Vapor-Liquid Equilibria for Ethylbenzene, Ethylcyclohexane, and Hexylene Glycol

Binary and Ternary Systems at 400 Mm. of Mercury

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COMPLETE binary vapor-liquid equilibrium data were determined for the ethylbenzene-ethylcyclohexane, ethylbenzene–hexylene glycol, and ethylcyclohexane–hexylene glycol systems at 400 mm. of mercury. The data were satisfactorily correlated by the Margules equations. Vapor-liquid equilibria for the ternary system including hexylene glycol were determined at selected concentrations and the change in relative volatility of ethylcyclohexane relative to ethylbenzene was noted. This investigation is one of a series to determine the effect of polar compounds on the relative volatility of hydrocarbons in binary and multicomponent mixtures. Houser (*2*), Lyvers (*3*), Murti (*4*), and Roberts (*7*) have completed portions of this over-all study.

APPARATUS

The equipment in which the equilibrium vapor and liquid samples were produced is the same type of modified Colburn still as that described by Haynes and Van Winkle (*1*).

Pressure was measured to within ± 0.5 mm. of mercury by a calibrated mercury manometer. The iron-Constantan thermocouple in conjunction with a Leeds & Northrup potentiometer allowed measurement of temperatures to within ± 0.1° C.

Compositions of the binary vapor and liquid samples for the ethylbenzene-cyclohexane and ethylbenzene–hexylene glycol systems were determined using Bausch & Lomb precision refractometer and a sodium *D* light source. The compositions of the ethylcyclohexane–hexylene glycol systems were determined by density measurements at 25° C. using a pycnometer.

MATERIALS AND PROCEDURE

The hydrocarbons and glycol were purified by distillation to satisfactory purity as indicated by the comparative experimental and literature values shown in Table I.

The procedures for evaluating vapor-liquid equilibrium data for the three binary systems were essentially those described by Haynes and Van Winkle (*1*). In determining the ternary data, binary hydrocarbon mixtures were prepared in volume ratios of 75 to 25, 50 to 50, and 25 to 75 of ethylbenzene to ethylcyclohexane. To these mixtures hexylene glycol was added in the volume ratios of 1 to 1, 3 to 1, and 5 to 1 volumes of hexylene glycol to volume of hydrocarbon mixture. These mixtures were subjected to equilibrium distillation in the Colburn still and the vapor and liquid samples obtained. Each of the vapor and liquid samples was extracted with water to remove the glycol. After the hydrocarbon phase was dried, composition of the phase with respect to ethylbenzene and ethylcyclohexane was determined by means of refractive index.

DISCUSSION OF RESULTS

Activity coefficients for the components in the binary mixtures were computed from the experimental data by the relation

$$\gamma = \frac{\nu y P_T}{xP} \qquad (1)$$

where

γ = activity coefficient
ν = fugacity coefficient
y = mole fraction in vapor phase
x = mole fraction in liquid phase
P_T = total pressure
P = vapor pressure

The fugacity coefficients for the components were essentially unity in all cases.

The temperature, vapor and liquid composition data, and activity coefficient data for the three binaries are reported in Table II and shown graphically in Figures 1 to 3. The

Table I. Properties of Materials

	Ethylbenzene		Ethylcyclohexane		Hexylene Glycol	
Index of refraction	Exptl.	Lit. (*8*)	Exptl.	Lit. (*8*)	Exptl.	Lit. (*9*)
n_D^{30}	1.49042	1.49042	1.42831	1.42861	1.42418	
n_D^{20}	1.49580	1.49588	1.4330	1.4330	1.4265	1.4263
Density, d_4^{25}	0.8623	0.8626	0.7835	0.7839	0.9152	0.9157
B. pt., 400 mm., ° C.	113.9	113.9	109.2	109.2	177.2	177.19
Antoine constants		6.95719		6.78041		7.8876
A		1424.255		1384.036		1890.38
B		213.206		215.128		180.46
C						

where $\log P = A - B/C + t$; P = mm. Hg., t = ° C.

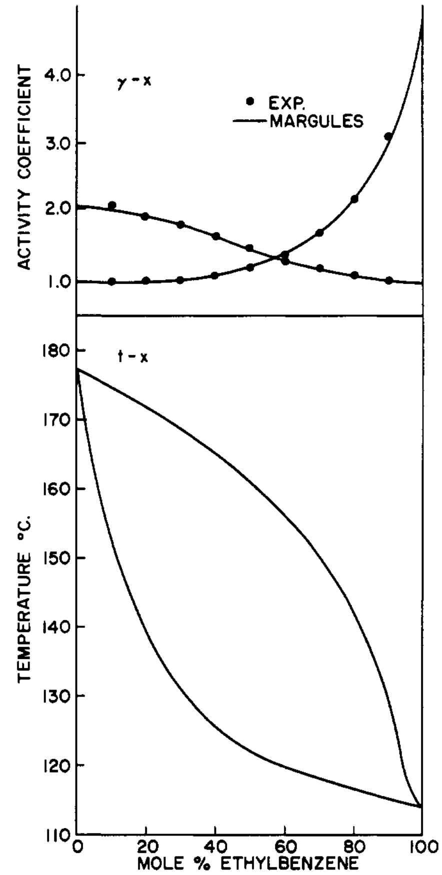

Figure 1. Ethylbenzene–hexylene glycol at 400 mm. of mercury

tendency shown by the ethylcyclohexane-ethylbenzene system is similar to that shown by the benzene-methylcyclohexane system reported by Myers (*5*).

The data were correlated by the Margules equations,

$$\log \gamma_1 = z_2^2\left[A + 2z_1\left(B\frac{q_1}{q_2} - A\right)\right] \tag{2a}$$

$$\log \gamma_2 = z_1^2\left[B + 2z_2\left(A\frac{q_2}{q_1} - B\right)\right] \tag{2b}$$

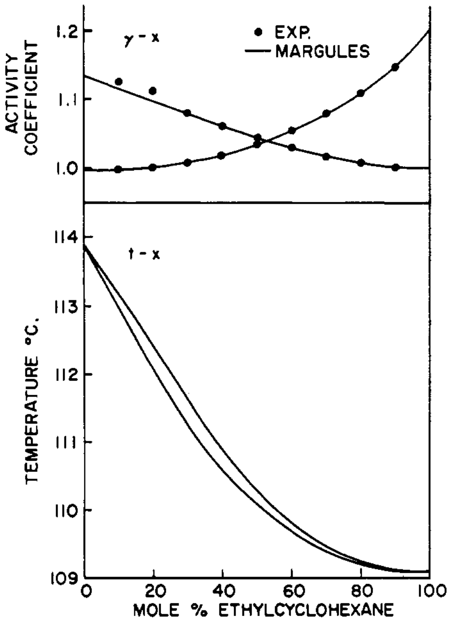

Figure 2. Ethylcyclohexane-ethylbenzene at 400 mm. of mercury

It was assumed that $q_1/q_2 = V_1/V_2$, the ratio of the molal volumes at the temperature of the equilibrium. The values of q_1/q_2 and A and B for the different binaries were as follows

	EB(2)-ECH(1)	ECH(1)-HG(3)	EB(2)-HG(3)
q_1/q_2	1.17	1.1	1.05
A	0.053	0.3	0.3
B	0.077	0.85	0.69

The average deviations of the calculated activity coefficients for the components in the binary mixtures from the experimental coefficients were: ethylbenzene-ethylcyclohexane, 0.5%; ethylbenzene-hexylene glycol, 2.0%; and ethylcyclohexane-hexylene glycol, 2.0%.

Table II. Binary Vapor Liquid Equilibria at 400 Mm. of Mercury

	Experimental		Calculated (Margules)			
Temp., ° C.	x_{EB}	y_{EB}	x_{EB}	y_{EB}	γ_{EB}	γ_{HG}
	Ethylbenzene–Hexylene Glycol					
177.2	0	0	0	0	2.08	1.00
154.2	0.1	0.64	0.1	0.61	2.02	1.00
139.8	0.2	0.82	0.2	0.82	1.95	1.01
130.6	0.3	0.89	0.3	0.89	1.83	1.03
125.3	0.4	0.92	0.4	0.93	1.66	1.09
122.0	0.5	0.94	0.5	0.94	1.48	1.19
119.7	0.6	0.945	0.6	0.942	1.32	1.37
118.0	0.7	0.952	0.7	0.944	1.19	1.69
116.6	0.8	0.96	0.8	0.946	1.09	2.19
115.2	0.9	0.973	0.9	0.96	1.02	3.11
113.9	1.0	1.00	1.0	1.00	1.00	4.84
	Ethylcyclohexane-Ethylbenzene					
	x_{ECH}	y_{ECH}	x_{ECH}	y_{ECH}	γ_{ECH}	γ_{EB}
113.9	0	0	0	0	1.13	1.0
113.04	0.1	0.13	0.1	0.13	1.12	1.00
112.11	0.2	0.24	0.2	0.24	1.10	1.00
111.26	0.3	0.35	0.3	0.35	1.08	1.01
110.6	0.4	0.45	0.4	0.45	1.06	1.02
110.1	0.5	0.54	0.5	0.54	1.05	1.03
109.7	0.6	0.63	0.6	0.63	1.03	1.05
109.4	0.7	0.72	0.7	0.72	1.02	1.08
109.22	0.8	0.81	0.8	0.81	1.01	1.11
109.14	0.9	0.90	0.9	0.90	1.00	1.15
109.1	1.0	1.0	1.0	1.00	1.00	1.20
	Ethylcyclohexane–Hexylene Glycol					
	x_{ECH}	y_{ECH}	x_{ECH}	y_{ECH}	γ_{ECH}	γ_{HG}
177.2	0	0	0	0	2.00	1.00
143.6	0.1	0.76	0.1	0.57	2.23	1.00
128.6	0.2	0.88	0.2	0.79	2.25	1.00
120.8	0.3	0.93	0.3	0.90	2.13	1.02
116.1	0.4	0.95	0.4	0.93	1.89	1.08
113.4	0.5	0.96	0.5	0.93	1.64	1.21
112.0	0.6	0.97	0.6	0.94	1.43	1.44
111.2	0.7	0.97	0.7	0.94	1.25	1.87
110.5	0.8	0.97	0.8	0.94	1.12	2.63
109.7	0.9	0.97	0.9	0.94	1.03	4.11
109.1	1.0	1.00	1.0	1.00	1.00	7.08

The Redlich-Kister consistency test (*6*) was applied to the activity coefficient–composition data of the binaries; the discrepancy in areas above and below the ordinate ($\log \gamma_1/\gamma_2 = 0$) was 4, 4, and 3% for the three systems.

In the case of the ternary system, because the samples were extracted with water, it was necessary to determine whether the glycol-free hydrocarbon concentration changed because of different solubilities of the hydrocarbon components in water. Laboratory tests as well as solubilities reported in the literature indicated this effect to be negligible.

Figure 4 shows the relative volatility of ethylcyclohexane relative to ethylbenzene to be at a maximum where the volumetric ratio of hexylene glycol to hydrocarbon is unity.

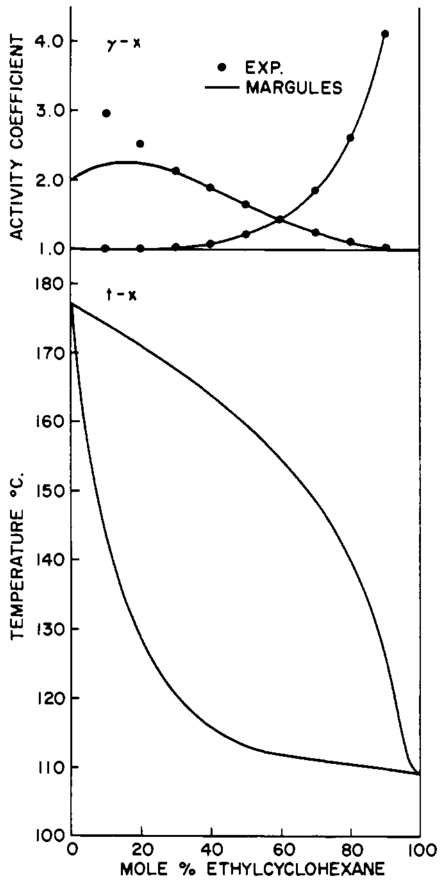

Figure 3. Ethylcyclohexane–hexylene glycol at 400 mm. of mercury

At a volumetric ratio of 5 to 1 the relative volatilities are approaching those of the original glycol-free mixture. Table III contains the ternary equilibrium data.

The maxima evidenced by the curves on Figure 4 are somewhat unusual. Usually increasing the proportion of the solvent in the mixture tends to increase the relative volatility of one of the original binary components relative to the other when the solvent has a marked affinity for only one of the components. The data were rechecked and the original data were reproduced within the limits of the estimated error. Therefore, for this system the trend shown can be assumed to be valid. Further data on other similar systems are needed before definite conclusions can be reached regarding this unexpected behavior.

The sum of possible experimental errors is estimated to be approximately 1.5%.

Table III. Ternary Vapor-Liquid Equilibria at 400 Mm. of Mercury

Binary Volume, %		Volume Ratio,				
EB	ECH	HG/HC	Temp., ° C.	x_{ECH}	y_{ECH}	$\gamma_{ECH\ EB}$
25	75	0	109.4	0.70	0.72	1.12
		1	121.7	0.67	0.76	1.58
		3	155.4	0.66	0.74	1.50
		5	166.2	0.68	0.74	1.35
50	50	0	110.2	0.48	0.52	1.17
		1	125.1	0.39	0.51	1.61
		3	157.0	0.40	0.50	1.51
		5	166.8	0.40	0.48	1.36
75	25	0	112.1	0.20	0.25	1.32
		1	127.0	0.18	0.26	1.67
		3	158.0	0.18	0.25	1.52
		5	167.4	0.19	0.24	1.38

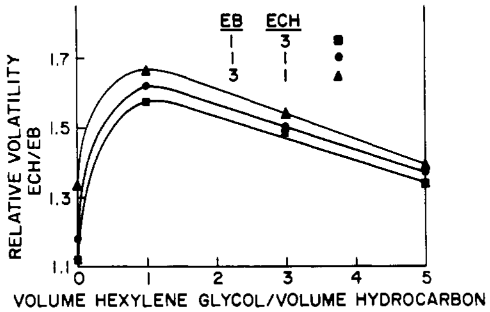

Figure 4. Solvent effect on hydrocarbon relative volatility

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