10.1021/je060174h CCC: $33.50

Table 4. Vapor−Liquid Equilibria for Acetone (1) + Diacetyl (2) System at (303.15 and 313.15) K

T/K = 303.15			T/K = 313.15		
P/kPa	y_1	x_1	P/kPa	y_1	x_1
8.62	0.000	0.000	14.33	0.000	0.000
9.36	0.074	0.018	15.25	0.071	0.018
9.86	0.129	0.034	16.05	0.128	0.035
10.56	0.196	0.057	16.95	0.181	0.058
12.15	0.358	0.118	19.24	0.341	0.116
15.35	0.544	0.231	23.54	0.536	0.231
18.75	0.704	0.350	28.83	0.671	0.356
23.44	0.818	0.518	35.42	0.804	0.513
30.43	0.930	0.756	45.41	0.923	0.749
33.82	0.967	0.868	50.60	0.963	0.867
35.22	0.979	0.913	52.50	0.976	0.913
36.42	0.990	0.956	53.60	0.985	0.943
36.82	0.992	0.965	54.50	0.991	0.966
38.04	1.000	1.000	56.64	1.000	1.000

Table 5. Vapor−Liquid Equilibria for Acetone (1) + Diacetyl (2) System at 323.15 K and 40 kPa

T/K = 323.15			P/kPa = 40		
P/kPa	y_1	x_1	T/K	y_1	x_1
22.77	0.000	0.000	336.67	0.000	0.000
23.74	0.061	0.018	334.11	0.152	0.052
24.84	0.114	0.035	331.61	0.267	0.101
26.23	0.175	0.061	327.32	0.446	0.189
29.73	0.318	0.121	323.20	0.595	0.297
35.82	0.506	0.228	319.22	0.715	0.413
43.01	0.670	0.357	315.71	0.809	0.530
52.20	0.795	0.519	312.54	0.879	0.649
66.08	0.914	0.754	309.73	0.930	0.768
73.17	0.959	0.868	307.76	0.962	0.857
75.77	0.974	0.912	306.18	0.983	0.931
77.76	0.985	0.943	305.70	0.989	0.956
79.06	0.991	0.967	305.37	0.994	0.973
81.65	1.000	1.000	305.16	0.996	0.983
			304.37	1.000	1.000

Table 6. Vapor−Liquid Equilibria for Methanol (1) + Diacetyl (2) System at (313.15 and 323.15) K

T/K = 313.15			T/K = 323.15		
P/kPa	y_1	x_1	P/kPa	y_1	x_1
14.33	0.000	0.000	22.77	0.000	0.000
17.15	0.205	0.072	26.93	0.209	0.070
18.95	0.323	0.125	30.13	0.325	0.119
21.54	0.447	0.198	34.02	0.445	0.191
24.04	0.577	0.301	38.32	0.550	0.282
26.33	0.653	0.395	42.11	0.644	0.400
28.83	0.724	0.532	46.01	0.722	0.533
31.03	0.791	0.666	49.40	0.787	0.669
32.63	0.858	0.781	51.90	0.855	0.782
34.32	0.940	0.918	54.10	0.939	0.914
34.72	0.968	0.957	54.40	0.964	0.956
35.02	0.980	0.973	54.99	0.986	0.984
35.32	0.989	0.985	55.69	1.000	1.000
35.52	1.000	1.000			

Table 7. Vapor−Liquid Equilibria for Methanol (1) + Diacetyl (2) System at 333.15 K and 40 kPa

T/K = 333.15			P/kPa = 40		
P/kPa	y_1	x_1	T/K	y_1	x_1
34.76	0.000	0.000	336.67	0.000	0.000
41.51	0.219	0.070	332.19	0.221	0.071
45.91	0.326	0.116	328.60	0.372	0.138
52.30	0.448	0.191	326.53	0.461	0.193
58.99	0.552	0.282	322.89	0.599	0.320
64.88	0.644	0.399	321.14	0.674	0.423
70.67	0.724	0.533	319.54	0.742	0.540
75.77	0.791	0.668	318.43	0.800	0.651
79.56	0.858	0.784	317.08	0.886	0.816
82.26	0.940	0.916	316.51	0.935	0.901
82.96	0.968	0.959	316.25	0.960	0.940
83.45	0.980	0.973	316.07	0.975	0.964
83.75	0.989	0.986	316.04	0.982	0.975
84.72	1.000	1.000	315.99	0.987	0.982
			315.73	1.000	1.000

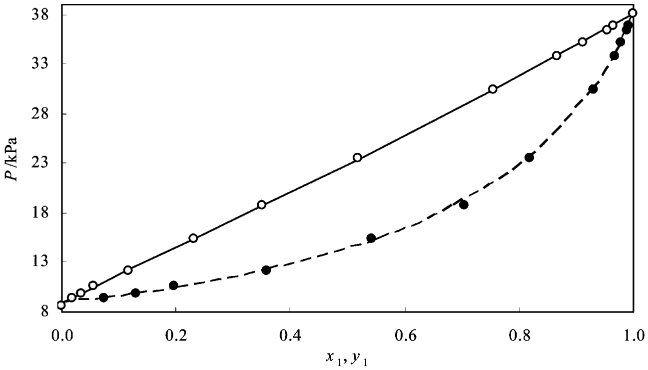

Figure 1. Measured VLE for acetone (1) + diacetyl (2) at 303.15 K compared to the UNIQUAC model fit: ●, y_1 this work; ○, x_1 this work; - -, y_1 UNIQUAC; —, x_1 UNIQUAC.

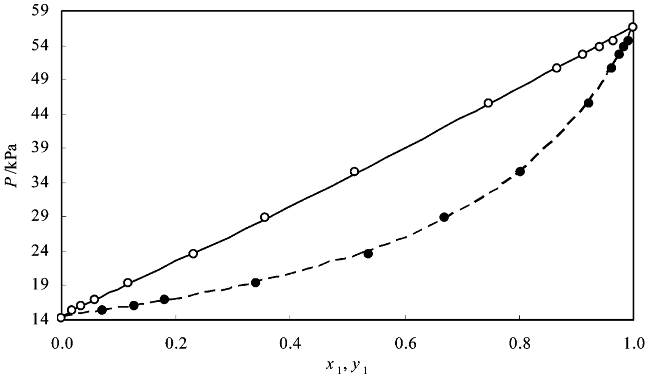

Figure 2. Measured VLE for acetone (1) + diacetyl (2) at 313.15 K compared to the NRTL model fit: ●, y_1 this work; ○, x_1 this work; - -, y_1 NRTL; —, x_1 NRTL.

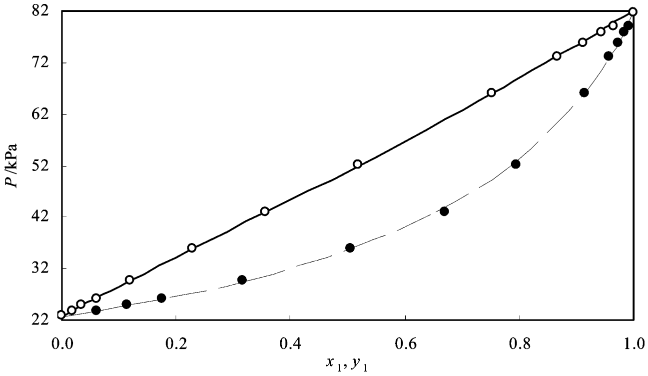

Figure 3. Measured VLE for acetone (1) + diacetyl (2) at 323.15 K compared to the UNIQUAC model fit: ●, y_1 this work; ○, x_1 this work; - -, y_1 UNIQUAC; —, x_1 UNIQUAC.

display was calibrated with a mercury manometer and a VAISALA electronic barometer (model PTB100A) with NIST traceable calibration. Isobaric measurements were made by allowing the vacuum pump-controller unit to control about a set-point (to approximately ± 0.05 kPa).

The equilibrium temperature was measured in the packed chamber by means of a Pt-100 sensor located near the bottom of the packed section. The uncertainty of the temperature measurement is estimated to be within ± 0.02 K. Isothermal operation was achieved manually (i.e., the pressure set-point was adjusted manually until each mixture reached the desired temperature). Temperature control was estimated to be better than ± 0.1 K.

The compositions of the samples were measured by GC analysis. A Shimadzu GC-17A gas chromatograph, fitted with a flame ionization detector, was used. The GC column used was a capillary type supplied by J&W Scientific (GS-Q) and

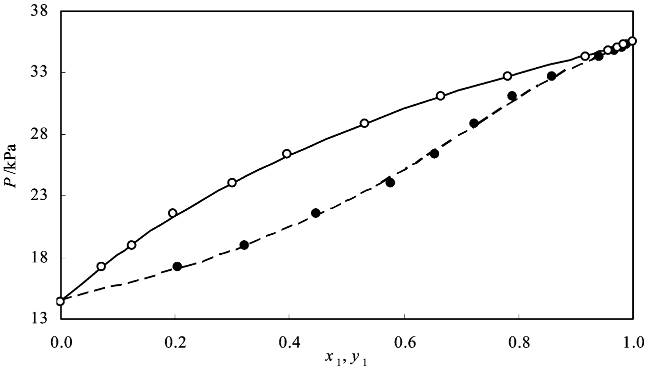

Figure 4. Measured VLE for methanol (1) + diacetyl (2) at 313.15 K compared to the UNIQUAC model fit: ●, y_1 this work; ○, x_1 this work; - -, y_1 UNIQUAC; —, x_1 UNIQUAC.

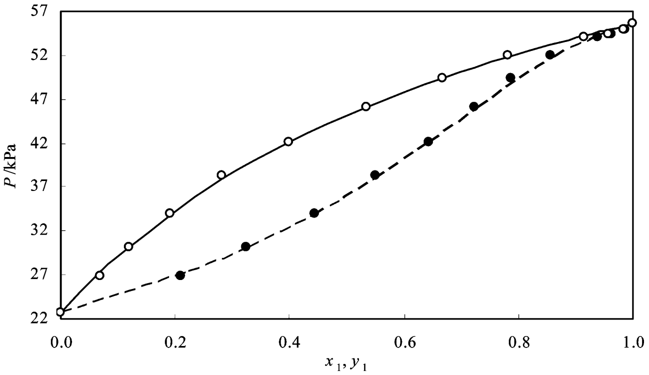

Figure 5. Measured VLE for methanol (1) + diacetyl (2) at 323.15 K compared to the NRTL model fit: ●, y_1 this work; ○, x_1 this work; - -, y_1 NRTL; —, x_1 NRTL.

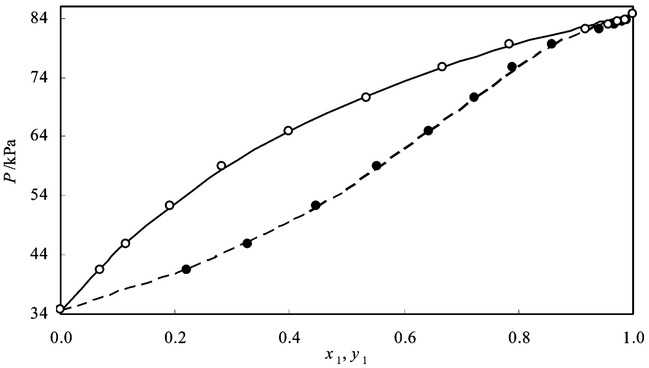

Figure 6. Measured VLE for methanol (1) + diacetyl (2) at 333.15 K compared to the UNIQUAC model fit: ●, y_1 this work; ○, x_1 this work; - -, y_1 UNIQUAC; —, x_1 UNIQUAC.

was operated at an oven temperature of 308.15 K. The uncertainty of the composition measurement is estimated to be ± 0.001 mole fraction.

Data Reduction

The VLE measurements were reduced using the $\gamma-\Phi$ approach:

$$y_i \Phi_i P = x_i \gamma_i P_i^{\text{sat}} \tag{2}$$

y_i is the vapor-phase mole fraction of species i, x_i is the liquid-phase mole fraction of species i, γ_i is the activity coefficient of species i, and P_i^{sat} is the saturation pressure of species i. The vapor correction term (Φ_i) was calculated from the truncated (two-term) Virial equation of state. The virial coefficients were calculated using the method of Hayden and O'Connell.[4]

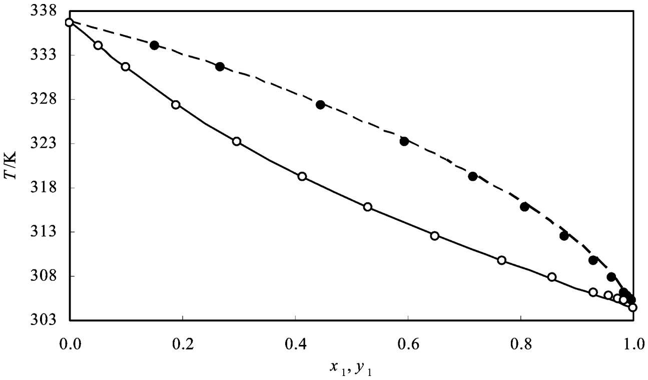

Figure 7. Measured VLE for acetone (1) + diacetyl (2) at 40 kPa compared to the Wilson model prediction: ●, y_1 this work; ○, x_1 this work; - -, y_1 Wilson; —, x_1 Wilson.

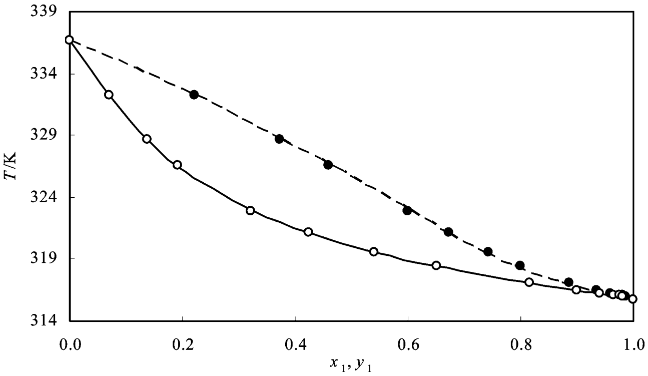

Figure 8. Measured VLE for methanol (1) + diacetyl (2) at 40 kPa compared to the NRTL model prediction: ●, y_1 this work; ○, x_1 this work; - -, y_1 NRTL; —, x_1 NRTL.

Parameters for three excess Gibbs energy models were computed viz. the Wilson, NRTL, and UNIQUAC equations. The data reduction procedure requires minimization of an objective function (OF). For the isothermal data the following objective function was used:

$$\text{OF} = \sum \text{abs}(\delta P) \tag{3}$$

The residual (δ) is the difference between the measured value of a property and the value calculated using the model (e.g., $\delta P = P_{\text{measured}} - P_{\text{calculated}}$). Only the pressure residual (δP) was used in the objective function (as suggested in ref 5). The objective function used to reduce the isobaric measurements consisted of the temperature residual only (δT):

$$\text{OF} = \sum \text{abs}(\delta T) \tag{4}$$

Thermodynamic Consistency Tests

The point test for thermodynamic consistency (Van Ness et al.[6]) requires the vapor composition residual (δy) to scatter evenly about the x-axis. Furthermore, the average absolute deviation (AAD) of the residual should be less than 0.01 mole fraction as suggested by Danner and Gess.[7] Van Ness[8] proposes the direct test (a plot of the residuals $\delta \ln(\gamma_1/\gamma_2)$ vs x_1) and suggests a scale ranging from 1 to 10 by which the reliability of the data can be measured (1 denotes data of the highest quality).

Results

The experimental data for the acetone + diacetyl system are listed in Tables 4 and 5, and data for the methanol + diacetyl

Table 8. Excess Gibbs Energy Model Parameters for the Acetone (1) + Diacetyl (2) Isothermal Data Sets

activity coeff model	T/K = 303.15	T/K = 313.15	T/K = 323.15
	UNIQUAC		
$(u_{12}-u_{11})$/J·mol^{-1}	−1051.989	−927.134	−1220.461
$(u_{12}-u_{22})$/J·mol^{-1}	1736.335	1535.946	2058.993
100 $(\delta P/P_{\text{measured}})^a$	0.61	0.55	0.36
$(\delta y)^a$	0.003	0.004	0.004
	Wilson		
$(\lambda_{12}-\lambda_{11})$/J·mol^{-1}	−90.483	−43.520	16.481
$(\lambda_{12}-\lambda_{22})$/J·mol^{-1}	90.827	46.103	−16.000
100 $(\delta P/P_{\text{measured}})^a$	0.86	0.72	0.72
$(\delta y)^a$	0.003	0.004	0.003
	NRTL		
$(g_{12}-g_{11})$/J·mol^{-1}	−2550.659	−2527.391	−2724.817
$(g_{12}-g_{22})$/J·mol^{-1}	3568.792	3476.265	3921.795
α	0.3	0.3	0.3
100 $(\delta P/P_{\text{measured}})^a$	0.73	0.52	0.54
$(\delta y)^a$	0.003	0.003	0.005

[a] Average absolute value.

Table 9. Excess Gibbs Energy Model Parameters for the Methanol (1) + Diacetyl (2) Isothermal Data Sets

activity coeff model	T/K = 313.15	T/K = 323.15	T/K = 333.15
	UNIQUAC		
$(u_{12}-u_{11})$/J·mol^{-1}	−1036.976	−1025.735	−1017.601
$(u_{12}-u_{22})$/J·mol^{-1}	3163.642	3382.082	3535.794
100 $(\delta P/P_{\text{measured}})^a$	0.57	0.73	0.61
$(\delta y)^a$	0.009	0.007	0.005
	Wilson		
$(\lambda_{12}-\lambda_{11})$/J·mol^{-1}	2748.535	2893.198	3054.824
$(\lambda_{12}-\lambda_{22})$/J·mol^{-1}	−1322.138	−1186.200	−1157.412
100 $(\delta P/P_{\text{measured}})^a$	0.59	0.74	0.73
$(\delta y)^a$	0.009	0.007	0.005
	NRTL		
$(g_{12}-g_{11})$/J·mol^{-1}	2780.543	2646.970	2878.722
$(g_{12}-g_{22})$/J·mol^{-1}	−1317.844	−938.333	−995.998
α	0.089	0.119	0.109
100 $(\delta P/P_{\text{measured}})^a$	0.58	0.73	0.71
$(\delta y)^a$	0.009	0.007	0.005

[a] Average absolute value.

Table 10. Excess Gibbs Energy Model Parameters for Isobaric Data Sets

	acetone (1) + diacetyl (2)	methanol (1) + diacetyl (2)
activity coeff model	P/kPa = 40	P/kPa = 40
	UNIQUAC	
$(u_{12}-u_{11})$/J·mol^{-1}	−1105.9	−1040.4
$(u_{12}-u_{22})$/J·mol^{-1}	1866.2	3569
100 $(\delta T/T_{\text{measured}})^a$	0.62	0.22
$(\delta y)^a$	0.002	0.004
	Wilson	
$(\lambda_{12}-\lambda_{11})$/J·mol^{-1}	2995.6	3120.6
$(\lambda_{12}-\lambda_{22})$/J·mol^{-1}	−2381.7	−1277
100 $(\delta T/T_{\text{measured}})^a$	0.64	0.24
$(\delta y)^a$	0.004	0.005
	NRTL	
$(g_{12}-g_{11})$/J·mol^{-1}	−7274.1	1395.8
$(g_{12}-g_{22})$/J·mol^{-1}	8554	388
α	0.057	0.3
100 $(\delta T/T_{\text{measured}})^a$	0.69	0.24
$(\delta y)^a$	0.007	0.006

[a] Average absolute value.

system are given in Tables 6 and 7. The data are also presented in Figures 1 to 8. The system acetone + diacetyl showed little deviation from Raoult's law. This is to be expected for mixtures of similar chemicals. The excess Gibbs energy model parameters regressed for the data are given in Tables 8 to 10.

Satisfactory modeling was obtained for both systems. The model parameters for the isothermal data are well-reproduced as functions of temperature by the quadratics or straight lines shown in Table 11 and as illustrated in Figure 9 for the methanol + diacetyl system. These temperature-dependent parameters permit accurate reproduction of the VLE data at arbitrary temperatures within the experimental range.

Table 11. Temperature Dependence of the UNIQUAC and NRTL Model Parameters

parameter^a	methanol (1) + diacetyl (2) for T = (313.15 to 333.15) K	acetone (1) + diacetyl (2) for T = (303.15 to 323.15) K
	$(u_{12}-u_{11})$/J·mol^{-1}	
a_1	0	−2.0909
a_2	0.9688	1301.1
a_3	−1339.8	203330
	$(u_{12}$-$u_{22})$/J·mol^{-1}	
a_1	0	3.6172
a_2	18.606	−2249.3
a_3	2652.1	351195
	$(g_{12}-g_{11})$/J·mol^{-1}	
a_1	1.8266	−1.1035
a_2	−1175.6	682.4
a_3	191808	−108010
	$(g_{12}-g_{22})$/J·mol^{-1}	
a_1	−2.1859	2.6903
a_2	1428.8	−1667.3
a_3	−234401	261766

[a] $(u_{12}-u_{ii})$/J·mol^{-1}, $(g_{12}-g_{ii})$/J·mol^{-1} = $a_1(T/\text{K})^2 + a_2(T/\text{K}) + a_3$.

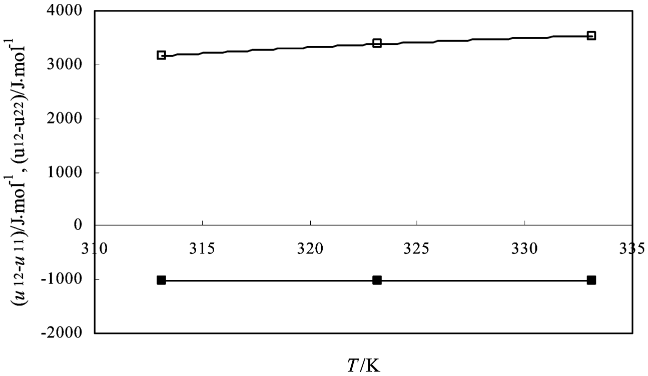

Figure 9. Temperature dependence of the UNIQUAC model parameters for the methanol (1) + diacetyl (2) system: ■, $(u_{12}-u_{11})$/J·mol^{-1}; □, $(u_{12}-u_{22})$/J·mol^{-1}.

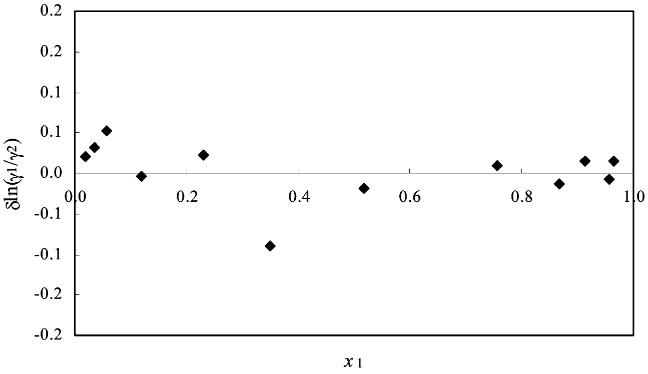

Figure 10. Direct test for thermodynamic consistency for acetone (1) + diacetyl (2) at 303.15 K.

The average absolute values of δy shown in Tables 8 to 10 were less than 0.01 mole fraction, which satisfies a consistency criterion suggested by Danner and Gess.[7] All the data were rated at worst "3" by the Van Ness direct test for thermodynamic consistency (the acetone + diacetyl isotherms were in fact given a rating of "2"). The results of the consistency tests are given in Table 12. The best fit models are shown in Figures 1 to 8, although it should be noted that the differences between the model fits were marginal and probably within the experimental

Table 12. Results of the Van Ness[8] Direct Test for Thermodynamic Consistency

system		index
acetone (1) + diacetyl (2)	T/K = 303.15	2
	T/K = 313.15	2
	T/K = 323.15	2
	P/kPa = 40	3
methanol (1) + diacetyl (2)	T/K = 313.15	3
	T/K = 323.15	3
	T/K = 333.15	3
	P/kPa = 40	3

uncertainty. An example of the Van Ness[8] consistency test is shown in Figure 10 for the acetone + diacetyl system at 303.15 K.

Conclusions

VLE data have been measured for the acetone + diacetyl system at 303.15 K, 313.15 K, 323.15 K, and 40 kPa and for the methanol + diacetyl system at 313.15 K, 323.15 K, 333.15 K, and 40 kPa. The data are new as these systems have not previously been measured. The data have been shown to be thermodynamically consistent. Satisfactory modeling was obtained for both systems using the UNIQUAC and NRTL equations for the liquid phase with temperature-dependent parameters.

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Received for review April 24, 2006. Accepted August 17, 2006. The authors thank the NRF Thuthuka Programme and Sasol R&D for financial support of this work.

JE060174H