ΔC_p	difference between specific heat of the liquid and the solid, cal/(mol K)
H	molar enthalpy, cal/mol
$\bar{H}$	partial molar enthalpy, cal/mol
ΔH	heat of fusion, cal/mol
K	dimerization equilibrium constant, mmHg^{-1}
p	pressure, mmHg
R	gas constant, cal/(mol K)
T	temperature, K
v	molar volume, cm^3/mol
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
γ	activity coefficient
λ	parameters of the Wilson equation, cal/mol

Subscripts

1	relative to the solvent
2	relative to acetic acid
f	at normal melting conditions
m	relative to the monomer
s	at saturation conditions
t	at the triple point

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Effect of Morpholine on Vapor–Liquid Equilibrium of the System Methylcyclohexane–Toluene

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The effect of morpholine on the vapor–liquid equilibrium of the methylcyclohexane–toluene system is reported at 760 mmHg and molar compositions of morpholine of 0.15, 0.30, and 0.45. An increase in the relative volatility and also a small increase in the boiling temperature with respect to the binary mixture are found. Vapor–liquid equilibrium data are also reported for the benzene–methanol and methylcyclohexane–toluene binary systems. Data for the latter systems have been correlated by the Wilson equation.

Vapor–liquid equilibrium data for the methylcyclohexane–toluene system have been determined at atmospheric (*1*) and at lower pressures (*2*). Activity coefficients, at constant composition, tend to increase as pressure is reduced (*2*), and therefore separation by distillation should be easier at low pressures.

The addition of a solvent to the binary mixture modifies the vapor–liquid equilibrium and therefore the relative volatilities, making possible the separation by extractive distillation. Morpholine and its derivatives have been used as extractive solvents for the separation of aromatic and aliphatic hydrocarbons (*3*). It is the purpose of this work to study the behavior of this solvent on a mixture of an aromatic and a cyclic aliphatic hydrocarbon.

Selectivities at infinite dilution for the mixture methylcyclohexane–toluene were determined by a chromatographic technique (*4*) and results were promising enough (*5*) to carry out a study of the vapor–liquid equilibrium in the presence of morpholine as a low volatile component.

Experimental Section

Vapor–liquid equilibrium data were determined in an Othmer still (*6*), similar to an apparatus previously described (*7*). Teflon stemmed valves were used to avoid greased stopcocks. The boiling point temperature was measured within an accuracy of ±0.05 °C by using a mercury-in-glass thermometer (0.1 °C divisions) calibrated against a standard thermometer.

To avoid concentration and temperature gradients in the liquid phase, magnetic stirring was provided at the bottom of the still. A pressure of 760 mmHg was maintained by using a water column and pumping through it a small amount of dried air. The difference with atmospheric local pressure was measured with a butyl phthalate manometer.

The local pressure in the laboratory was measured by a mercury manometer and a cathetometer with an accuracy of ±0.05 mmHg. All pressures were corrected to the equivalent height of a mercury column at 0 °C and standard gravity.

The operation of the equilibrium still was checked with the binary system benzene–methanol. Analysis of vapor and liquid samples was made by measuring densities and refractive indices (PAY refractometer of the Abbe type) and by gas–liquid chromatography (Hewlett-Packard 5710, flame ionization detector). Calibration curves had been previously determined for mixtures of known composition.

Densities were measured with an Ostwald type picnometer with an accuracy estimated of ±0.0002 g/cm^3.

Refractive indices were determined with an accuracy of ±0.0001 at 25.00 ± 0.10 °C. A deviation of ±0.0001 in refractive index is equivalent to a variation of 0.002 in mole fraction.

For the ternary system studied in this work, gas chromatography was used as the analytical method, obtaining compositions by the internal standard technique. This method is insensitive to changes in sample size and makes it possible to check the composition of the extractive solvent in the liquid phase. A previous calibration of the chromatograph with benzene–methylcyclohexane–morpholine mixtures of known composition showed an accuracy in the analysis of liquid and

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Table I. Physical Properties of Pure Compounds

compound	property	exptl	lit.
benzene	n_D (25 °C)	1.4979	1.49790[a]
	ρ (25 °C)	0.8736	0.87368[a]
methylcyclohexane	n_D (25 °C)	1.4206	1.42058[a]
methanol	n_D (25 °C)	1.3266	1.32663[a]
	ρ (25 °C)	0.7866	0.78685[a]
morpholine	n_D (25 °C)	1.4525	1.45265[b]
	ρ (25 °C)	0.9954	0.99545[c]
toluene	n_D (25 °C)	1.4941	1.49413[a]

[a] Reference 15. [b] Reference 14. [c] Reference 13.

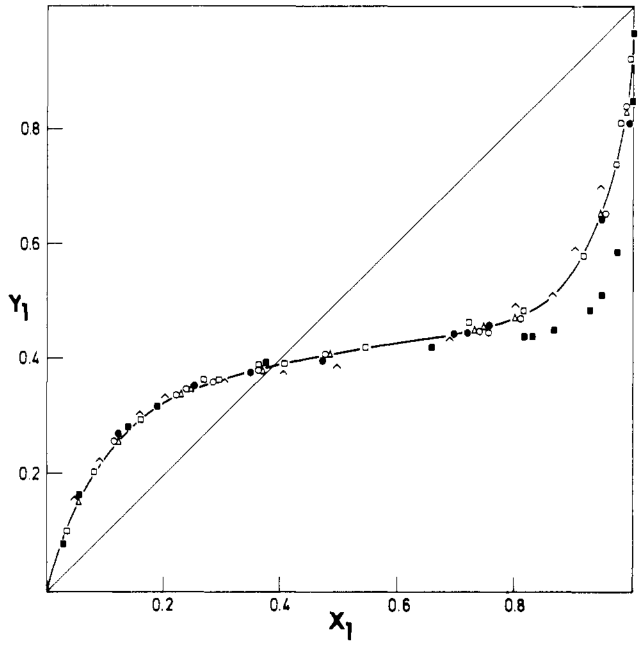

Figure 1. x-y diagram for the system benzene (1)-methanol (2) at 760 mmHg: ●, GLC; O, refractometry; Δ, picnometry; □, Ocón (*8*); Λ, Vilcu (*9*); ■, Williams (*10*).

vapor samples within ±(0.001-0.004) mole fraction, depending on the composition level.

The products used to determine vapor-liquid equilibrium data were supplied by Fluka and guaranteed 99% minimum purity. However, they were further purified by distillation in a packed column of the Oldershaw type. The products were kept out of contact with moisture by using burets provided with a reservoir at the top and fitted to silica gel tubes. Some of the physical properties of the pure compound are shown in Table I.

Gas chromatographic analysis showed no detectable impurities. The column used in gas chromatography analysis for benzene, methanol, and its mixtures was stainless steel (180 × 0.32 cm) with 10% of UCC W982 as liquid phase on a Chromosorb W-AW support.

For methylcyclohexane, toluene, and morpholine a stainless steel column (150 × 0.64 cm) with 20% Amine 220 as liquid phase on a Chromosorb P-AW support was used.

Results and Discussion

1. Benzene-Methanol. This system has been extensively studied (*8-10*) and is therefore suitable for testing the performance of the equilibrium still used in this work. However, discrepancies are common among the different published data. Experimental data obtained in the present work are shown in Table II. In Figure 1 data reported in the literature are presented.

Results for the binary systems were checked by applying the Herington thermodynamic consistency test (*11*) to the liquid-phase activity coefficients. Activity coefficients were calculated making no corrections for the vapor-phase nonideality.

Table II. Vapor-Liquid Equilibrium Data for the System Benzene (1)-Methanol (2) at 760 mmHg

analysis by picnometry			analysis by refractometry			analysis by GLC		
x_1	y_1	T, °C	x_1	y_1	T, °C	x_1	y_1	T, °C
0.056	0.160	61.15	0.055	0.155	61.15	0.055	0.161	61.15
0.122	0.258	59.33	0.177	0.253	59.33	0.121	0.266	59.33
0.231	0.340	58.20	0.222	0.336	58.20	0.232	0.337	58.20
0.257	0.350	58.07	0.250	0.349	58.07	0.250	0.340	58.07
0.285	0.357	57.89	0.284	0.356	57.89	0.286	0.357	57.89
0.364	0.378	57.77	0.365	0.380	57.77	0.350	0.372	57.77
0.483	0.402	57.85	0.480	0.402	57.85	0.473	0.393	57.85
0.733	0.442	58.33	0.736	0.440	58.33	0.696	0.436	58.33
0.746	0.447	58.45	0.755	0.442	58.45	0.720	0.441	58.45
0.802	0.466	59.23	0.810	0.466	59.23	0.760	0.445	59.23
0.885	0.524	61.16	0.900	0.518	61.16	0.890	0.516	61.16
0.948	0.648	66.72	0.954	0.646	66.72	0.950	0.640	66.72
0.990	0.825	74.04	0.990	0.831	74.04	0.990	0.805	74.04

Table III. Parameters in the Wilson Equation for the Systems Benzene (1)-Methanol (2) and Methylcyclohexane (1)-Toluene (2)

system	$\lambda_{12} - \lambda_{11}$	$\lambda_{12} - \lambda_{22}$
benzene-methanol	213.4	1775.8
methylcyclohexane-toluene	226.0	42.5

Table IV. Parameters to Calculate Molar Volumes as a Function of Temperature[a]

compound	a	b	c
benzene	70.85	0.0149	0.000 159
methanol	64.49	−0.197	0.000 387
methylcyclohexane	84.195	0.143	0.000 017
toluene	76.13	0.143	0.000 011

[a] Reference 12.

Table V. Vapor-Liquid Equilibrium Data for the System Methylcyclohexane (1)-Toluene (2) at 760 mmHg

x_1	y_1	T, °C	γ_1	γ_2	Δy
0.066	0.108	108.70	1.359	1.009	0.0021
0.163	0.234	106.85	1.254	1.020	0.0021
0.222	0.304	105.90	1.227	1.025	0.0072
0.306	0.393	104.90	1.183	1.032	0.0122
0.382	0.470	104.15	1.157	1.035	0.0196
0.475	0.553	103.35	1.120	1.052	0.0228
0.555	0.615	102.77	1.083	1.088	0.0189
0.631	0.676	102.26	1.062	1.121	0.0188
0.717	0.747	101.78	1.047	1.157	0.0204
0.783	0.804	101.45	1.043	1.176	0.0249
0.803	0.825	101.31	1.046	1.167	0.0297
0.850	0.866	101.15	1.042	1.179	0.0310
0.928	0.935	100.91	1.037	1.200	0.0328

Wilson equation parameters were calculated following the method described by Holmes-van Winkle (*12*) and results are shown in Table III.

Liquid molar volumes, to obtain parameters Λ_{ik} in the Wilson equation, were calculated by the equation

$$V_i^L = a + bT + cT^2$$

Parameters a, b, and c are shown in Table IV.

The composition and temperature of the azeotrope are in fairly good agreement with data reported by Williams (*10*) and Ocón et al. (*8*). The maximum discrepancy in the data obtained by the three methods of analysis used in this work is no higher than 1% in moles.

2. Methylcyclohexane-Toluene-(Morpholine). Vapor-liquid equilibrium results for the binary system methylcyclohexane-toluene are presented in Table V; the analysis of the vapor and liquid phases was made by refractometry. Activity coefficients are shown in Table V and Wilson parameters in Table III.

In Table V values of Δy are shown for the system methylcyclohexane-toluene. The agreement between experimental

Table VI. Vapor-Liquid Equilibrium Data for the System Methylcyclohexane (1)-Toluene (2) at 760 mmHg in the Presence of Morpholine

morpholine 15%			morpholine 30%			morpholine 45%		
x_1*	y_1*	T, °C	x_1*	y_1*	T, °C	x_1*	y_1*	T, °C
0.131	0.207	108.60	0.111	0.201	109.72	0.131	0.259	111.23
0.208	0.283	107.40	0.166	0.277	108.65	0.235	0.371	109.95
0.260	0.348	107.00	0.237	0.358	107.50	0.265	0.391	109.30
0.287	0.373	106.23	0.292	0.418	106.55	0.329	0.479	108.30
0.307	0.391	106.22	0.340	0.476	105.70	0.410	0.555	106.75
0.335	0.434	105.40	0.392	0.532	105.05	0.477	0.618	105.85
0.395	0.505	104.75	0.462	0.592	104.35	0.567	0.680	104.75
0.436	0.531	104.07	0.462	0.586	104.35	0.625	0.742	104.15
0.454	0.562	103.65	0.536	0.656	103.65	0.719	0.813	103.30
0.491	0.574	103.35	0.612	0.715	102.95	0.781	0.863	102.85
0.520	0.590	103.30	0.720	0.793	102.30	0.851	0.902	102.50
0.551	0.644	102.90	0.827	0.875	101.65	0.893	0.924	102.15
0.572	0.645	102.65	0.900	0.930	101.20			
0.631	0.699	102.20						
0.713	0.772	101.65						
0.814	0.851	101.05						
0.895	0.918	101.04						

Table VII. Effect of Morpholine on the Relative Volatilities of the System Methylcyclohexane-Toluene

morpholine x_S	0.0	0.15	0.30	0.45
$\bar{\alpha}_{12}$	1.33	1.45	1.69	1.78

and calculated vapor-phase compositions can be considered quite satisfactory.

Vapor-liquid equilibrium data for the ternary system have been obtained under conditions of constant concentration of morpholine. The still was charged with methylcyclohexane and toluene, and morpholine was added to obtain the desired initial composition. Before starting every new experiment, the composition of the mixture was adjusted so that morpholine would be at the established composition. Results, on solvent-free basis, for constant molar concentration of 15, 30, and 45% of morpholine are shown in Table VI.

The effect of morpholine as an extractive solvent is shown in Figure 2, where equilibrium data are represented on a solvent-free basis. An increase of morpholine concentration makes the relative volatilities α_{12} increase; average values of α_{12} are shown in Table VII.

From the former results it can be concluded that morpholine could be use as an extractive solvent for the separation by distillation of mixtures of methylcyclohexane-toluene. Although there is a remarkable increase in α_{12}, particularly at $x_S = 0.30$, morpholine does not increase the boiling point of the mixture too much, only 1 °C for equimolecular mixtures of methylcyclohexane and toluene at $x_s = 0.30$ and less then 3 °C for $x_S = 0.45$ on the same conditions.

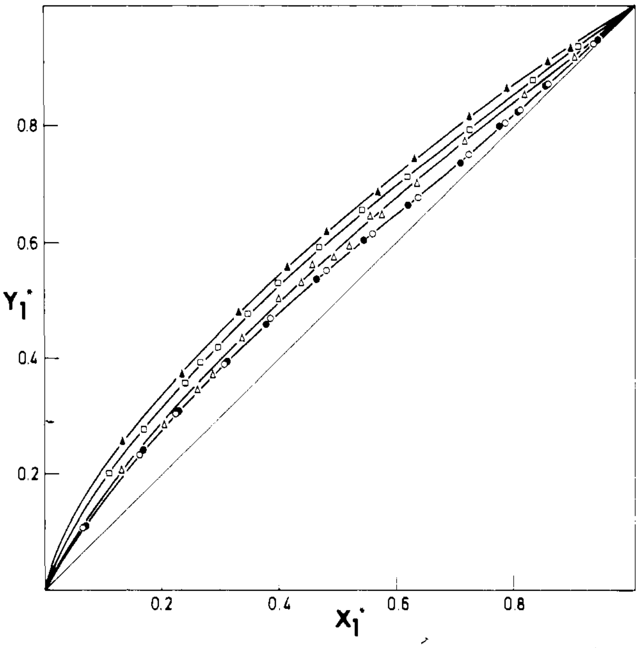

Figure 2. x-y diagram for the system methylcyclohexane (1)-toluene (2)-(morpholine) at 760 mmHg (solvent-free basis): ○, $x_S = 0$ (refractometry); ●, $x_S = 0$ (GLC); △, $x_S = 0.15$; □, $x_S = 0.30$; ▲, $x_S = 0.45$.

Glossary

a, b, c	parameters in the molar volume equation
n_D	refractive index
T	temperature, °C or K
V_i^L	liquid molar volume of the "ith" component, cm^3/g-mol
x_i	liquid mole fraction of the "ith" component
x_i*	liquid mole fraction of the "ith" component on solvent-free basis
x_S	liquid mole fraction of the solvent
y_i	vapor mole fraction of the "ith" component
y_i*	vapor mole fraction of the "ith" component on solvent-free basis
Δy	difference between calculated and experimental vapor composition
α_{ij}	relative volatility
$\bar{\alpha}_{ij}$	mean relative volatility
Λ_{ij}	Wilson parameter
γ_i	activity coefficient of the "ith" component
$\lambda_{ij} - \lambda_{ii}$, $\lambda_{ij} - \lambda_{jj}$	parameters in the Wilson equation, cal/g-mol
ρ	density, g/cm^3

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