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Liquid−Liquid Equilibria on Three Binary Systems: Methyl Cyclopropanecarboxalate + Water; Dimethyl Sulfide + Water; and Dimethyl Disulfide + Water[†]

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Liquid−liquid equilibria are reported at each of three temperatures for the following three binary systems: methyl cyclopropanecarboxalate + water; dimethyl sulfide + water; and dimethyl disulfide + water. These data were obtained by withdrawing and analyzing multiple samples from each of the two equilibrium liquid phases at each run temperature. No previously measured liquid−liquid equilibrium data were found in the literature for any of these three binary systems.

Introduction

This work is part of an ongoing investigation of phase equilibria for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Properties, DIPPR, of the American Institute of Chemical Engineers. This paper reports measurements that have been made under Project 805/98 to obtain liquid−liquid equilibrium data on three binary systems. These systems and their measurement temperatures are as follows:

1. methyl cyclopropanecarboxalate + water at 25 °C, 50 °C, and 75 °C.
2. dimethyl sulfide + water at 5 °C, 25 °C, and 50 °C.
3. dimethyl disulfide + water at 25 °C, 50 °C, and 75 °C.

Liquid−liquid equilibria (LLE) were obtained for these systems by directly measuring the composition of each equilibrium liquid phase at each of the three measurement temperatures. No previously measured LLE data were found in the literature for any of these three binary systems.

Experimental Section

The apparatus for the LLE measurements has been described previously.[1,2] Temperatures were measured with platinum resistance thermometers that were calibrated using ice and steam points and referenced to a standard resistance thermometer with a NIST traceable calibration. Temperatures were measured with an estimated uncertainty of ± 0.05 K using the ITS-90 temperature scale.

The measurements were performed by charging the cell with approximately equal quantities of each of the two compounds of interest. The contents of the cell were vigorously stirred and allowed to come to equilibrium at the desired temperature. The cell contents were then maintained on temperature for 1 h or more, after which the stirrer was turned off.

The two liquid phases were allowed to completely separate, and the aqueous liquid sample line was purged by withdrawing liquid through the line and into a weighed, evacuated vial. Four or more samples from the aqueous phase were then withdrawn into weighed, evacuated vials. A known amount of an organic solvent was added to each vial, and the organic component was extracted into the solvent. The aqueous samples were analyzed by gas chromatography (GC) with a flame ionization detector to quantify the results. Four or more injections of the organic layer were made onto the GC, and the results were used to determine the composition of each sample. Isopropyl acetate was the solvent used for the methyl cyclopropanecarboxalate measurements while ethyl benzene was used to extract the sulfur compounds.

GC standards were prepared covering the composition ranges of interest, and these standards were injected daily in order to determine GC response factors. A minor correction was applied to account for the small amount of the organic compounds that remained in the aqueous phase. This correction was directly determined by preparing and analyzing calibration standards with and without water present. The correction was less than 0.01 g/g of methyl cyclopropanecarboxalate, less than 0.025 g/g of dimethyl sulfide and less than 0.002 g/g of dimethyl disulfide in each respective sample. The estimated uncertainty in the GC analyses of the aqueous phase is better than ± 3 % of the reported values, and the standard deviations from the replicate samples are reported with the results.

The organic liquid sample line was purged by withdrawing liquid into a weighed syringe. Four or more samples of the organic phase were withdrawn into weighed syringes and analyzed for water by Karl Fischer titration. The Karl Fischer titrant was standardized by titrating known quantities of water. This standardization was checked on a daily basis and remained constant to within ± 0.5 % of the original value during the entire period of time that these measurements were performed. The estimated uncertainty in the water analyses of the organic phase is ± 1 % of the reported values, and the standard deviations from the replicate samples are reported with the results.

Results and Discussion

The results of the LLE measurements are reported in Tables 1 through 3. These tables list the system temperature and the

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Table 1. Liquid−Liquid Equilibrium Measurements on Methyl Cyclopropanecarboxalate (A) + Water (B)

		mass composition		mole composition	
t/°C	phase[a]	$100w_A$	$100w_B$	$100x_A$	$100x_B$
25.0	organic	97.584 ± 0.005	2.416 ± 0.005	87.905 ± 0.024	12.095 ± 0.024
	aqueous	3.559 ± 0.008	96.441 ± 0.008	0.660 ± 0.002	99.340 ± 0.002
50.0	organic	96.708 ± 0.003	3.292 ± 0.003	84.090 ± 0.012	15.910 ± 0.012
	aqueous	3.267 ± 0.013	96.733 ± 0.013	0.604 ± 0.003	99.396 ± 0.003
75.0	organic	95.553 ± 0.013	4.447 ± 0.013	79.451 ± 0.051	20.549 ± 0.051
	aqueous	3.432 ± 0.007	96.568 ± 0.007	0.635 ± 0.001	99.365 ± 0.001

[a] The organic phase was the upper liquid, and the aqueous phase was the lower liquid.

Table 2. Liquid−Liquid Equilibrium Measurements on Dimethyl Sulfide (A) + Water (B)

		mass composition		mole composition	
t/°C	phase[a]	$100w_A$	$100w_B$	$100x_A$	$100x_B$
5.0	organic	99.728 ± 0.001	0.272 ± 0.001	99.067 ± 0.005	0.933 ± 0.005
	aqueous	2.428 ± 0.037	97.572 ± 0.037	0.716 ± 0.011	99.284 ± 0.011
25.0	organic	99.566 ± 0.002	0.434 ± 0.002	98.519 ± 0.007	1.481 ± 0.007
	aqueous	2.169 ± 0.029	97.831 ± 0.029	0.639 ± 0.009	99.361 ± 0.009
50.0	organic	99.258 ± 0.001	0.742 ± 0.001	97.488 ± 0.005	2.512 ± 0.005
	aqueous	2.073 ± 0.017	97.927 ± 0.017	0.610 ± 0.005	99.390 ± 0.005

[a] The organic phase was the upper liquid, and the aqueous phase was the lower liquid.

Table 3. Liquid−Liquid Equilibrium Measurements on Dimethyl Disulfide (A) + Water (B)

		mass composition		mole composition	
t/°C	phase[a]	$100w_A$	$100w_B$	$100x_A$	$100x_B$
25.0	aqueous	0.260 ± 0.007	99.740 ± 0.007	0.050 ± 0.001	99.950 ± 0.001
	organic	99.870 ± 0.001	0.130 ± 0.001	99.325 ± 0.004	0.675 ± 0.004
50.0	aqueous	0.316 ± 0.004	99.684 ± 0.004	0.061 ± 0.001	99.939 ± 0.001
	organic	99.753 ± 0.001	0.247 ± 0.001	98.720 ± 0.005	1.280 ± 0.005
75.0	aqueous	0.421 ± 0.013	99.579 ± 0.013	0.081 ± 0.003	99.919 ± 0.003
	organic	99.543 ± 0.004	0.457 ± 0.004	97.656 ± 0.021	2.344 ± 0.021

[a] The aqueous phase was the upper liquid, and the organic phase was the lower liquid.

Table 4. Source and Purity of Chemicals

			purity, mass %	
compound	CAS Registry No.	supplier	Wiltec analysis	supplier analysis
methyl cyclopropanecarboxalate	2868-37-3	Aldrich	99.9+	99.9
dimethyl sulfide	75-18-3	Aldrich	99.4	99.49
dimethyl disulfide	624-92-0	Aldrich	99.0[a]	99.58
water	7732-18-5	Mt. Olympus	99.9+	99.9+

[a] The value of 99.0 % is the area % obtained from the GC analysis of this compound. It should be noted that with the flame detector used for these analyses, aromatic hydrocarbons such as toluene and ethyl benzene gave responses on the order of 8 to 10 times higher than the response obtained for the sulfide. Thus, if some of the impurities were not sulfides, it is possible that the actual purity was higher than 99.0 mass %.

composition of each of the liquid phases on both a mass and a mole basis. The standard deviations obtained from the analysis of four or more replicate samples are also included in the tables. A brief description of the results of these measurements for each of the three systems follows.

1. Methyl Cyclopropanecarboxalate + Water. Results of LLE measurements on the methyl cyclopropanecarboxalate + water system at 25 °C, 50 °C, and 75 °C are shown in Table 1. This table includes the standard deviations obtained from the analysis of four or more replicate samples from each liquid phase. These deviations show the excellent repeatability that was obtained upon sampling and analyzing each liquid phase. The solubility of water in the organic phase shows a steady increase with increasing temperature while the solubility of methyl cyclopropanecarboxalate in the aqueous phase decreases from 25 °C to 50 °C and then increases between 50 °C and 75 °C.

2. Dimethyl Sulfide + Water. Liquid−liquid equilibria for dimethyl sulfide + water at 5 °C, 25 °C, and 50 °C are reported in Table 2. Standard deviations from the four or more replicate samples from each liquid phase are also reported. The solubility of water in the organic phase shows a steady increase with increasing temperature while the solubility of dimethyl sulfide in the aqueous phase decreases with increasing temperature over the reported temperature range.

3. Dimethyl Disulfide + Water. Liquid−liquid equilibria for dimethyl disulfide + water at 25 °C, 50 °C, and 75 °C are reported in Table 3 together with the standard deviations that were obtained from sampling and analyzing four or more replicate samples from each liquid phase. At the measured conditions, the density of dimethyl disulfide is higher than that of water. Thus, the upper liquid phase is the aqueous phase for this system. The solubility of water in the organic phase and the solubility of dimethyl disulfide in the aqueous phase both show a steady increase in solubility with increasing temperature at the conditions that were studied.

Ancillary Data. Table 4 lists the source and purity of the chemicals used in this study. The chemicals were thoroughly degassed before being used. Table 4 also lists the Chemical Abstracts Service Registry number for each chemical.

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Literature Cited

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