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Vapor-Liquid Equilibria in Mixtures of *o*-Methyl-cyclohexanol and *o*-Methyl-cyclohexyl Acetate from 50–296 mm Hg

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Vapor-liquid equilibrium data were measured for mixtures of *o*-methyl-cyclohexanol and *o*-methyl-cyclohexyl acetate over the pressure range 50–296 mm Hg. Vapor-pressure data for the pure components were also determined.

In a previous paper (*2*), we described an apparatus suitable for determination of vapor-liquid equilibrium of thermally sensitive materials. This paper reports the results of measurements on the system *o*-methyl-cyclohexanol–*o*-methyl-cyclohexyl acetate.

Experimental

The acetate was obtained from Laporte Industries Limited, and the alcohol from B.D.H. Ltd., UK. Each of the components was actually a mixture of cis and trans isomers. The properties of the isomers are, however, so similar that no attempt was made to separate them. Other impurities were removed by fractionation at 50 mm Hg in a 3-ft laboratory column packed with Fenske helices. The distillates were dried using a molecular sieve and contained less than 0.01 wt % of water. The refractive indices of the components are given in Table I, where they are compared with the literature values (*1*) for the cis and trans isomers. The flow still that was used in this investigation has been described previously (*2*). No changes in operational procedure were made.

The compositions of the liquid and condensed vapor samples obtained from the flow still were determined using a Perkin-Elmer Model 900 gas-liquid chromatograph. The 2-meter column contained Chromosorb W coated with Silicone fluid MS550 + Bentone 34. The system was calibrated with samples of accurately known composition. The precision of the analysis was 0.2 mol %. Under the conditions used for analysis, separate peaks corresponding to the cis and trans isomers were not detected. The compositions quoted later for both the alcohol and acetate are calculated without regard to the existence of geometric isomers.

Results

The boiling points of the pure components determined at different pressures, together with the fitted constants of the Antoine equation (*3*), are given in Table II. The root-mean-square deviations of the measured boiling-point temperatures are 0.16° for the alcohol and 0.23°C for the acetate. The still pressures could be controlled and measured to ±0.1 mm Hg.

The equilibrium vapor and liquid compositions for the binary mixture and boiling points at a series of pressures are given in Table III. Figure 1 is a plot of $y_1 - x_1$ against x_1, and the average deviation in the vapor mole

Table I. Refractive Indices (Na D-line) for o-Methyl-cyclohexanol and o-Methyl-cyclohexyl Acetate at 25°C

	This work, mixture of isomers	Arnold et al. (*1*) Cis isomer	Trans isomer
o-Methyl-cyclohexanol	1.4613	1.4620	1.4596
o-Methyl-cyclohexyl acetate	1.4365	1.4376	1.4353

Table II. Boiling-Point Temperatures and Antoine Constants for o-Methyl-cyclohexanol and o-Methyl-cyclohexyl Acetate

o-Methyl-cyclohexanol		o-Methyl-cyclohexyl Acetate	
P, mm Hg	*t*, °C	*P*, mm Hg	*t*, °C
396.6	144.6	750.0	183.5
297.6	135.5	297.5	150.8
198.7	124.8	270.8	147.8
100.0	106.6	190.6	136.8
50.0	91.6	100.0	118.5
11.2	63.5	52.9	101.9
3.95	47.3	50.0	100.5
2.82	42.4	21.5	81.9
2.15	38.9	9.7	64.9
Antoine constants			
$A = 6.8542$		$A = 7.4600$	
$B = 1293.3$		$B = 1860.4$	
$C = 159.41$		$C = 222.28$	

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Table III. Vapor-Liquid Equilibrium Data for o-Methyl-cyclohexanol(1)–o-Methyl-cyclohexyl Acetate(2)

P, mm Hg	x_1	y_1	t, °C
296.0	0.026	0.046	149.8
	0.093	0.170	148.8
	0.216	0.334	146.5
	0.394	0.518	143.0
	0.501	0.617	142.0
	0.640	0.727	140.0
	0.733	0.803	138.5
	0.910	0.936	136.6
100.0	0.027	0.060	117.9
	0.099	0.173	116.7
	0.215	0.315	114.9
	0.382	0.498	112.7
	0.498	0.605	111.5
	0.640	0.737	110.2
	0.741	0.811	109.2
	0.818	0.863	108.4
	0.913	0.933	107.4
50.0	0.028	0.046	100.0
	0.127	0.195	98.3
	0.228	0.334	96.8
	0.388	0.496	95.5
	0.496	0.587	94.6
	0.642	0.710	93.5
	0.736	0.795	93.1
	0.818	0.855	92.5
	0.914	0.929	92.2

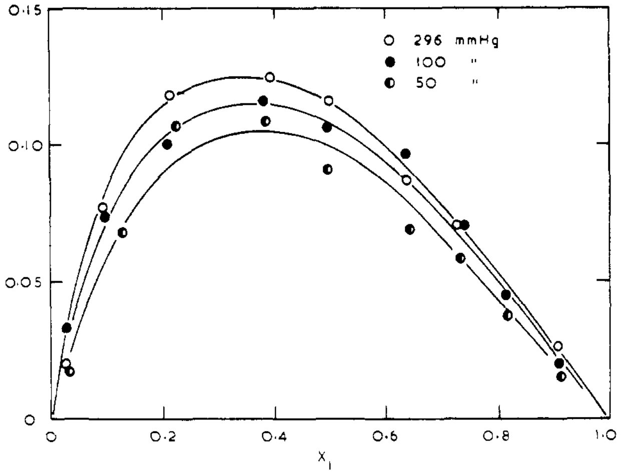

Figure 1. Equilibrium vapor and liquid compositions for o-methyl-cyclohexanol(1) and o-methyl-cyclohexyl acetate(2) at 296, 100, and 50 mm Hg

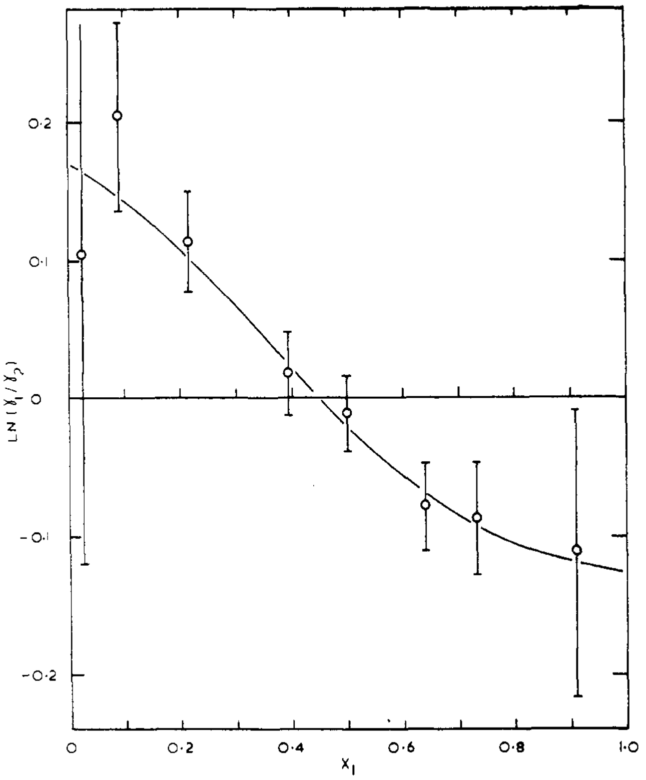

Figure 2. Thermodynamic consistency test for o-methyl-cyclohexanol(1)–o-methyl-cyclohexyl acetate(2) at 296 mm Hg

fraction is 0.005. The results have been tested for thermodynamic consistency in the usual way. Figure 2 is a plot of ln (γ_1/γ_2) against x_1 for the data at 296 mm Hg. The error bars correspond to errors of ±0.005 in the vapor and liquid mole fractions. Within these limits, the data satisfy the equal area test. The enthalpies of mixing for this system can be estimated from the temperature dependence of the activity coefficients and are too small to affect the result of the area test. Similar conclusions apply to the results at 100 and 50 mm Hg.

The deviations from ideal behavior are quite small for this system which becomes increasingly nonideal at low pressures. At 50 mm Hg, the equimolar excess Gibbs energy is 120 J mol^{-1} (t = 94.6°C). The relative volatility of the alcohol to the acetate decreases with pressure and at some pressure lower than 50 mm Hg, this system would be expected to form an azeotrope.

Nomenclature

A, B, C = Antoine constants $\cdot \log_{10} P/\text{mm Hg} = A - B/(C + t/°\text{C})$

t = Celsius temperature, °C

P = total pressure, mm Hg

y_i = vapor-phase mole fraction

x_i = liquid-phase mole fraction

γ_i = liquid-phase activity coefficient, pure liquid reference state

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