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Vapor–Liquid Equilibrium for Binary Systems of 2,3-Pentanedione with Diacetyl and Acetone

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2,3-Pentanedione and diacetyl are byproducts of sugar manufacture and have many food related uses. Vapor−liquid equilibrium (VLE) data for the systems presented in this paper are required to determine thermodynamic model parameters which will be used to simulate the design of a purification process. A vapor and liquid recirculating still was used to measure data for diacetyl + 2,3-pentanedione at 333.15 K, 343.15 K, 353.15 K, and 40 kPa, as well as for acetone + 2,3-pentanedione at 323.15 K, 30 kPa, and 40 kPa. The $\gamma-\varphi$ correlation approach for VLE modeling was used to correlate the data with excess Gibbs energy models. The vapor phase nonideality was computed 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 thermodynamically consistent by both the Van Ness point and direct tests.

Introduction

2,3-Pentanedione (acetyl propionyl) and diacetyl (2,3-butanedione) are byproducts of sugar manufacture. Diacetyl's main use is as a flavor component in beer, wine, and dairy products. 2,3-Pentanedione also has many food related uses ranging from use as a flavor component to a starting material for antioxidants. It is a biodegradable solvent, a polymerization inhibitor, and a starting material for pharmaceutical intermediates. Distillation is being considered as a separation technique for purification of both diketones, and therefore vapor−liquid equilibrium (VLE) data are required for the systems presented. Both isothermal and isobaric VLE measurements of binary mixtures of 2,3-pentanedione + diacetyl and acetone + 2,3-pentanedione were undertaken in this study. A highly refined VLE still[1–3] was used to perform the measurements. VLE data were measured for the system diacetyl + 2,3-pentanedione at 333.15 K, 343.15 K, 353.15 K, and 40 kPa. Measurements for acetone + 2,3-pentanedione were undertaken at 323.15 K, 30 kPa, and 40 kPa. VLE measurements for diacetyl with methanol and acetone have previously been reported by our group.[4] The measurements for 2,3-pentanedione with diacetyl and acetone constitute new data to the open literature.

Experimental

Chemicals. The specifications and physical properties of the chemicals used in this study are shown in Tables 1 and 2. GC (gas chromatographic) analysis using a TCD detector showed no significant impurities for any of the chemicals used, and they were therefore not purified further. Table 1 also shows the minimum specified weight fraction of the chemicals as provided by the supplier, as well as the fractional GC peak area for each chemical. Measured vapor pressures compared well with those available in the 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. As the vapor pressure measurements for 2,3-pentanedione constitute new data, no value for ΔT is listed. 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. The vapor pressure data were fitted to eq 1 to determine the Antoine equation constants

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

Table 1. Purity of the Chemicals Used in this Study

chemical	supplier	100 w	$100A/(A_{\text{total}})$	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]
2,3-pentanedione	Illovo (Pty) Ltd.	min 98.52	99.722	–

[a] Literature data sourced from ref 10. [b] Literature data sourced from ref 2.

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

	acetone	2,3-pentanedione	diacetyl
P_c/kPa	4700[a]	4007[b]	4590[b]
T_c/K	508.1[a]	616.6[b]	536.1[b]
V_c/cm$^3\cdot$mol^{-1}	209[a]	315.38[b]	271.5[b]
R	2.57[c]	4.02[c]	3.34[c]
Q	2.34[c]	3.52[c]	2.98[c]
A (eq 1)	14.209	13.771	14.968
B (eq 1)	2705.12	2756.64	3224.09
C (eq 1)	−50.166	−82.096	−50.939

[a] Literature data sourced from ref 10. [b] Calculated using the Ambrose method.[10] [c] Ref 1.

There is the possibility of thermal degradation of the components as well as of keto–enol tautomerization for the binary systems studied, and therefore GC analysis of the samples before and after experimentation was undertaken. Results indicated that there were no thermal degradation or tautomerization effects.

Equipment. A vapor and liquid recirculating still as described by Raal and Muhlbauer[1] and Joseph et al.[2,3] was used to perform 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.

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Table 3. Vapor Pressure Data for 2,3-Pentanedione

acetone			diacetyl			2,3-pentanedione[a]	
P/kPa	T/K	T^b/K	P/kPa	T/K	T^c/K	P/kPa	T/K
30.23	297.67	297.71	19.06	314.30	314.99	15.37	331.84
35.22	301.25	301.30	24.04	320.55	320.89	20.36	338.38
45.21	307.33	307.39	29.03	325.62	325.93	25.35	343.73
50.40	310.08	310.14	33.91	329.85	330.07	30.35	348.13
55.29	312.52	312.52	39.00	333.64	333.63	35.34	352.15
60.29	314.76	314.79	43.59	336.76	336.72	40.33	355.74
65.08	316.80	316.82	48.97	339.99	340.12	45.32	358.85
70.07	318.77	318.82	53.85	342.80	342.78	50.21	361.89
			58.83	345.41	345.30	55.21	364.69
			63.83	347.62	347.64	60.20	367.09
			68.81	349.90	349.82	65.19	369.44
			737.93	351.89	351.87	70.18	371.61
						75.27	373.80

[a] Literature data not available. [b] Literature data from ref 10. [c] Literature data from ref 2.

Table 4. Vapor–Liquid Equilibria for Diacetyl (1) + 2,3-Pentanedione (2) at (333.15 and 343.15) K

T/K = 333.15			T/K = 343.15		
P/kPa	y_1	x_1	P/kPa	y_1	x_1
16.30	0.000	0.000	24.80	0.000	0.000
16.57	0.066	0.033	25.25	0.066	0.035
17.17	0.140	0.072	25.95	0.126	0.068
18.36	0.233	0.133	27.65	0.233	0.132
21.16	0.434	0.276	31.44	0.410	0.273
23.66	0.574	0.418	35.04	0.568	0.413
25.75	0.699	0.538	38.33	0.684	0.534
27.65	0.779	0.647	41.13	0.771	0.643
29.55	0.844	0.737	48.32	0.963	0.916
34.76	1.000	1.000	49.02	0.973	0.939
			51.20	1.000	1.000

Table 5. Vapor–Liquid Equilibria for Diacetyl (1) + 2,3-Pentanedione (2) at 353.15 K and 40 kPa

T/K = 353.15			P/kPa = 40		
P/kPa	y_1	x_1	T/K	y_1	x_1
36.60	0.000	0.000	355.52	0.000	0.000
37.13	0.067	0.034	353.97	0.100	0.054
38.53	0.128	0.071	352.18	0.223	0.130
40.63	0.231	0.132	349.41	0.407	0.264
45.62	0.401	0.276	343.94	0.695	0.548
50.91	0.570	0.418	342.06	0.783	0.652
55.80	0.691	0.546	339.21	0.897	0.828
59.30	0.778	0.648	338.27	0.933	0.885
69.18	0.963	0.916	337.22	0.984	0.970
70.48	0.974	0.940	336.78	1.000	1.000
73.20	1.000	1.000			

Table 6. Vapor–Liquid Equilibria for Acetone (1) + 2,3-Pentanedione (2)

T/K = 323.15			P/kPa = 30			P/kPa = 40		
P/kPa	y_1	x_1	T/K	y_1	x_1	T/K	y_1	x_1
10.30	0.000	0.000	347.94	0.000	0.000	355.52	0.000	0.000
11.48	0.108	0.016	344.58	0.028	0.139	353.19	0.017	0.084
13.97	0.322	0.053	342.26	0.048	0.222	351.42	0.034	0.152
22.76	0.614	0.179	338.16	0.089	0.387	348.83	0.057	0.251
31.44	0.768	0.3	335.76	0.123	0.468	340.30	0.153	0.523
44.92	0.88	0.496	324.05	0.281	0.727	331.64	0.275	0.718
57.10	0.944	0.665	315.56	0.425	0.857	325.15	0.396	0.842
77.37	0.993	0.945	309.47	0.577	0.931	316.75	0.576	0.926
80.07	0.997	0.976	297.53	1.000	1.000	308.82	0.825	0.980
81.90	1.000	1.000				306.95	0.899	0.989
						305.89	0.943	0.994
						304.37	1.000	1.000

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 receivers were stirred via magnetic coupling.

The pressure was maintained subatmospheric using a KNF vacuum pump-controller unit (type NC800). The pressure 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 (within approximately ± 0.05 kPa).

The equilibrium temperature was measured in the packed chamber by means of a Class 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 determined 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 which was supplied by J&W Scientific (GS-Q) and was operated at an oven temperature of 308.15 K. The uncertainty of the composition measurement is estimated to be ± 0.001 mol fraction.

Data Reduction

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

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

γ_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.[5] 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. For the isothermal data, the following objective function was used

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

The residual (δ) is the difference between the experimental value of a property and the value calculated using the model (e.g.,

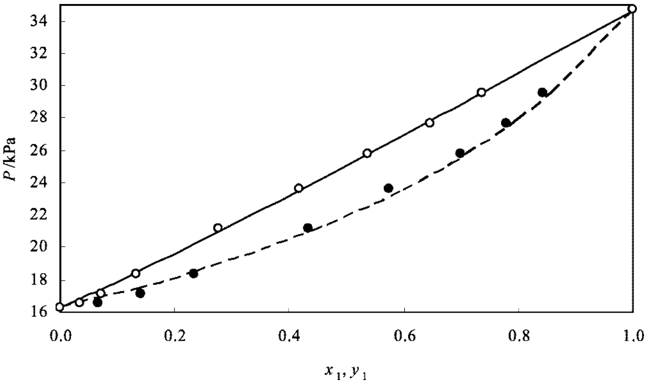

Figure 1. Measured VLE for diacetyl (1) + 2,3-pentanedione (2) at 333.15 K compared to the Wilson model fit: •, y_1 this work; ○, x_1 this work; — —, y_1 Wilson; ——, x_1 Wilson.

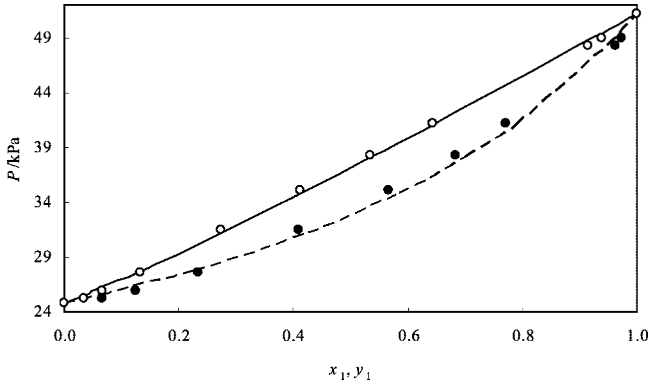

Figure 2. Measured VLE for diacetyl (1) + 2,3-pentanedione (2) at 343.15 K compared to the Wilson model fit: •, y_1 this work; ○, x_1 this work; — —, y_1 Wilson; ——, x_1 Wilson.

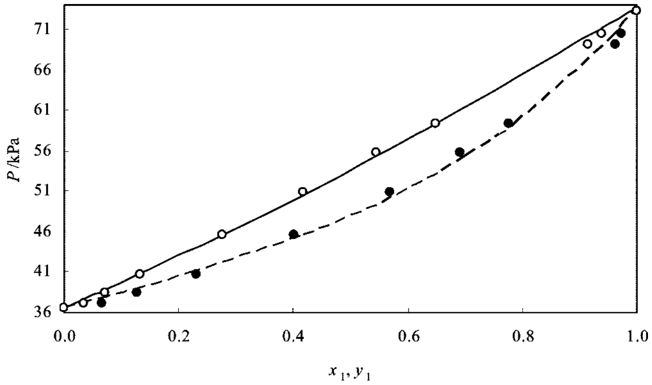

Figure 3. Measured VLE for diacetyl (1) + 2,3-pentanedione (2) at 353.15 K compared to the UNIQUAC model fit: •, y_1 this work; ○, x_1 this work; — —, y_1 UNIQUAC; ——, x_1 UNIQUAC.

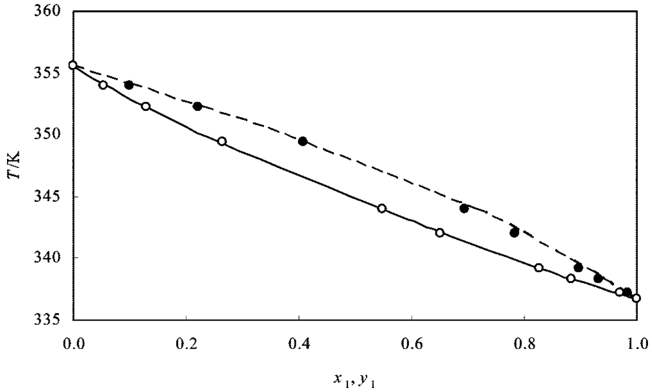

Figure 4. Measured VLE for diacetyl (1) + 2,3-pentanedione (2) at 40 kPa compared to the Wilson model fit: •, y_1 this work; ○, x_1 this work; — —, y_1 Wilson; ——, x_1 Wilson.

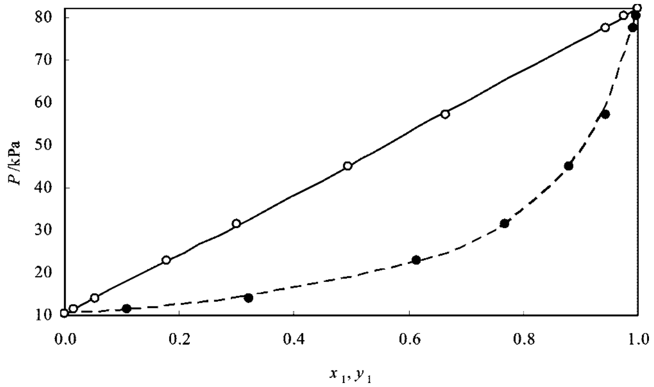

Figure 5. Measured VLE for acetone (1) + 2,3-pentanedione (2) at 323.15 K compared to the NRTL model fit: •, y_1 this work; ○, x_1 this work; — —, y_1 NRTL; ——, x_1 NRTL.

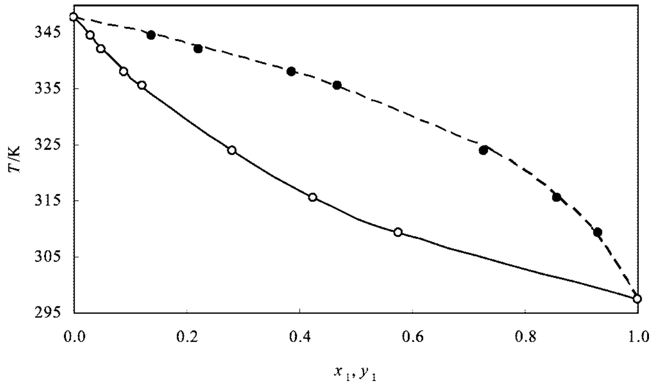

Figure 6. Measured VLE for acetone (1) + 2,3-pentanedione (2) at 30 kPa compared to the UNIQUAC model fit: •, y_1 this work; ○, x_1 this work; — —, y_1 UNIQUAC; ——, x_1 UNIQUAC.

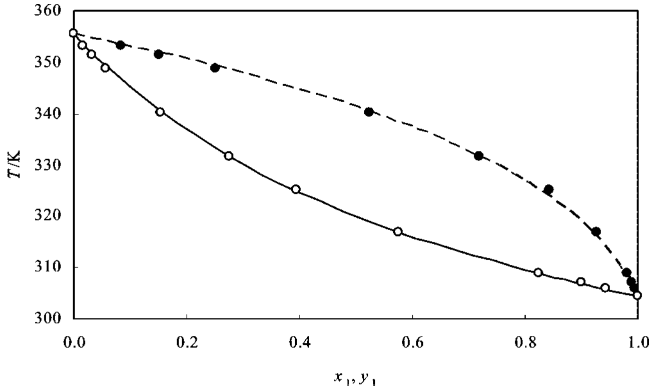

Figure 7. Measured VLE for acetone (1) + 2,3-pentanedione (2) at 40 kPa compared to the Wilson model prediction: •, y_1 this work; ○, x_1 this work; — —, y_1 Wilson; ——, x_1 Wilson.

$\delta P = P_{\text{exptl}} - P_{\text{calcd}}$). Only the pressure residual (δP) was used in the objective function (as suggested by Van Ness and Abbott[6]). 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.[7]) requires the vapor composition residual (δy) to scatter evenly about the x-axis. Furthermore, the average absolute deviation of the residual should be less than 0.01 mol fraction as suggested by Danner and Gess.[8] Van Ness[9] 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 vapor pressure measurements for 2,3-pentanedione constitute new data (Table 3). The Antoine parameters (eq 1) for 2,3-pentanedione are given in Table 2. The experimental data for the diacetyl + 2,3-pentanedione system are listed in Tables 4 and 5, and the data for the acetone + 2,3-pentanedione system are given in Table 6. The data are also presented graphically in Figures 1 to 7. Both systems showed little deviation from Raoult's law. This is to be expected for mixtures

Table 7. Excess Gibbs Energy Model Parameters for the Isothermal Data Sets

	diacetyl (1) + 2,3-pentanedione (2)			acetone (1) + 2,3-pentanedione (2)
parameter	T/K = 333.15	T/K = 343.15	T/K = 353.15	T/K = 323.15
		UNIQUAC		
$(u_{12} - u_{11})$/J·mol^{-1}	1484.872	767.862	886.137	448.875
$(u_{12} - u_{22})$/J·mol^{-1}	−1237.009	−767.923	−885.832	−448.400
$100(\delta P/P_{\mathrm{measured}})^a$	0.535	0.608	0.655	0.433
$(\delta y)^a$	0.008	0.008	0.008	0.006
		Wilson		
$(\lambda_{12} - \lambda_{11})$/J·mol^{-1}	801.205	988.544	−1504.140	3397.488
$(\lambda_{12} - \lambda_{22})$/J·mol^{-1}	−801.215	−978.958	1490.195	−2557.570
$100(\delta P/P_{\mathrm{measured}})^a$	0.524	0.586	0.658	0.498
$(\delta y)^a$	0.008	0.009	0.008	0.005
		NRTL		
$(g_{12} - g_{11})$/J·mol^{-1}	8505.421	5491.949	−8981.612	1955.294
$(g_{12} - g_{22})$/J·mol^{-1}	−7712.616	−5185.405	9987.226	−1954.880
α	0.041	0.053	0.042	0.008
$100(\delta P/P_{\mathrm{measured}})^a$	0.516	0.602	0.672	0.377
$(\delta y)^a$	0.009	0.009	0.008	0.006

[a] Average absolute value.

Table 8. Excess Gibbs Energy Model Parameters for the Isobaric Data Sets

	diacetyl (1) + 2,3-pentanedione (2)	acetone (1) + 2,3-pentanedione (2)	
parameter	P/kPa = 40	P/kPa = 30	P/kPa = 40
	UNIQUAC		
$(u_{12} - u_{11})$/J·mol^{-1}	−1091.2	637.78	−1957
$(u_{12} - u_{22})$/J·mol^{-1}	1972	−540.65	1587.2
$100(\delta P/P_{\mathrm{measured}})^a$	0.108	0.555	0.261
$(\delta y)^a$	0.005	0.005	0.005
	Wilson		
$(\lambda_{12} - \lambda_{11})$/J·mol^{-1}	2405.4	2388.4	3789.6
$(\lambda_{12} - \lambda_{22})$/J·mol^{-1}	−1621.8	−2177.1	−2830.5
$100(\delta P/P_{\mathrm{measured}})^a$	0.087	0.562	0.209
$(\delta y)^a$	0.004	0.006	0.005
	NRTL		
$(g_{12} - g_{11})$/J·mol^{-1}	1001.3	−571.26	2637.1
$(g_{12} - g_{22})$/J·mol^{-1}	−980.8	432.88	−2465.6
α	0.229	0.109	0.119
$100\ (\delta P/P_{\mathrm{measured}})^a$	0.100	0.554	0.319
$(\delta y)^a$	0.005	0.005	0.006

[a] Average absolute value.

Table 9. Temperature Dependence of the UNIQUAC Model Parameters for the System Diacetyl (1) + 2,3-Pentanedione (2) for T = (333.15 to 353.15) K

parameter^a	$(u_{12} - u_{11})$ / J·mol^{-1}	$(u_{12} - u_{22})$ / J·mol^{-1}
a_1*	4.1664	−2.935
a_2*	−2889.3	2031.8
a_3*	501611	−352391

[a] $(u_{12} - u_{ii})/\mathrm{J \cdot mol^{-1}} = a_1^*(T/\mathrm{K})^2 + a_2^*(T/\mathrm{K}) + a_3^*$.

of similar compounds. The excess Gibbs energy model parameters regressed for the data are given in Tables 7 and 8.

Satisfactory modeling was obtained for both systems. The model parameters for the diacetyl + 2,3-pentanedione isothermal data are well reproduced as functions of temperature by quadratics or straight lines shown in Table 9 and illustrated in Figure 8. These temperature-dependent parameters permit accurate reproduction of the VLE data at arbitrary temperatures within the experimental range.

The average absolute values of δy shown in Tables 7 and 8 were less than 0.01 mol fraction, which satisfies the consistency criterion suggested by Danner and Gess.[8] All the data were rated "3" by the Van Ness direct test for thermodynamic consistency.

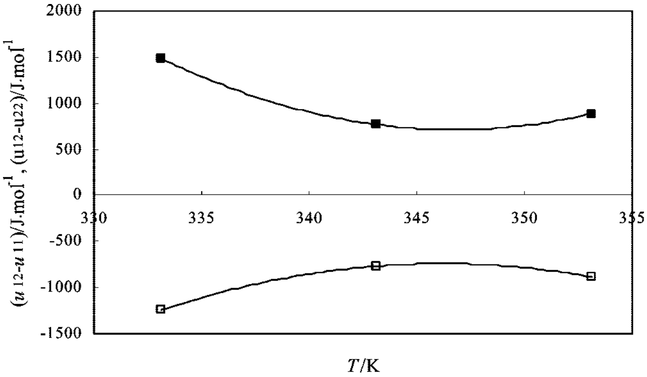

Figure 8. Temperature dependence of the UNIQUAC model parameters for the acetone (1) + 2,3-pentanedione (2) system: □, $(u_{12} - u_{11})$/J·mol^{-1}; ■, $(u_{12} - u_{22})$/J·mol^{-1}.

Table 10. Results of the Van Ness[9] Direct Test for Thermodynamic Consistency

system		index
diacetyl + 2,3-pentanedione	333.15 K	3
	343.15 K	3
	353.15 K	3
	40 kPa	3
acetone + 2,3-pentanedione	323.15 K	3
	30 kPa	3
	40 kPa	3

The results of the consistency tests are given in Table 10. The best fit models are shown in Figures 1 to 7, although it should be noted that the differences between the model fits were marginal and probably within the experimental uncertainty. An example of the Van Ness[9] consistency test is shown in Figure 9 for the acetone + 2,3-pentanedione system at 323.15 K.

Conclusions

Vapor–liquid equilibrium data have been measured for the diacetyl + 2,3-pentanedione system at 333.15 K, 343.15 K, 353.15 K, and 40 kPa and for the acetone + 2,3-pentanedione system at 323.15 K, 30 kPa, and 40 kPa. The data constitute new contributions to the literature as these systems have not been measured previously. The data have been shown to be thermodynamically consistent. Satisfactory modeling was obtained for both systems using the Wilson, NRTL, and UNIQUAC equations for the liquid phase, with temperature-

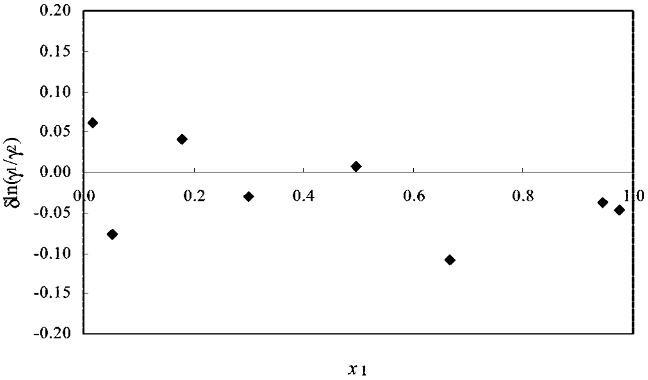

Figure 9. Direct test for thermodynamic consistency for acetone (1) + 2,3-pentanedione (2) at 323.15 K.

dependent parameters given for the UNIQUAC model within the experimental range.

Literature Cited

(1) Raal, J. D.; Mühlbauer A. L. *Phase Equilibria: Measurement and Computation*; Taylor & Francis: Washington D. C., 1998; Chapters 2 and 4.

(2) Joseph, M. A.; Raal, J. D.; Ramjugernath, D. Phase Equilibrium Properties of Binary Systems with Diacetyl from a Computer Controlled Vapour-Liquid Equilibrium Still. *Fluid Phase Equilib.* **2001**, *182*, 157–176.

(3) Joseph, M. A.; Raal, J. D.; Ramjugernath, D. Computer-aided measurement of vapour-liquid equilibria in a dynamic still at sub-atmospheric pressures. *Dev. Chem. Eng. Mineral Proc.* **2002**, *10*, 615–637.

(4) Soni, M.; Ramjugernath, D.; Raal, J. D. Vapor-liquid Equilibrium for Binary Systems of Diacetyl with Methanol and Acetone. *J. Chem. Eng. Data* **2006**, *51* (6), 2083–2087.

(5) Hayden, J. G.; O′ Connell, J. P. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Proc. Des. Dev.* **1975**, *14*, 209–215.

(6) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Non Electrolyte Solutions: With Applications to Phase Equilibria*; McGraw-Hill: New York, 1982.

(7) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-Liquid Equilibrium: Part I. An Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238–244.

(8) Danner, R. P.; Gess, M. A. A Data Base Standard for the Evaluation of Vapor-Liquid Equilibrium Models. *Fluid Phase Equilib.* **1990**, *56*, 285–301.

(9) Van Ness, H. C. Thermodynamics in the Treatment of Vapor /Liquid Equilibrium (VLE) Data. *Pure Appl. Chem.* **1995**, *67*, 859–872.

(10) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; Appendix A; McGraw-Hill: New York, 1987.

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