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Vapor−Liquid Equilibrium in a Ternary System Cyclohexane + Ethanol + Water[†]

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Experimental vapor−liquid equilibrium (*p*, *T*, *x*, *y*) data of the cyclohexane + ethanol + water system have been determined by an ebulliometric method at the temperatures (323, 333, and 343) K. The vapor pressures of pure components have been measured by the ebulliometric method in the range from (310 to 340) K.

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 Project 805(B)/96. This ternary system cyclohexane + ethanol + water has a liquid−liquid miscibility gap.[1] The total pressure data for the investigated system have been reported by Connemann et al.[2] The same authors used a distillation method to determine the composition of the ternary heteroazeotrope under pressures from (25 to 99) kPa. These results are in reasonable agreement with the earlier results obtained by an ebulliometric method.[3] The industrial importance of the mixture cyclohexane + ethanol + water is evident. Cyclohexane is an entrainer for the binary (ethanol + water) mixture, which alters the activity coefficients of the component to be separated. The low-boiling ternary heterogeneous azeotrope causes a composition in the vicinity of the coexistence curve to frequently split into two phases during condensation. In the literature, there are no ternary *p*, *T*, *x*, *y* data for this system. It is difficult to sample and analyze the compositions of coexisting phases in a system that splits into two liquid phases. In this paper, measurements are reported of vapor−liquid equilibrium (VLE) data (*p*, *T*, *x*, *y*) for the homogeneous part of the system.

Experimental Section

Chemicals. Cyclohexane (CA Reg. No. 110-82-7) was purchased from Sigma-Aldrich (HPLC grade) with a purity of 99.9+% and a water content of <0.01%; it was used without further purification. Butanol (CA Reg. No. 71-36-3) was purchased from Sigma-Aldrich, in a synthesis grade (purity > 98% by gas−liquid chromatography (GLC), with a water content below 0.02%); it was used without further purification. Anhydrous 99.8% ethanol (CA Reg. No. 64-17-5) was purchased from POCH S.A. Gliwice (ISO, ACS); it was distilled to obtain a purity of 99.9% by mass and a water content of <0.01%. The content of water was determined by GLC analysis with a thermal conductivity detector (TCD) and a glass 2.5 m by 3 mm column filled with Chromosorb 101 (60/80 Mesh) to be <0.05 mass %. Water (CA Reg. No. 7732-18-5) was used after it was twice distilled and was deionized.

Table 1. Vapor Pressure *p* as Function of Temperature *T* of the Pure Components

cyclohexane		water		ethanol	
T/K	*p*/kPa	*T*/K	*p*/kPa	*T*/K	*p*/kPa
302.92	16.060	327.13	15.000	312.17	17.001
304.19	16.951	328.16	15.752	313.43	18.154
306.91	19.052	330.78	17.846	318.15	23.068
308.27	20.165	333.15	19.937	318.24	23.181
309.90	21.561	335.82	22.530	320.87	26.390
313.16	24.613	338.15	25.021	323.15	29.484
318.19	30.027	340.67	27.981	326.13	33.996
323.14	36.231	343.16	31.206	326.16	34.017
328.16	43.514	346.13	35.419	328.14	37.336
331.90	49.684	348.14	38.552	328.17	37.387
333.16	51.899	353.14	47.359	330.65	41.898
333.17	51.903	358.14	57.789	333.16	46.935
338.16	61.559			336.10	53.467
343.16	72.528			336.14	53.564
345.42	77.943			338.16	58.476
348.05	84.731			343.15	72.304
				348.14	88.772
				351.38	101.114
				351.42	101.231

Vapor Pressure Measurements. Measurements of pure-compound vapor pressure were carried out in a Świetosławski ebulliometer modified for total pressure measurements.[4] The ebulliometer was connected to the pressure-stabilizing system consisting of a 0.6 m^3 buffer vessel combined with a vacuum pump and a pressurized argon container. The pressure was adjusted manually by using a system of vessels and a rubber balloon filled with argon until the boiling temperature of the compound in the ebulliometer was reached within ±0.005 K. The temperature was measured by using a SYSTEMTEKNIK AB S1228 thermometer with a platinum resistance probe and the resolution of 0.001 K. The calibration was made by comparison with readings of a Tinsley & Co. Muller Bridge type 4772 with a platinum resistance temperature sensor type 5187 SA calibrated by NPL to Type I (uncertainty,

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[†] This contribution will be part of a special print edition containing papers reporting experimental results from the various projects of the Design Institute for Physical Properties of the American Institute of Chemical Engineers.

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Table 2. Vapor−Liquid Equilibria for Cyclohexane (1) + Ethanol (2) + Water (3)

x_1	x_2	x_3	y_1	y_2	y_3	p/kPa
			T/K = 323.15			
0.0152	0.8734	0.1114	0.2315	0.6787	0.0898	36.942
0.0355	0.8603	0.1042	0.3407	0.5832	0.0761	41.654
0.0509	0.8499	0.0992	0.3517	0.5846	0.0637	44.700
0.0181	0.9788	0.0031	0.1515	0.8462	0.0023	34.808
0.0146	0.9416	0.0438	0.1466	0.8127	0.0407	34.665
0.0101	0.8667	0.1232	0.1483	0.749	0.1027	34.965
0.0049	0.7714	0.2237	0.1122	0.7215	0.1663	33.243
0.0015	0.6334	0.3651	0.078	0.6777	0.2443	30.797
0.0448	0.9528	0.0024	0.2686	0.7295	0.0019	40.889
0.0409	0.9076	0.0515	0.2797	0.6775	0.0428	41.894
0.0267	0.8162	0.1571	0.2737	0.6144	0.1119	41.694
0.0468	0.7999	0.1533	0.3484	0.5423	0.1093	47.245
0.0058	0.8664	0.1278	0.0969	0.7949	0.1082	32.812
0.0212	0.8541	0.1247	0.2182	0.6835	0.0983	38.614
0.0013	0.7364	0.2623	0.0462	0.7512	0.2026	30.603
0.0058	0.7339	0.2603	0.1262	0.6876	0.1862	34.205
			T/K = 333.15			
0.0050	0.6403	0.3547	0.1616	0.6145	0.2239	53.8729
0.0035	0.6479	0.3486	0.1243	0.6442	0.2315	51.7211
0.0071	0.6879	0.3050	0.1685	0.6196	0.2119	55.4448
0.0022	0.7065	0.2913	0.0818	0.6995	0.2187	49.9132
0.0072	0.7213	0.2715	0.1608	0.6421	0.1971	55.2728
0.0093	0.7157	0.2750	0.2219	0.5975	0.1806	57.0740
0.1006	0.8925	0.0069	0.3919	0.6013	0.0068	70.9915
0.0960	0.8430	0.0610	0.4159	0.5403	0.0438	73.1926
0.0867	0.7654	0.1479	0.3733	0.5102	0.1165	76.4364
0.0639	0.7062	0.2299	0.3099	0.5192	0.1709	76.6417
0.0462	0.9506	0.0032	0.1489	0.8488	0.0023	54.2929
0.0158	0.9396	0.0446	0.1362	0.8216	0.0422	54.4755
0.0105	0.8663	0.1232	0.1325	0.7617	0.1058	54.4382
0.0065	0.7712	0.2223	0.1186	0.7138	0.1676	53.3383
0.0465	0.9508	0.0027	0.2500	0.7478	0.0022	62.9775
0.0421	0.9063	0.0516	0.2692	0.6850	0.0458	64.1467
0.0307	0.8126	0.1567	0.2737	0.6144	0.1119	65.0600
0.0529	0.7940	0.1531	0.3061	0.5730	0.1209	73.4006
0.0068	0.8660	0.1272	0.0928	0.7960	0.1112	32.8120
0.0225	0.8538	0.1237	0.2129	0.6867	0.1004	59.8911
0.0018	0.7329	0.2653	0.0501	0.7492	0.2007	49.0240
0.0078	0.7294	0.2628	0.0887	0.7163	0.1950	54.6982
			T/K = 343.15			
0.0000	0.8816	0.1184	0.0000	0.8847	0.1153	72.641
0.0060	0.8828	0.1112	0.0693	0.8239	0.1068	77.596
0.0140	0.8750	0.1110	0.1494	0.7501	0.1005	82.879
0.0262	0.8664	0.1074	0.2715	0.6442	0.0843	89.926
0.0402	0.8508	0.1090	0.2933	0.6174	0.0893	94.539
0.0582	0.8338	0.1080	0.3720	0.5444	0.0836	102.162
0.0098	0.7147	0.2755	0.1801	0.6313	0.1886	84.321
0.0141	0.7147	0.2712	0.2468	0.5829	0.1703	89.494
0.0176	0.9785	0.0039	0.1278	0.8694	0.0028	82.056
0.0163	0.9383	0.0454	0.1289	0.8267	0.0444	82.780
0.0105	0.8663	0.1232	0.1232	0.7702	0.1066	82.320
0.0073	0.7714	0.2213	0.1145	0.7161	0.1694	81.721
0.0025	0.6321	0.3654	0.0761	0.6768	0.2471	76.863
0.0483	0.9493	0.0024	0.1798	0.8186	0.0016	94.142
0.0422	0.9072	0.0506	0.2623	0.6915	0.0462	95.261
0.0359	0.8111	0.1530	0.2768	0.6046	0.1186	98.867
0.0071	0.8670	0.1259	0.0875	0.7991	0.1134	79.639
0.0216	0.8536	0.1248	0.1873	0.7081	0.1046	88.934
0.0023	0.7343	0.2634	0.0493	0.7476	0.2031	75.636
0.0237	0.7263	0.2500	0.1360	0.6819	0.1821	83.118

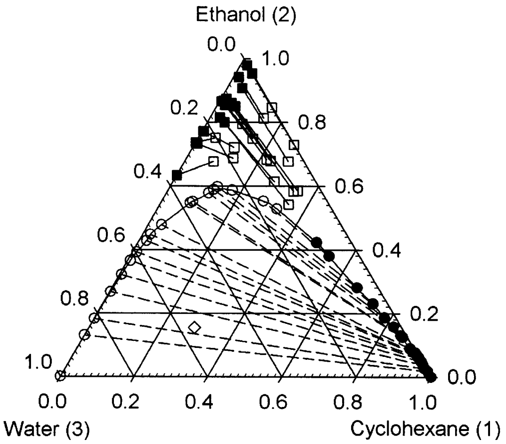

Figure 1. Composition of coexisting liquid (■) and vapor phases (□) at 323.15 K: Moriyoshi et al. (ref 1) data for LLE for the cyclohexane-rich liquid phase (●) and water-rich liquid phase (○); ◇, heteroazeotrope at 320.3 K from Connemann et al. (ref 2).

Table 3. Correlation of Pure-Component Vapor Pressure with the Antoine Equation

		cyclohexane	ethanol	water
temp range/K		302−348	312−351	327−359
A		5.949609	7.205835	7.081330
B		1191.969	1574.107	1662.617
C		51.663	48.736	45.587
errors	RMSD(p)/Pa	13.6	12.2	4.8
	RMSD(p_{lit})/Pa	6.8[d]	4.6[e]	6.3[f]
$\Delta_{vap}H$/kJ·mol^{-1} at T/K = 298.15	calculated	33.05	42.99	43.87
		32.8[a]	42.5[a]	43.9[b]
	literature	33.01[b] 33.04[c]	42.32[b]	43.99[c]
$\Delta_{vap}H$/kJ·mol^{-1} at boiling pt T/K		353.80	351.41	373.14
	calculated	30.02	39.12	40.67
		29.9[a]	38.65[a]	40.80[b]
	literature	29.97[b] 29.96[c]	38.56[b]	40.66[c]

[a] Reference 5. [b] Reference 6. [c] Reference 7. [d] Reference 8. [e] Reference 9. [f] Reference 10.

±0.001 K). In the course of the measurements, the ice point temperature was repeated within ±0.002 K. No systematic deviations of the temperature during measurements were observed. The pressure was measured with a Texas Instruments 144-01 precision pressure gauge with a no. 8, type 2 quartz Bourdon tube frequently recalibrated against a high-precision mercury manometer (resolution, ±0.08 Pa) connected to the same system. The pressure resolution was ±0.3 Pa, and a vacuum pressure of less than 10^{-2} Pa was used to fix the 144-01 gauge null point. The estimated accuracy of the pressure measurement was ±10 Pa, and that of the temperature measurement was ±10 mK. The results obtained are given in Table 1.

Vapor−Liquid Equilibrium Measurements. The VLE measurements were carried out by means of an ebulliometer that enabled collection of coexisting liquid and vapor condensate. It was connected to the same pressure-stabilizing system as for vapor pressure measurements. The method is fully described elsewhere.[4] The ternary VLE measurements were made at (323, 333, and 343) K for the compositions outside of the miscibility region in this temperature range. The binary mixtures ethanol + cyclohexane or ethanol + water, of known composition, were prepared by weighing. The mixture was introduced into the ebulliometer and heated with a continuous adjustment of pressure until a steady-state boiling was reached after approximately 30 min of boiling at constant temperature. The measure of a steady state was the stability of temperature within ±0.003 K for about 5 min. Samples of vapor condensate and boiling liquid, in equilibrium, were taken for analysis. A small amount of 1-butanol was added to the collected sample by the same hypodermic syringe to avoid phase splitting. Next, a precise amount of the third component (water or cyclohexane, respectively) was added in small amounts. In general, the time between introducing samples was about 30 min. Then, the readouts of pressure and temperature were taken. The procedure was repeated until a splitting of the liquid phase was visible in the

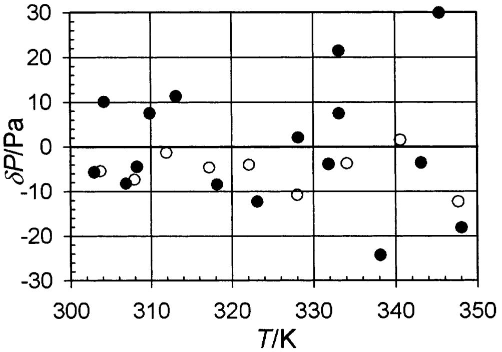

Figure 2. Deviation of cyclohexane saturation pressure data from a correlation with the Antoine (●) equation: ○, Williamham et al. (ref 8) data.

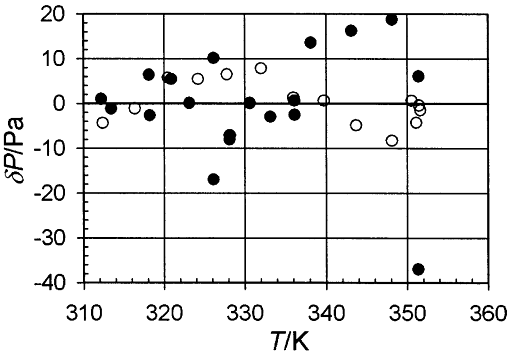

Figure 3. Deviation of ethanol saturation pressure data from a correlation with the Antoine (●) equation: ○, Ambrose and Sprake (ref 9) data.

ebulliometer. The temperature was measured with an accuracy of ±0.01 K, and that of pressure was ±10 Pa.

The sample composition was determined by using an HP 5890 series II gas chromatograph. The HP-FFAP column (poly(ethylene glycol)−TPA modified 30 m × 0.53 mm × 0.01 μm film thickness) and an HP 3396 injector and TCD were used. An appropriate calibration procedure was used. The accuracy of the composition determination of the liquid phase was ±0.001, and that of the vapor phase was ±0.002 mole fraction.

The results obtained for the equilibrium pressure (p/kPa), temperature (T/K), and mole fraction of the components in the liquid (x) and vapor (y) phases are listed in Table 2. The composition of coexisting vapor and liquid phases (VLE and liquid−liquid equilibrium (LLE)) for $T = 323.15$ K is given in Figure 1.

Correlation

Vapor Pressure. The vapor pressure data were correlated by means of the Antoine equation,

$$\log(p/\mathrm{kPa}) = A - \frac{B}{T/\mathrm{K} - C} \tag{1}$$

where p is pressure, T is temperature, and A, B, and C are adjustable parameters.

The results of the correlation are summarized in Table 3. The root-mean-square deviations of pressure (RMSD(p)/Pa) are calculated from the equation

$$\mathrm{RMSD}(p) = \sqrt{\frac{\sum_{i=1}^{n}(p_i^{\mathrm{exp}} - p_i^{\mathrm{calc}})^2}{n - m}} \tag{2}$$

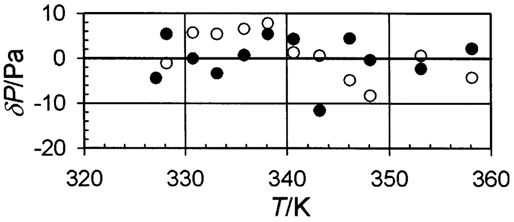

Figure 4. Deviation of water saturation pressure data from a correlation with the Antoine (●) equation: ○, Bridgeman and Aldrich (ref 10) data.

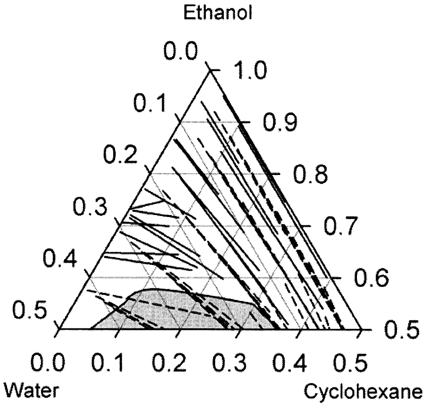

Figure 5. VLE tie lines: solid, experimental; dotted, computed by Connemann et al. (ref 2). Gray area, two liquid phase region.

where m is the number of adjustable parameters, n is the number of experimental points, p_i^{exp} is the pressure measured at point number i, and p_i^{calc} is the pressure calculated from eq 1 at point number i. The best evidence of the accuracy of the vapor pressure determination is a calculation of the enthalpy of vaporization from the measured vapor pressure and a comparison with those obtained by a calorimetric method. The Daubert and Danner[5] correlations were used for computation of necessary liquid molar volume and second virial coefficients. The resulting enthalpies are given in Table 3. The calculated values exhibit small deviations from the literature calorimetric data (see Figures 2−4).

The system investigated is very difficult to correlate. The VLE data were measured for a limited concentration range, and due to this no correlation has been made. In almost half of the investigated concentration range, there is a significant difference in the slopes of the tie lines calculated by Connemann et al.[2] from total pressure data and directly measured in this work (Figure 5).

Note Added after ASAP Posting. This article was released ASAP on 5/15/2003. In Table 1, the headings for the water and ethanol columns were transposed to be correct. The paper was reposted on 11/14/2003.

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