Registry No. CO_2, 124-38-9; *n*-dotriacontane, 544-85-4; *n*-docosane, 629-97-0.

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Vapor–Liquid Equilibria in Mixtures of Cyclohexane and Methyl Methacrylate

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Isothermal vapor–liquid equilibrium values were measured for mixtures of cyclohexane and methyl methacrylate at 318.12, 333.13, and 348.14 K by using a modified Dvorak and Boublik recirculating still. The experimental results were correlated with the Wilson equation by fitting the total pressure and vapor composition values. A binary azeotrope was found to exist at all three temperatures.

Introduction

An ester interchange reaction between methyl methacrylate (MMA) and higher alcohols can be carried out in the presence of a catalyst to produce higher esters. This transesterification of alcohols is usually conducted in an inert solvent, such as hexane, benzene, or cyclohexane, which can form a low-boiling azeotrope with the liberated alcohols.

The data available in the literature on the vapor–liquid equilibrium (VLE) values for mixtures of cyclohexane and MMA are limited to those reported by Frolova et al. (*1*) at 760 mmHg (101.325 kPa). It appears that these values are of uncertain quality. The purpose of this work is to establish isothermal VLE values for the mixture at three temperatures by means of a recirculating still.

Experimental Section

Chemicals. Phillips 66 Research-grade cyclohexane, supplied by the Phillips Petroleum Co., and Aldrich Analyzed-grade MMA, containing 65 ppm hydroquinone monomethyl ether, supplied by the Aldrich Chemical Co., were used without further purification. The purity of both liquids was estimated to be 99 mol % minimum. Physical constants of these materials are given in Table I. The vapor pressure data available in the literature for pure MMA are generally not in good agreement, and for this reason those that were obtained in this work were preferred.

Apparatus. Vapor–liquid equilibria were established by means of a modified Dvorak and Boublik recirculating still, whose operation has been previously described (*2*, *3*). The temperature of the equilibrium mixture was measured by using a Hewlett-Packard (Model 2801 A) quartz thermometer, which was checked at the triple point of water. The accuracy of the temperature measurement is estimated to be ±0.01 K. For pressure measurements, a Texas Instruments pressure gauge (type 144-01) together with a Bourdon Capsule (0–174 kPa) was used. This instrument was calibrated by measuring the vapor pressure of distilled and demineralized water in a Swietoslawski type ebulliometer, and checked by a mercury manometer in conjunction with a cathometer. The system pressure was controlled by a two-liquid manostat. The accuracy of the pressure measurements is estimated to be ±0.05 torr.

Analyses of the condensed vapor and liquid samples were made with an Anton-Paar K.G. (Model DMA 02A) digital densimeter with its temperature maintained at 288.15 ± 0.01 K. The accuracy of the determined composition is estimated to be ±0.002 mole fraction.

Results and Discussion

The experimentally determined equilibrium pressure, P, and liquid and vapor compositions, x and y, together with the calculated activity coefficients, γ_i, are listed in Table II.

The values of $\ln \gamma_1$ were obtained from

$$\ln \gamma_1 = \ln [y_1P/(x_1p_1^\circ)] + (B_{11} - v_1^\circ)(P - p_1^\circ)/RT + (1 - y_1)^2\delta_{12}P/RT \quad (1)$$

and similarly for $\ln \gamma_2$. In these equations

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (2)$$

and x_1 and y_1 are the equilibrium mole fractions of cyclohexane in the liquid and vapor phases at pressure P. The quantities p_i°, B_{ii}, and v_i° are the vapor pressure, second virial coefficient, and liquid molar volume of component i and B_{12} is the cross second virial coefficient. The experimentally obtained p_i° values as listed in Table I were used in the calculation. The values of v_i° for cyclohexane and MMA were taken from Timmermans (*4*) and Matheson et al. (*5*).

Since values of B_{ii} and B_{12} are not available at the three temperatures investigated, they were estimated by using the

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Table I. Physical Properties of Pure Components Used

	ρ(288.15 K), g/cm^3		molar vol, cm^3/g-mol		
	exptl	lit.	318.12 K	333.13 K	348.14 K
cyclohexane	0.7832	0.783 15 (*4*)	111.57 (*4*)	113.78 (*4*)	116.08 (*4*)
methyl methacrylate	0.9491	0.948 8 (*5*)	109.49 (*5*)	111.67 (*5*)	114.00 (*5*)

	vapor press., torr					
	318.12 K		333.13 K		348.14 K	
	exptl	lit.	exptl	lit.	explt	lit.
cyclohexane	224.24	224.62 (*6*)	388.86	388.91 (*6*)	637.32	637.32 (*6*)
methyl methacryalte	94.74	90.9 (*7*) 95.29 (*8*)	180.59	178.6 (*7*) 181.37 (*8*)	322.89	316.3 (*7*) 323.13 (*8*)

	second virial coeff, cm^3/g-mol							
	318.12 K	333.13 K	348.14 K	T_c, K	P_c, atm	V_c, cm^3/g-mol	ω	μ, D
cyclohexane	−1529.0	−1333.3	−1178.2	553.4 (*9*)	40.2 (*9*)	308.0 (*9*)	0.213 (*9*)	0.3 (*9*)
methyl methacrylate	−2260.0	−1915.8	−1650.0	554.75 (*10*)	35.8 (*10*)	332.9 (*10*)	0.330	1.675 (*11*)

empirical correlation of Tsonopoulos (*12*). The calculated B_{ii} values together with all the pure-component properties used in their calculation are also listed in Table I. It should be noted that the acentric factor that was used for MMA was that of its homomorph, 2-methylhexane (*9*). The B_{12} values obtained are −1757.7, −1520.3, and −1333.6 cm^3/g-mol for the temperatures 318.12, 333.13, and 348.14 K, respectively.

An attempt was made to detect the possible occurrence of polymerization of MMA throughout the work. The results indicate that the volatility of the shipping inhibitor is adequate for preventing the polymerization of MMA in the condensed vapor.

The thermodynamic consistency of the data was tested by the area test of Redlich-Kister (*13*). The net areas obtained were 1.2%, 0.8%, and 0.2% of the total area for the temperatures 318.12, 333.13, and 348.14 K, respectively.

The data were correlated by using the Wilson equation (*14*) where

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \quad (3)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \quad (4)$$

$$\Lambda_{12} = (v_2^\circ/v_1^\circ)\exp(-\Delta\lambda_{12}/RT)$$

$$\Lambda_{21} = (v_1^\circ/v_2^\circ)\exp(-\Delta\lambda_{21}/RT) \quad (5)$$

The quantities v_1° and v_2° are the liquid molar volumes of cyclohexane and MMA, respectively. The parameters $\Delta\lambda_{12}$ ($=\lambda_{12} - \lambda_{11}$) and $\Delta\lambda_{21}$ ($=\lambda_{12} - \lambda_{22}$) were obtained by fitting the total pressure and vapor composition with the maximum likelihood principle and are reported in Table III. The calculated y_1 and P at given T and x_1 are compared with the experimental values in Figure 1. The average absolute deviations obtained in the calculated y_1 and P values are also reported in Table III.

Using the parameter values reported in Table III, we calculated values of γ_i and compared them with the experimental values. The average absolute deviations between experimental and calculated γ_1 values, $|\Delta\gamma_1|_{av}$, are 0.01, 0.01, and 0.01 and the corresponding $|\Delta\gamma_2|_{av}$ values are 0.02, 0.01, and 0.01 for the temperatures 318.12, 333.13, and 348.14 K, respectively.

An azeotrope exists in the binary mixture at the three temperatures studied. The calculated azeotropic composition and pressure at these temperatures agree well with those obtained graphically as shown in Table IV.

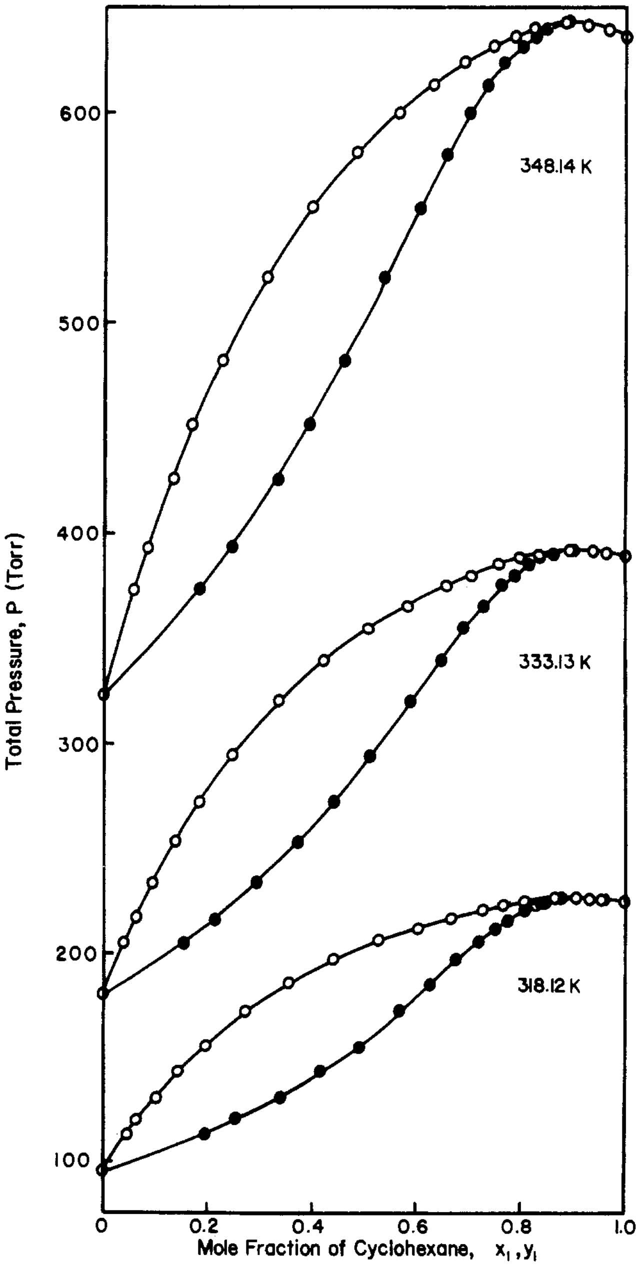

Figure 1. Comparison of calculated total pressures and vapor mole fractions with experimental results for cyclohexane (1) and methyl methacrylate (2) mixtures at three isothermal conditions.

Glossary

B_{ii}	second virial coefficient of pure component i
B_{12}	cross virial coefficient
G^E	molar excess Gibbs free energy of mixing
N	number of observations

Table II. Isothermal Vapor-Liquid Equilibrium Results for Cyclohexane (1) and Methyl Methacrylate (2)

x_1	y_1	P, torr	γ_1	γ_2
		318.12 K		
0.047	0.198	112.93	2.14	1.00
0.066	0.258	119.60	2.11	1.00
0.103	0.346	131.33	1.98	1.01
0.145	0.421	142.91	1.86	1.02
0.197	0.494	156.21	1.76	1.03
0.273	0.569	171.66	1.60	1.07
0.357	0.630	185.60	1.47	1.12
0.443	0.680	196.53	1.35	1.18
0.529	0.722	205.63	1.25	1.27
0.605	0.753	211.73	1.18	1.38
0.671	0.782	216.63	1.13	1.50
0.731	0.810	220.13	1.09	1.62
0.771	0.831	222.15	1.07	1.71
0.807	0.849	223.78	1.05	1.82
0.867	0.882	225.76	1.02	2.09
0.907	0.912	226.34	1.01	2.23
0.935	0.933	225.98	1.01	2.43
0.956	0.953	225.71	1.00	2.51
0.964	0.961	225.53	1.00	2.55
		333.13 K		
0.039	0.152	204.63	2.08	1.00
0.061	0.215	216.56	1.99	1.00
0.094	0.291	232.93	1.88	1.00
0.137	0.372	253.03	1.79	1.01
0.183	0.441	271.90	1.70	1.02
0.247	0.510	294.15	1.57	1.05
0.335	0.587	319.52	1.45	1.09
0.421	0.644	339.28	1.34	1.14
0.506	0.688	354.70	1.24	1.22
0.581	0.726	365.94	1.18	1.30
0.656	0.762	375.61	1.12	1.41
0.702	0.785	380.39	1.09	1.49
0.756	0.815	385.93	1.07	1.59
0.798	0.836	388.24	1.05	1.72
0.833	0.860	390.31	1.04	1.78
0.893	0.900	391.87	1.02	1.99
0.937	0.933	391.50	1.00	2.27
0.963	0.958	390.75	1.00	2.41
		348.14 K		
0.058	0.183	372.68	1.88	1.00
0.084	0.245	393.26	1.83	1.00
0.132	0.333	426.37	1.71	1.01
0.168	0.393	451.79	1.68	1.01
0.227	0.460	482.33	1.55	1.03
0.311	0.537	521.63	1.42	1.07
0.399	0.604	554.20	1.32	1.11
0.483	0.658	581.20	1.25	1.17
0.562	0.700	599.83	1.18	1.25
0.631	0.735	613.38	1.12	1.34
0.689	0.768	623.62	1.09	1.41
0.746	0.801	631.84	1.07	1.50
0.786	0.824	636.53	1.05	1.59
0.824	0.849	639.92	1.03	1.66
0.882	0.888	643.16	1.02	1.85
0.927	0.924	642.38	1.00	2.03
0.967	0.963	640.00	1.00	2.18

P	total pressure
p_i°	vapor pressure of pure component i
R	gas constant
T	absolute temperature

Table III. Wilson Parameters and Average Absolute Deviations in the Calculated y_1 and P Values

	318.12 K	333.13 K	348.14 K
$\Delta\lambda_{12}$, cal/g-mol	138.67	120.25	112.68
$\Delta\lambda_{21}$, cal/g-mol	557.01	529.03	490.85
$\lvert\Delta y_1\rvert_{av}$[a]	0.0023	0.0023	0.0019
$\lvert\Delta P\rvert_{av}$,[a] torr	0.1476	0.3190	0.4996

[a] Average deviation $\lvert\Delta X\rvert_{av} = (\sum\lvert X_{exptl} - X_{calcd}\rvert)/N$.

Table IV. Azeotropic Mole Fraction and Pressure for Cyclohexane and Methyl Methacrylate Mixtures

	azeotropic compn, mole fraction of cyclohexane		azeotropic press., torr	
temp, K	exptl	calcd	exptl	calcd
318.12	0.921	0.923	226.4	226.2
333.13	0.915	0.916	392.5	392.3
348.14	0.906	0.909	643.8	643.2

v_i°	molar volume of pure liquid i
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapor
γ_i	liquid activity coefficient of component i
Λ_{12}, Λ_{21}, $\Delta\lambda_{12}$, $\Delta\lambda_{21}$	parameters in Wilson equation
μ	dipole moment
ρ	density
ω	acentric factor

Registry No. Cyclohexane, 110-82-7; methyl methacrylate, 80-62-6.

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