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Vapor−Liquid Equilibrium for Benzaldehyde with 1-Methylethylbenzene and for 2-Methyl-propan-2-ol with 2,4,4-Trimethyl-1-pentene

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The saturation pressure of 2-methylpropan-2-ol and 2,4,4-trimethyl-1-pentene at (305 to 356) K was measured by the ebulliometric method. The vapor−liquid equilibrium (VLE) (*P*, *T*, *x*, *y*) was measured by the ebulliometric method for the system benzaldehyde + 1-methylethylbenzene at 373.15 K and for the system 2-methyl-propan-2-ol + 2,4,4-trimethyl-1-pentene at (313.16, 333.14, and 353.18) K. A positive azeotrope was found in the last system. The experimental vapor pressures were correlated with Antoine equation and for 2-methyl-propan-2-ol. VLE was correlated with Redlich−Kister four-parameter equation.

Introduction

This work is part of an ongoing investigation of the phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data, DIPPR, of the American Institute of Chemical Engineers. In this paper, we report part of the experimental measurements that have been made under Projects 805(E)/01 and 805(E)/02. Vapor−liquid equilibrium (VLE) data for the investigated systems have not been reported in the literature, and the results cannot be predicted with sufficient accuracy either by using pure component property data or using a semi-empirical method (e.g., based on a group contribution concept such as ASOG[1] or UNIFAC[2]).

Experimental Section

Chemicals. Benzaldehyde (Chemical Abstract Service Registry No. (CASRN) 100-52-7) purchased from Sigma-Aldrich Chemie GmbH as a physicochemical standard of purity better than 99.5 % (w = 99.94 % by mass of pure compound was found by using GC analysis). Cumene (1-methylethylbenzene, CASRN 98-82-8) was purchased from Sigma-Aldrich Chemie GmbH as a GC standard of purity better than 99 % (w = 99.95 % was found by using GC analysis). *tert*-Butyl alcohol (2-methyl-propan-2-ol, CASRN 75-65-0) was purchased from Sigma-Aldrich Chemie GmbH as a physicochemical standard of purity better than 99.5 % (anhydrous, w = 99.92 % was found by using GC analysis of 78 % by mass solution of 2-methyl-2-propanol in 2,4,4-trimethyl-1-pentene). 2,4,4-Trimethyl-1-pentene (CASRN 107-39-1) was purchased from Sigma-Aldrich Chemie GmbH as a physicochemical standard of purity better than 99 % (w = 99.98 % was found by using GC analysis). Substances were used without further purification. No traces of water were measured by GC.

Analytical Procedure. For determination of purity and for analysis of samples equilibrated in the course of VLE measurements, the GLC method with the HP 5890 series II gas chromatograph equipped with an HP 3396 integrator, a thermal conductivity detector (TCD), and HP-FFAP (polyethylene glycol−TPA modified) 30 m × 0.53 mm × 0.01 μm film thickness column was used. An internal standard was used in the calibration procedure.

Table 1. Vapor Pressure *P* of Pure Components at Temperature *T* with Pressure Difference *δP* between Calculated and Experimental Values[a]

2-methylpropan-2-ol			2,4,4-trimethyl-1-pentene		
T/K	*P*/kPa	*δP*/Pa	*T*/K	*P*/kPa	*δP*/Pa
305.87	8.957	9.1	306.23	8.664	−1.5
310.08	11.512	−8.3	309.74	10.150	−0.5
313.14	13.717	−10.5	313.14	11.778	6.6
316.04	16.106	2.9	316.42	13.564	−3.1
319.50	19.431	−3.4	319.61	15.492	2.6
322.94	23.276	−2.1	323.20	17.940	−5.2
326.30	27.620	1.7	326.72	20.627	−4.3
329.74	32.736	13.3	330.07	23.472	5.3
333.15	38.574	10.4	333.14	26.373	−5.7
336.41	44.935	4.3	336.41	29.748	7.1
339.74	52.288	4.8	339.75	33.568	1.7
343.25	61.091	−9.0	343.12	37.809	−1.2
346.50	70.274	−13.9	346.79	42.896	5.2
349.84	80.847	−13.8	349.50	47.012	−8.6
353.15	92.534	15.1	353.14	53.001	−2.5
355.31	100.91	−1.2	356.24	58.567	4.3

[a] Standard uncertenities: $u(T)$/K = 0.010; $u(P_i^0)$/Pa = 7.

Vapor Pressure. The vapor pressure of the investigated substances has been measured by various authors. Data for benzaldehyde were reported by de Mare et al.[3] and by Ambrose et al.[4] Data for 1-methylethylbenzene were reported by Willingham et al.,[5] Forziati et al.,[6] and Cepeda et al.[7] For 2-methyl-propan-2-ol, numerous data were reported. The most significant[8] are by Beynon and McKetta,[9] Biddiscombe et al.[10] and Brown et al.[11] There are some discrepances in these data. For 2,4,4-trimethyl-1-pentene, Camin and Rossini[12] have measured vapor pressure. For all compounds, the thermodynamic properties have been estimated by Daubert and Danner.[13] When processing results of VLE measurements, the most crucial data are the saturation pressures of the pure components.

The direct measurements of the vapor pressure were made for 2-methyl-propan-2-ol and for 2,4,4-trimethyl-1-pentene in a Swietoslwski ebulliometer modified for the determination of VLE (*x, y, p, T)* by Rogalski and Malanowski.[14] The detailed procedure and equipment for determination of saturation pressure were described earlier.[15] The results obtained are given in

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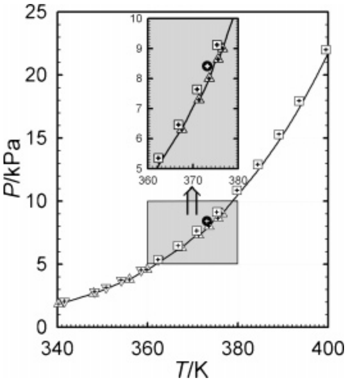

Figure 1. Vapor pressure of benzaldehyde. Comparison with literature data: solid circle with + inside, this work; open upward-facing triangle with + inside, ref 3; open downward-facing triangle with + insdie, ref 4 set I (mercury as reference material); open box with + inside, ref 4 set II (water as reference material); —, ref 14 estimation.

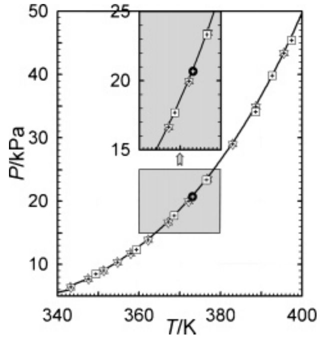

Figure 2. Vapor pressure of 1-methylethylbenzene. Comparison with literature data: solid circle with + inside, this work; open upward-facing triangle with + inside, ref 5; open downward-facing triangle with + inside, ref 6; open box with + inside, ref 7; —, ref 14 estimation.

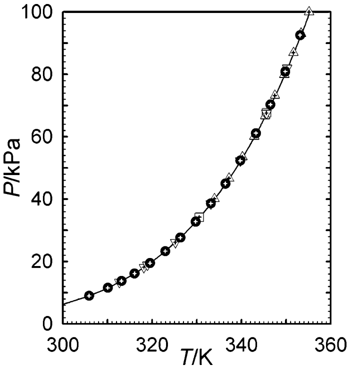

Figure 3. Vapor pressure of 2-methyl-propan-2-ol. Comparison with literature data: solid circle with + inside, this work; open upward-facing triangle with + inside, ref 9; open downward-facing triangle with + inside, ref 10; open box with + inside, ref 11; —, ref 14 estimation.

Table 1, and comparisons with literature data are made in Figures 1 to 4. The estimated standard uncertainty of pressure measurement is $u(p_i^0)$/Pa = 7 and that of temperature is $u(T)$/mK = 10.

Vapor−Liquid Equilibrium. The VLE measurements were carried out for both systems at isothermal conditions by means of the ebulliometric method described elsewhere.[14] The ebulliometers were the same that were used for vapor pressure determination. The known mass of pure compound was introduced to the ebulliometer and heated under variable pressure until the desired boiling point was reached at steady pressure. The readouts of pressure and temperature were taken. Next, the precise amount of the second component was added,

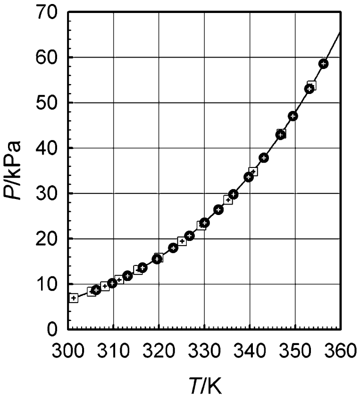

Figure 4. Vapor pressure of 2,4,4-trimethyl-1-pentene. Comparison with literature data: solid circle with + inside, this work; open upward-facing triangle with + inside, ref 12; —, ref 14 estimation.

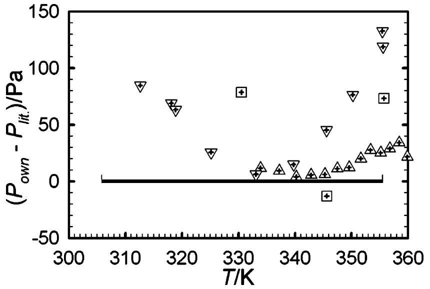

Figure 5. Deviations of measured vapor pressure data for 2-methyl-propan-2-ol from literature data: open box with + inside, ref 9; open upward-facing triangle with + inside, ref 10; open downward-facing triangle with + inside, ref 11; thick line, correlation by Antoine or AEOS equations.

Table 2. Experimental Results of Vapor−Liquid Equilibrium

Benzaldehyde (1) + 1-Methylethylbenzene (2)[a]					
T/K = 373.15					
x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0000	0.0000	20.661	0.6214	0.3666	15.054
0.1091	0.0683	19.934	0.6661	0.4003	14.448
0.2169	0.1256	19.097	0.7186	0.4487	13.683
0.3001	0.1728	18.391	0.8414	0.6112	11.619
0.3631	0.2024	17.819	0.9543	0.8599	9.326
0.4171	0.2363	17.277	1.0000	1.0000	8.4109

2-Methyl-2-propanol (1) + 2,4,4-Trimethyl−1-pentene (2)[b]								
T/K = 313.16			T/K = 333.14			T/K =3 53.18		
x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0000	0.000	11.778	0.0000	0.000	26.373	0.0000	0.000	53.002
0.0731	0.302	15.833	0.0728	0.347	36.202	0.0728	0.316	72.364
0.1633	0.376	17.142	0.1606	0.447	40.184	0.1576	0.433	82.854
0.2588	0.422	17.705	0.2606	0.494	42.499	0.2583	0.501	89.385
0.3435	0.456	18.020	0.3408	0.521	43.599	0.3349	0.546	92.674
0.4059	0.475	18.191	0.4042	0.512	44.282	0.4050	0.578	95.065
0.4627	0.496	18.248	0.4639	0.581	44.777	0.4620	0.601	96.659
0.5250	0.524	18.272	0.5191	0.585	45.070	0.5225	0.639	93.036
0.5253	0.523	18.266	0.6215	0.623	45.375	0.6264	0.675	99.675
0.6176	0.550	18.178	0.6300	0.628	45.380	0.6993	0.714	100.236
0.6981	0.597	17.933	0.6911	0.657	45.335	0.7340	0.734	100.302
0.7645	0.633	17.581	0.7591	0.689	44.874	0.7648	0.753	100.237
0.8017	0.664	17.270	0.7999	0.722	44.398	0.8000	0.777	99.982
0.8451	0.709	16.795	0.8406	0.759	43.761	0.8399	0.799	99.465
0.8861	0.755	16.196	0.8815	0.799	42.854	0.8810	0.813	98.577
1.0000	1.000	13.717	1.0000	1.000	38.574	1.0000	1.000	92.536
Azeotropic Parameters[c]								
0.525	0.525	18.27	0.630	0.630	45.38	0.760	0.760	100.31

[a] Standard uncertenities: $\delta(T)$/K = 0.03; $\delta(x_1) = 0.0003$; $\delta(y_1) = 0.001$; $\delta(P)$/Pa = 7. [b] Standad uncertenities: $\delta(T)$/K = 0.01; $\delta(x_1) = 0.0003$; $\delta(y_1) = 0.002$; $\delta(P)$/Pa = 5. [c] Standard uncertenities: $\delta(T)$/K = 0.03; $\delta(x_1) = 0.005$; $\delta(y_1) = 0.005$; $\delta(P)$/Pa = 70.

Table 3. Correlation of Vapor Pressure

	2-methyl-propan-2-ol	2,4,4-trimethyl-1-pentene
	T/K = 305−355	T/K = 306−356
Parameters of Antoine Equation (T/K, p/kPa)		
A	6.512711	5.938261
B	1178.906	1261.986
C	93.841	53.744
errors: rmsd(p)/Pa	9.1	4.7
Enthalpy of Vaporization ($\Delta_{\text{vap}}H°$/kJ·mol^{-1}) at T/K = 298.15		
calcd from own vapor pressure:	47.37	35.66
calorimetric or other	46.94 ± 0.02[a]	35.69[d]
Daubert and Danner prediction	46.39[b]	35.90[b]
	T/K = 355.4	T/ = 374.6
Enthalpy of Vaporization ($\Delta_{\text{vap}}H°$/kJ mol^{-1}) at Boiling Point		
calcd from own vapor pressure	39.62	31.09
calorimetric or other	39.07[c]	30.69[d]
Daubert and Danner prediction	40.13[b]	31.03[b]

[a] Ref 17. [b] Ref 13. [c] Ref 18. [d] Ref 19.

and the system was equilibrated until the steady state was reached at the desired temperature. Next without interruption of boiling, the samples of boiling liquid and vapor condensate were collected for analysis. The measure of steady state was the stability of temperature within ± 0.003 K for about 5 min. In general, the time between introducing samples was about 30 min. The whole procedure was repeated until the volume fracttion of second component exceeds 0.5. The sample composition was determined by using gas chromatograph. For each system, the calibration procedure was used.

The estimated uncertenity of the pressure measurement was ± 10 Pa and that of temperature was ± 10 mK. The sample composition was determined by the GLC method, with an uncertainty of $x = 0.001$ for liquid phase and $x = 0.003$ for vapor phase. The results obtained are given in Table 2. The consistency check was made for each isotherm with the method proposed by Eubank et al.[16] (test 1). The auxiliary data were taken from Daubert and Danner.[13] The differences between calculated and experimental liquid-phase compositions do not exceed 0.015, which is an acceptable value.

Correlation

Vapor Pressure. The vapor pressure data were correlated with the Antoine equation:

$$\log(P_i^0/\text{kPa}) = A - \frac{B}{T/\text{K} - C} \qquad (1)$$

where A, B, and C are adjustable parameters; P_i^0 is the saturation pressure; and T is the corresponding temperature.

The values of parameters obtained by fitting the Antoine equation to vapor pressure data are given in Table 3. The deviations of computed and values calculated ($\delta P_i/\text{Pa} = P_i^{\text{calcd}} - P_i^{\text{exptl}}$) by both equations are given in Table 1. The distribution of deviations is random.

The root-mean-square deviations (δ_{rms}) of P are calculated from

$$\delta_{\text{rms}}(p) = \sqrt{\frac{\sum_{i=1}^{n} (P_i^{\text{calcd}} - P_i^{\text{exptl}})^2}{n}} \qquad (2)$$

The parameters of Antoine equation are listed in Table 3 together with the $\delta_{\text{rms}}(P/\text{kPa})$. The results are satisfactory.

Table 4. Correlation of VLE with Redlich−Kister Equation

parameters						RMSD(y)	RMSD (p)
A_0	A_1	A_2	A_3	A_4	A_5	mole fraction	Pa
Benzaldehyde (1) + 1-Methylethylbenzene (2)							
T/K = 373.15							
0.483332						0.0063	86.4
0.470905	−0.063184					0.0033	33.6
0.471598	−0.073177	−0.032669				0.0022	25.3
0.467975	−0.058014	−0.033343	−0.069764			0.0013	9.2
0.467665	−0.057889	−0.029432	−0.071247	−0.010190		0.0013	8.9
0.468042	−0.060274	−0.031992	−0.055734	−0.007224	−0.021995	0.0013	8.7
2-Methyl-propan-2-ol (1) + 2,4,4-Trimethyl-1-pentene (2)							
T/K = 313.16							
1.45538						0.0245	422
1.47034	−0.29420					0.0120	178
1.40445	−0.28063	0.27281				0.0079	65
1.45090	−0.23464	0.22140	−0.229159			0.0042	60
1.45126	−0.23502	0.21687	−0.224875	0.011587		0.0041	56
1.45120	−0.23715	0.21770	−0.215218	0.010681	−0.020844	0.0042	55
T/K = 333.14							
1.33321						0.0270	851
1.35540	−0.23216					0.0181	387
1.33462	−0.22560	0.23013				0.0175	127
1.33918	−0.18633	0.19379	−0.178048			0.0174	85
1.33909	−0.18588	0.19529	−0.179863	−0.005017		0.0173	84
1.33916	−0.18444	0.19211	−0.189103	−0.004359	0.022225	0.0173	79
T/K = 353.18							
1.20338						0.0575	1293
1.22380	−0.15031					0.0115	655
1.20798	−0.15752	0.17076				0.0085	80
1.20949	−0.14646	0.16484	−0.046126			0.0080	12
1.20953	−0.14667	0.16418	−0.045551	−0.001949		0.0080	11
1.20959	−0.14509	0.16009	−0.057360	0.010787	0.024604	0.0082	8

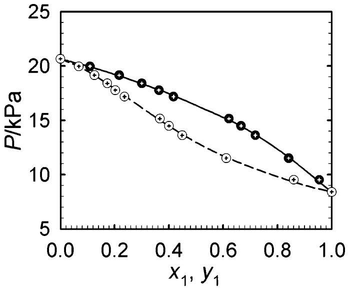

Figure 6. VLE, isotherm 373.15 K for benzaldehyde (1) + 1-methylethylbenzene (2). Computed with Redlich−Kister four-parameter equation: —, bubble points line; − −, dew points line. Experimental: closed circle with + inside, bubble points; open circle with + inside, dew points.

The best evidence of the accuracy of the vapor pressure determination is the calculation of the enthalpy of vaporization from the measured vapor pressure and comparison with these obtained by other methods. This is presented in Table 3. The calculated values exhibit small deviations from published calorimetric data.

Vapor−Liquid Equilibrium. The *P*, *T*, *x*, *y* data were reduced to activity coefficients according

$$x_1\gamma_1P_1^{0=y}{}_iP\phi_i \qquad (3)$$

The Redlich−Kister equations in the following form, with one to six adjustable parameters (A_0, ..., A_6), were used as activity coefficients models:

$$\ln\gamma_1 = x_2^2\sum_{k=0}^{m-1} A_k(x_1(2k+1) - x_2)(x_1 - x_2)^k$$

$$\ln\gamma_2 = x_1^2\sum_{k=0}^{m-1} A_k(x_1 - x_2(2k+1))(x_2 - x_1)^k \qquad (4)$$

where *m* is the number of adjustable parameters. The necessary fugacity coefficients (ϕ_i) of the component *i* in the vapor phase were calculated from

$$\phi_i = \exp\left(\frac{(v_i^{\mathrm{L}} - \beta_i)(P - P_i^0) - P(1 - y_i)^2(\beta_1 + \beta_2)/2}{RT}\right) \qquad (5)$$

where second virial coefficients β_i and liquid volumes v_i^{L} as functions of *T* were calculated from DIPPR data and formula:[13]

$$\beta_i = A + \frac{B}{T} + \frac{C}{T^3} + \frac{D}{T^8} + \frac{E}{T^9} \qquad (6)$$

$$v_i^{\mathrm{L}} = a/b^{(1 + (1 - T/c)^d)} \qquad (7)$$

A, *B*, *C*, *D*, *E* and *a*, *b*, *c*, *d* are the parameters recommended by Daubert and Danner.[13] The results obtained are summarized in Table 4.

The root-mean-square deviations of total pressure $\delta_{\mathrm{rms}}(P)$/Pa and vapor-phase composition $\delta_{\mathrm{rms}}(y)$ were calculated for all experimental points by eq 2. The correlation results are summarized in Table 4 and presented in Figures 6 and 7.

Conclusions

The VLE in both systems was measured for the first time. The binary positive homoazeotrope was found in the system 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene. The azeotropic data are given in Table 2. Comparison of vapor pressure obtained in course of present work show that good agreement was obtained for benzaldehyde with Ambrose et al.[4] data obtained with the use of water as reference material. For 1-methylethylbenzene the agreement is good; the best with data of Willingham et al.[5] For 2-methyl-2-propanol, deviations from literature data are observed; the best agreement is with the data of Biddiscombe et al.[10] (Figures 3 and 5). For 2,4,4-trimethyl-1-pentene, there was good agreement with the data of Camin and Rossini.[12] The best results for the correlation of VLE data for both systems were obtained with the Redlich−Kister equation with four adjustable parameters. Other equations gave poorer fits and are not reported in this paper.

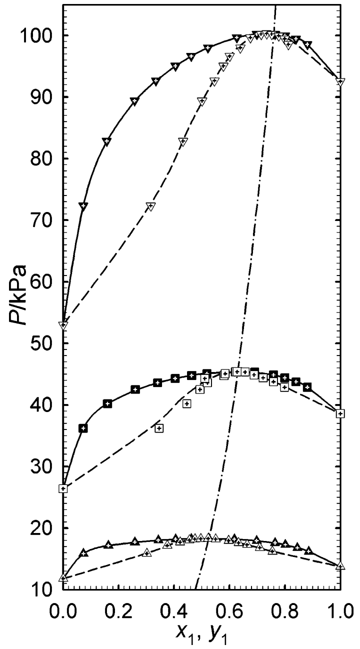

Figure 7. VLE for 2-methyl-2-propanol (1) + 2,4,4-trimethyl-1-pentene (2). Computed with Redlich−Kister four-parameter equation: —, bubble points line; − −, dew points line. Experimental: solid smbols, bubble points; hollow symbols, dew points; open upward-facing triangle with + inside, *T*/K = 313.16; open box with + inside, *T*/K = 333.14; open downward-facing triangle with + inside, *T*/K = 353.18; − • −, azeotropic composition line.

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