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Isobaric Vapor−Liquid and Vapor−Liquid−Liquid Equilibria Data for the System Water + Isopropanol + Isooctane

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Isobaric vapor−liquid and vapor−liquid−liquid equilibria were measured for the ternary system water + isopropanol (2-propanol) + isooctane (2,2,4-trimethylpentane) at 101.3 kPa. The experimental determination was carried out in a dynamic equilibrium still, with circulation of both the vapor and liquid phases equipped with an ultrasonic homogenizer. The experimental data demontrated the existence of a ternary heterogeneous azeotrope at 70.9 °C with a composition of 0.31, 0.31, and 0.38 mole fraction of water, isopropanol, and isooctane, respectively.

Introduction

Isopropanol (2-propanol) is a well-known solvent which has several applications in the industry. It is used mainly as a solvent for coatings, inks, surfactants, pharmaceutical products, cosmetics, paints, and so on.[1] For all these applications, it is interesting to obtain pure isopropanol by eliminating the water that has dissolved. One possible way to carry out this separation process is by azeotropic distillation, since this forms an azeotrope with water with a molar composition of 68% isopropanol and 32% water. Usually in the industry, isopropyl ether is used as an entrainer in this process.[1] In this paper, vapor−liquid equilibrium (VLE) and vapor−liquid−liquid equilibrium (VLLE) for mixtures of water, isopropanol, and isooctane will be discussed that show a ternary azeotrope. This could be used to develop a new suitable column sequence to separate water and isopropanol using isooctane as an entrainer.

Experimental Section

Chemicals. All chemicals were used as supplied after gas chromatography failed to show measurable amounts of organic impurities. The nominal purities of 2-propanol and isooctane obtained from Merck were 99.8 and 99.5 mass %. For the ethanol, which was used as the internal standard for chromatographic analysis, the nominal purity was >99.5 mass %. The Karl Fischer titration method was used to determine the water content for isooctane, ethanol, and 2-propanol that is 0.005, 0.05, and 0.07, respectively. Ultrapure water was purified using a Milli Q-Plus system.

Apparatus and Procedures. The equipment used for the determination of VLLE data was a commercial unit (Labodest model 602) built in Germany by Fischer Labor und Verfahrenstechnik, that was modified by Gomis et al.[2] by coupling an ultrasonic homogenizer (Braun Labsonic L) to the boiling flask. The still allows good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium. The ultrasound system ensures a good dispersion of partly miscible liquid phases, and consequently this equipment works perfectly for the determination of VLLE data. For VLE determinations, the same equipment without modifications was used.

The temperature in the still was measured with a Pt-100 thermometer connected to an ERTCO-Hart (model 5614), with an uncertainty of 0.006 °C according to the certificate of calibration (on the ITS 90[3]). A Fischer M101 phase equilibrium control system was used to measure and control the pressure and the heating power. The pressure in the still was 101.3 kPa, measured and controlled with an accuracy of 0.1 kPa. To guarantee the correct operation of the equipment, the boiling point of pure water was measured and compared with the accepted value.

All analytical work was carried out by gas chromatography on a Shimadzu GC-14B coupled with a personal computer by using the Shimadzu CLASS-VP Chromatography Data System. Separation of the components was obtained on a 2 m × 3 mm column packed with Porapack Q 80/100. The oven temperature was 210 °C, and the helium flow rate was 50 $\mathrm{mL \cdot min^{-1}}$.

Sampling was carried out using different methods depending on the phase treated:

(a) The sampling of the gaseous phase was carried out using a UW Type, 6-port valve from Valco Instruments Co., which injected the samples automatically into the GC.

(b) For the sampling of the liquid phase in the heterogeneous region, a small amount of the liquid coming from the separation chamber of the instrument was diverted to a tube using a solenoid valve. In this tube, the dispersed liquid phases enter and separate into two layers at their bubble point. A sample of each layer was taken and placed in a vial with a small amount of an internal standard.

(c) Liquid samples in the homogeneous region were withdrawn with a syringe of the liquid coming from the separator chamber and put into a vial.

To obtain quantitative results in the analysis of the liquid phases, an internal standard method was used. For this reason, ethanol (which is completely miscible in water, 2-propanol, and isooctane) was also added to the sample vials. Furthermore, the addition of the standard prevents phase-separation effects when changing the temperature after the separation of the phases. A further description of the sample take off is given in a previous paper.[2]

Depending on the composition of the samples, detection was carried out by two different techniques: TCD (thermal conductivity detector) for organic-rich samples (analyzing water, 2-propanol, and isooctane) and FID (flame ionization

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Table 1. Vapor−Liquid−Liquid Equilibrium Data (Mole Fraction) for the Ternary System Water (1) + Isopropanol (2) + Isooctane (3) at 101.3 kPa

	organic phase			aqueous phase			vapor phase			
	x_1	x_2	x_3	x_1	x_2	x_3	y_1	y_2	y_3	t_b/°C
BIN	0.006	0.000	0.994	0.997	0.000	0.003	0.473	0.000	0.527	79.03
1	0.035	0.165	0.800	0.912	0.081	0.008	0.329	0.282	0.389	71.27
2	0.061	0.250	0.690	0.859	0.128	0.013	0.322	0.295	0.384	71.04
3	0.071	0.262	0.667	0.823	0.160	0.018	0.302	0.301	0.397	70.97
4	0.072	0.285	0.643	0.798	0.181	0.021	0.312	0.308	0.380	70.91
5	0.103	0.344	0.554	0.747	0.223	0.030	0.300	0.320	0.380	70.85
6	0.227	0.410	0.363	0.661	0.281	0.058	0.314	0.327	0.359	70.91
7	0.260	0.427	0.314	0.612	0.297	0.091	0.308	0.328	0.364	70.99

Table 2. Vapor−Liquid Equilibrium Data (Mole Fraction) for the Ternary System Water (1) + Isopropanol (2) + Isooctane (3) at 101.3 KPa

	liquid phase			vapor phase			
	x_1	x_2	x_3	y_1	y_2	y_3	t_b/°C
1	0.380	0.426	0.194	0.314	0.305	0.381	70.96
2	0.070	0.422	0.508	0.281	0.334	0.385	71.35
3	0.153	0.376	0.471	0.315	0.306	0.379	70.97
4	0.129	0.432	0.439	0.266	0.375	0.359	71.62
5	0.178	0.517	0.305	0.265	0.374	0.361	71.62
6	0.157	0.476	0.367	0.278	0.362	0.360	71.51
7	0.273	0.412	0.315	0.292	0.329	0.379	70.94
8	0.267	0.481	0.252	0.282	0.349	0.369	71.25
9	0.292	0.549	0.159	0.282	0.362	0.356	71.76
10	0.421	0.492	0.087	0.295	0.341	0.364	71.65
11	0.215	0.693	0.092	0.223	0.513	0.264	74.10
12	0.036	0.528	0.436	0.137	0.491	0.372	73.68
13	0.060	0.607	0.333	0.137	0.510	0.353	73.81
14	0.068	0.689	0.243	0.115	0.565	0.320	74.65
15	0.254	0.694	0.052	0.253	0.544	0.203	75.82
16	0.134	0.725	0.141	0.174	0.555	0.271	74.30
17	0.167	0.645	0.188	0.216	0.469	0.315	72.95
18	0.249	0.649	0.102	0.250	0.457	0.293	73.38
19	0.289	0.662	0.049	0.269	0.498	0.233	75.33
20	0.351	0.556	0.093	0.286	0.387	0.327	72.10
21	0.242	0.618	0.140	0.25	0.437	0.313	72.55
22	0.177	0.590	0.233	0.226	0.444	0.330	72.24

Table 3. Antoine Equation Parameters[5] of the Pure Substances

compound	*A*	*B*	*C*	temperature range/°C
water	8.07131	1730.630	233.426	1−100
isopropanol	8.87829	2010.330	252.636	−26−83
isooctane	6.81189	1257.840	220.735	23−100

detector*)* for water-rich samples (analyzing 2-propanol and isooctane). The temperature of the detector was 230 °C, and the current for the TCD was 100 mA.

The water content in the organic phase was also measured with a Metroohm 735 Karl Fischer coulometer. These measurements were carried out to check the results of the chromatographic analysis for the organic phase. The water content in the aqueous phase is inferred from a mass balance.

The accuracy of the mole fraction measurements was estimated at 0.002 for all the compounds except for the water in the liquid organic phase and isooctane in the aqueous phase, where the accuracy was approximately 0.0005.

Results and Discussion

The experimental VLLE data of the studied ternary system are summarized in Table 1. This table also includes the VLLE for the binary water−isooctane (BIN). VLE data for the homogeneous region are shown in Table 2. In these tables, the bubble point (t_b, °C) and the composition (mole fraction) of the liquid phases (x_i) and the vapor phase (y_i) are presented.

The ternary VLLE and VLE experimental data were tested by the point-to-point L/W Wisniak[4] method and were found to be thermodynamically consistent. All the values of L/W are between 0.94 and 1.00. Similarly, these data were tested with the McDermott−Ellis consistency test which checks thermodynamic consistency every two consecutive experimental points taken in pairs. Since the calculated D were lower than D_{max}, it can be said that all the points are consistent. Vapor pressures were calculated

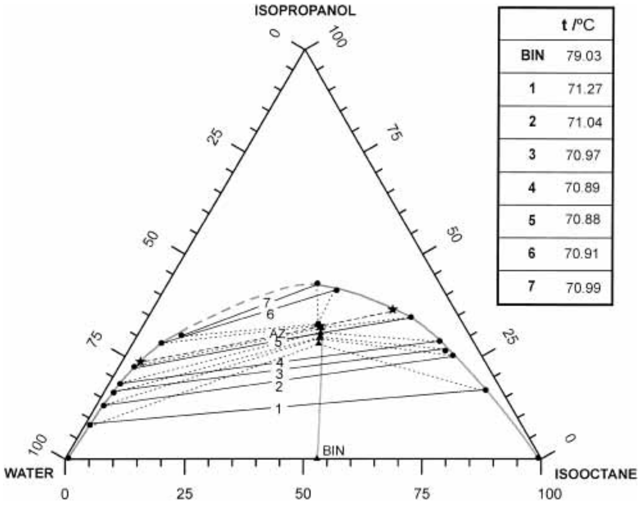

Figure 1. VLLE diagram for the ternary system Water (1) + 2-Propanol (2) + Isooctane (3) at 101.3 kPa. ●, liquid phase; ▲, vapor phase; ★, azeotrope.

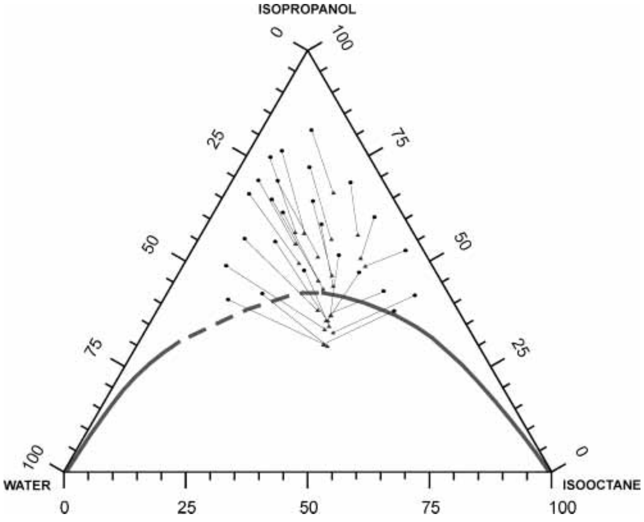

Figure 2. VLE diagram for the ternary system Water (1) + 2-Propanol (2) + Isooctane (3) at 101.3 kPa. ●, liquid phase; ▲, vapor phase.

with the Antoine equation, whose parameters A_i, B_i, and C_i for water, 2-propanol, and isooctane were taken from the literature[5] and are given in Table 3. This test does not reveal any substantial inconsistency in the data.

Figure 1 represents the graphical diagram that includes the nonisothermal binodal curve and the vapor line. This figure shows the presence of a ternary azeotrope in the heterogeneous region. The points of the vapor line corresponding to the liquid−liquid equilibrium lines 1 to 3 are above the tie line. However, the points corresponding to lines 4 and 5 are under the tie line. Therefore, there is a point between lines 3 and 4 where the composition of the vapor coincides with that of a liquid heterogeneous mixture. The composition of the ternary azeotrope determined by numerical interpolation is approximately 0.303, 0.321, and 0.376 mole fraction of water, ethanol, and isooctane, respectively, and the temperature is 70.84 °C. The composition of the two liquid phases in equilibrium is 0.74, 0.23, and 0.03 in the aqueous phase and 0.13, 0.36, and 0.51 in the organic-rich phase. This composition is similar to that reported by Kudryavtseva (azeotropic composition = 0.299, 0.334, 0.367, t = 70.38 °C) and compiled by Gmehling et al.[6] Figure 2 shows the VLE data and the nonisothermal binodal curve.

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