and $P_{Hg}°$ is the vapor pressure of pure mercury at the temperature, T, under study. P_{Hg} is the mercury vapor pressure at the temperature, T, under study. The variations of the activity coefficient with the temperature are within the range of the precision of the measurements:

$$\left(\frac{\Delta\nu_{Hg}}{\nu_{Hg}} \simeq 1\text{-}2\%\right)$$

The values of γ_{Hg} are indicated in Table II. For the solid liquid phase, we used the liquidus curve given by Ito et al. (*5*). The activity coefficient of mercury in the presence of indium can be considered as independent of the temperature in the range of temperature studied. On the other hand, the dependence as regards the concentration of indium is important and the mercury-indium amalgams deviate negatively from ideality.

CONCLUSION

The method used has allowed the determination of the mercury vapor pressure of mercury above the indium amalgams with an accuracy at least equal to that of the absorption method. However, under the experimental conditions chosen here, the measuring field is more limited. These results allow the calculation of the temperatures of the walls corresponding to the maximum luminous efficiency of fluorescent lamps containing an indium amalgam. For example, a 60-W fluorescent lamp, with an incorporated amalgam of 80% indium, has an optimum mercury temperature of 87°C, whereas the measured value is 84.5°C.

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NOMENCLATURE

M = molecular mass, grams
m = effused mass, grams
P = vapor pressure, Baryes or torr
R = universal gas constant, $8.31 \cdot 10^7$ erg/K
S = area of the effusion opening, cm^2
t = time, sec
T = temperature, K

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Vapor-Liquid Equilibrium Data for Systems Ethylbenzene—Anisole and *p*-Xylene—Anisole

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Isobaric vapor-liquid equilibrium data were obtained for the binary systems ethylbenzene—anisole and *p*-xylene—anisole at 760 mm of Hg pressure. The *t-x-y* data for these systems were tested for thermodynamic consistency. The experimental phase compositions were compared with those calculated by Raoult's law

This work forms part of a program on the evaluation of nonideality characteristics for mixtures of close-boiling hydrocarbons and other types of compounds. Vapor-liquid equilibrium data were determined for the systems ethylbenzene-anisole and *p*-xylene-anisole at 760 mm of Hg pressure.

EXPERIMENTAL

Materials. Ethylbenzene, laboratory reagent grade, obtained from British Drug Houses, Poole, England; *p*-xylene, pure grade, obtained from Riedel-De Haen AG, Seelze-Hannover, Germany; and anisole, pure grade, obtained from W. G. Bush and Co., London, were dried over anhydrous calcium chloride and further purified by distillation in a 30-mm glass column packed to a height of 1 meter with 4-mm helices made from Nichrome wire. The column was provided with an air jacket and a 125-W heater to minimize heat losses and run at total reflux for 30 min, and the low-boiling impurities were drawn off as rejects at a very low rate. When the desired boiling temperature was attained and remained constant for 15 min, the fraction was collected and near total reflux conditions were maintained until the contents of the distillation flask were reduced to about one

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fifth of the original charge. Adequate precautions were taken to minimize moisture absorption by the materials. Table I summarizes some of the physical properties of the compounds employed.

Apparatus and Analytical Techniques. A modified version of the equilibrium still with circulating vapor phase described by Rao and co-workers (*15*) was used for the determination of the vapor-liquid equilibrium data. The data were obtained at 760 ± 1.0 mm of Hg pressure. Fluctuations in the pressure were minimized by the use of ballast vessels having a total volume of about 35 liters. Fine control was achieved by the use of a needle valve. An open mercury manometer was used to measure the pressure which is read by means of a magnifying lens. Temperatures were measured by means of standard Anschutz short-range thermometers with an accuracy of ±0.1°C. These thermometers were calibrated against another precision mercury thermometer calibrated by checking at the ice point and normal boiling point of distilled water. Stem corrections for the exposed mercury column were applied. Absorption of moisture into the systems was prevented by using sulfuric acid bubblers and calcium chloride U-tubes in the air supply system.

The equilibrated mixtures were analyzed by the density method, using pycnometers calibrated with distilled water. An Ultra Thermostat with a mercury thermoregulator was used to maintain the samples at 30 ± 0.1°C for a minimum period of 20 min before filling into the pycnometers maintained at the same temperature. The accuracy of the density measurements was of the order of ±0.0003 g/cm^{-3}. Table II gives the density-composition data. Figures 1 and 2 represent the boiling point-composition diagrams for the two systems, ethylbenzene-anisole and *p*-xylene-anisole, respectively.

Table I. Physical Properties of Materials

		Anisole	Ethylbenzene	*p*-Xylene
Mol wt		108.13	106.16	106.16
Normal bp, °C	Exptl	153.50	135.85	138.21
	Lit	153.75 (*3*)	136.19 (*6*)	138.35 (*6*)
Refractive index, 30°C	Exptl	1.5160	1.4922	1.4904
	Lit	...	1.4905 (*6*)	1.4905 (*6*)
Density, 30°C	Exptl	0.9829	0.8599	0.8539
	Lit	...	0.8583 (*6*)	0.8525 (*6*)

Table II. Density-Composition Data at 30°C

Ethylbenzene–anisole system		*y*-Xylene–Anisole system	
Mole fraction ethylbenzene	Density	Mole fraction *p*-xylene	Density
0.0000	0.9829	0.0000	0.9829
0.0434	0.9764	0.0474	0.9761
0.0956	0.9690	0.0890	0.9704
0.1363	0.9628	0.1390	0.9629
0.1754	0.9572	0.1823	0.9563
0.2256	0.9523	0.2323	0.9501
0.2733	0.9449	0.2725	0.9432
0.3281	0.9377	0.3244	0.9361
0.3631	0.9335	0.3599	0.9317
0.4202	0.9266	0.4202	0.9225
9.4741	0.9202	0.4646	0.9179
0.5127	0.9142	0.5210	0.9091
0.5728	0.9075	0.5680	0.9037
0.6173	0.9022	0.6197	0.8976
0.6788	0.8957	0.6782	0.8895
0.7299	0.8884	0.7307	0.8825
0.7700	0.8855	0.7759	0.8768
0.8312	0.8781	0.8340	0.8703
0.8880	0.8709	0.8851	0.8640
0.9433	0.8649	0.9402	0.8575
1.0000	0.8599	1.0000	0.8539

RESULTS AND DISCUSSION

The liquid phase activity coefficients were calculated from the experimental data using Equation 1 (*9*):

$$\gamma_i = \pi y_i / P_i^0 x_i \exp \left[(\pi - P_i^0)(B_i - V_i)/RT \right] \qquad (1)$$

Antoine's equation (*2*) was used to represent the vapor pressure data for the pure components. It gave the following average absolute deviations when compared with the literature data:

Compound	Temp range, °C	Av abs dev, mm of Hg	Data sources
Anisole	123–156	12.51	(*3, 7, 13, 16*)
Ethylbenzene	79–167	2.06	(*1, 4, 5, 18*)
p-Xylene	80–167	0.18	(*1, 5, 6, 16*)

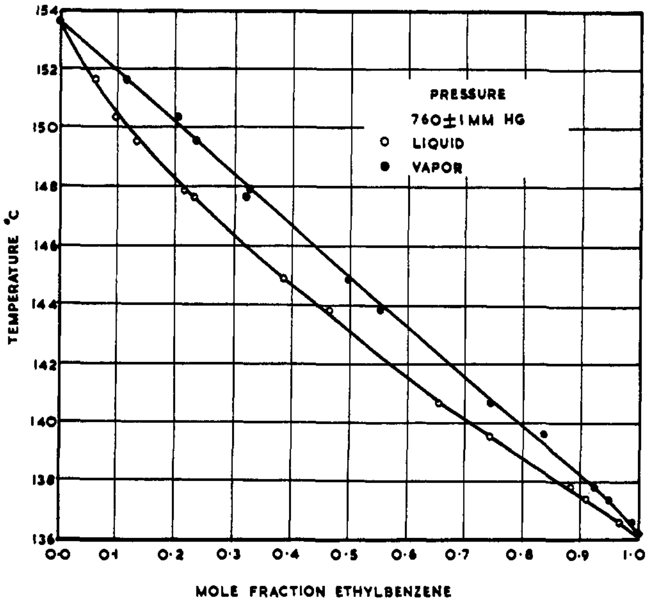

Figure 1. Temperature-composition diagram for ethyl benzene–anisole system

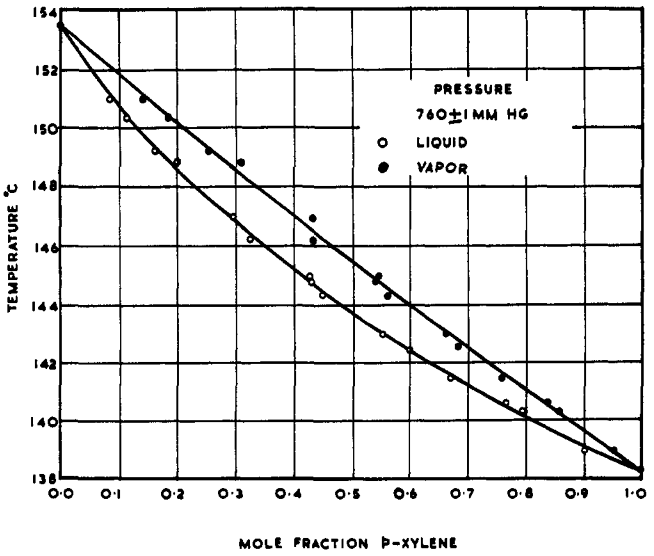

Figure 2. Temperature-composition diagram for *p*-xylene–anisole system

The gas phase second virial coefficients for ethylbenzene and *p*-xylene were estimated by the correlation of Pitzer and Curl (*14*) and for anisole by the correlation of O'Connell and Prausnitz (*11*). Liquid molar volumes were estimated by the method of Yen and Woods (*19*). The exponential term in Equation 1, which represents the vapor phase imperfection, was found to be close to unity for both the systems. A maximum of a 2% increase in the values of relative volatility results, if vapors are assumed to be perfect gases. In Table III, besides the *t-x-y* and activity coefficient data, the deviations of the vapor and liquid compositions, from the corresponding Raoult's law values, are given for these systems which indicate that these deviations are not appreciable, the average deviations being 0.018 mol fraction in x and 0.023 mol fraction in y for the ethylbenzene-anisole system and 0.028 in x and 0.033 in y for the *p*-xylene-anisole system.

The *t-x-y* data for these systems have been tested for thermodynamic consistency by applying the following form of the Gibbs-Duhem equation applicable to isobaric data if the vapors are regarded as perfect gases (*8, 10, 12*)

$$\frac{x - y}{y(1 - y)}\left[\frac{dy}{dt}\right]_{\pi} = \frac{h^E}{RT^2} \tag{2}$$

The left-hand side of Equation 2 was estimated from the *t-x-y* data obtained experimentally. The h^E term on the right-hand side of the equation was calculated from a knowledge of the pure component heats of vaporization at the normal boiling points using the following equation which assumes ideal mixture vaporization enthalpy:

$$h^E = x_1 h_{v_1} + x_2 h_{v_2} \tag{3}$$

The heats of vaporization at the system temperatures were estimated from those at the normal boiling points, using the Watson correlation (*17*). Table IV gives the results obtained in this test for the two systems. The deviations are not high for values of x in the middle concentration region indicating that the data are acceptably consistent within the bounds of the assumptions made in the calculations, namely, the vapor phase was regarded as a perfect gas and the molar average heats of vaporization were used in place of the partial molar average heats of vaporization.

Table III. Vapor-Liquid Equilibrium Data at 760 ± 1.0 Mm of Hg Pressure

t, °C	x_1	y_1	$x_1 - x_1^{*a}$	$y_1 - y_1^{*a}$	γ_1	γ_2
System Ethylbenzene (1)–Anisole (2)						
151.58	0.063	0.115	−0.015	0.022	1.263	1.002
150.34	0.095	0.205	−0.047	0.068	1.525	0.963
149.52	0.133	0.235	−0.033	0.047	1.273	0.989
147.90	0.215	0.325	−0.025	0.033	1.132	1.006
147.67	0.232	0.320	−0.005	0.007	1.038	1.043
144.85	0.388	0.499	−0.010	0.013	1.037	1.040
143.80	0.468	0.550	0.017	−0.021	0.972	1.106
140.68	0.654	0.744	−0.007	0.007	1.016	1.055
139.55	0.744	0.837	−0.021	0.023	1.033	0.939
137.77	0.885	0.922	0.002	−0.002	1.000	1.058
137.39	0.909	0.950	−0.011	0.012	1.014	0.857
136.57	0.954	0.989	−0.025	0.025	1.027	0.397
System *p*-Xylene (1)–Anisole (2)						
151.00	0.084	0.138	−0.016	0.022	1.204	0.937
150.40	0.114	0.184	−0.021	0.028	1.202	1.008
149.19	0.162	0.252	−0.028	0.038	1.192	1.009
148.76	0.202	0.309	−0.034	0.044	1.184	0.990
146.93	0.296	0.434	−0.050	0.063	1.183	0.967
146.20	0.325	0.434	−0.028	0.035	1.098	1.028
144.98	0.428	0.547	−0.032	0.038	1.083	1.003
144.75	0.428	0.541	−0.030	0.035	1.079	1.021
144.30	0.450	0.560	−0.029	0.034	1.072	1.032
142.97	0.553	0.663	−0.034	0.038	1.068	1.010
142.40	0.600	0.680	−0.011	0.012	1.023	1.088
141.40	0.669	0.756	−0.029	0.031	1.047	1.029
140.58	0.767	0.839	−0.024	0.026	1.034	0.987
140.28	0.796	0.857	−0.018	0.019	1.025	1.012
138.88	0.900	0.950	−0.037	0.037	1.041	0.751

[a] Difference between the experimental and Raoult's law composition.

Table IV. Thermodynamic Consistency of *t-x-y* Data

t, °C	x_1	y_1	dy_1/dt	L.H.S. of Eq. 2	R.H.S. of Eq. 2	Deviation
System Ethylbenzene (1)–Anisole (2)						
151.58	0.063	0.115	−0.0074	0.0038	0.0262	−0.0224
150.34	0.095	0.205	−0.0725	0.0489	0.0263	0.0225
149.52	0.133	0.235	−0.0582	0.0330	0.0264	0.0066
147.90	0.215	0.325	−0.0570	0.0286	0.0264	0.0021
147.67	0.232	0.320	−0.0524	0.0212	0.0264	−0.0052
144.85	0.388	0.499	−0.0570	0.0254	0.0263	−0.0009
143.80	0.468	0.550	−0.0559	0.0186	0.0263	−0.0076
140.68	0.654	0.744	−0.0577	0.0273	0.0262	0.0011
139.55	0.744	0.837	−0.0600	0.0408	0.0261	0.0146
137.77	0.885	0.922	−0.0583	0.0294	0.0259	0.0034
137.39	0.909	0.950	−0.0588	0.0512	0.0259	0.0253
136.57	0.954	0.989	−0.0581	0.1791	0.0259	0.1532
System *p*-Xylene (1)–Anisole (2)						
151.00	0.084	0.138	−0.0109	0.0049	0.0263	−0.0213
150.40	0.114	0.184	−0.0758	0.0354	0.0263	0.0090
149.19	0.162	0.252	−0.0627	0.0299	0.0263	0.0035
148.76	0.202	0.309	−0.0761	0.0381	0.0263	0.0118
146.93	0.296	0.434	−0.0726	0.0406	0.0263	0.0142
146.20	0.325	0.434	−0.0616	0.0272	0.0263	0.0009
144.98	0.428	0.547	−0.0678	0.0325	0.0262	0.0063
144.75	0.428	0.541	−0.0645	0.0295	0.0263	0.0032
144.30	0.450	0.560	−0.0629	0.0281	0.0263	0.0017
142.97	0.553	0.663	−0.0653	0.0321	0.0262	0.0059
142.40	0.600	0.680	−0.0630	0.0231	0.0261	−0.0029
141.40	0.669	0.756	−0.0644	0.0305	0.0261	0.0044
140.58	0.767	0.839	−0.0672	0.0361	0.0259	0.0104
140.28	0.796	0.857	−0.0670	0.0333	0.0259	0.0074
138.88	0.900	0.950	−0.0669	0.0705	0.0258	0.0447

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NOMENCLATURE

B = gas phase second virial coefficient of pure components, cm^3 mol^{-1}
h^E = excess enthalpy of mixing, cal mol^{-1}
h_v = heat of vaporization at the system temperature, cal mol^{-1}
P^0 = vapor pressure of pure components, mm of Hg
R = gas constant
T = absolute temperature, K
t = system temperature, °C
V = liquid molar volume of pure component, cm^3 mol^{-1}
x = mole fraction in liquid phase
y = mole fraction in gas phase
x^* = mole fraction in liquid phase calculated by Raoult's law
y^* = mole fraction in gas phase calculated by Raoult's law
γ = activity coefficient
π = system pressure, mm of Hg

SUBSCRIPTS

i = component i
1 = more volatile component
2 = less volatile component

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Vapor-Liquid Equilibria

Systems 1,2-Dichloroethane–Ethylbenzene and 1,2-Dichloroethane–p-Xylene

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Vapor-liquid equilibrium data were obtained for the wide-boiling systems 1,2-dichloroethane–ethylbenzene and 1,2-dichloroethane–*p*-xylene at 735 mm of Hg pressure using a vapor recirculating type of equilibrium still. The experimental equilibrium compositions were compared with those calculated by Raoult's law. The vapor-phase nonideality was estimated and found to be moderate.

This work is part of an investigation on the evaluation of vapor-liquid equilibrium characteristics of systems involving close-boiling hydrocarbons and other compounds. Isobaric vapor-liquid equilibria at 735 mm of Hg pressure were determined for two binary systems.

EXPERIMENTAL

The purification of materials and apparatus has already been described (*2*). Table I gives the physical properties of 1,2-dichloroethane whereas the physical properties of ethylbenzene and *p*-xylene are given in Table I of ref. *2*. The atmospheric pressure during the runs remained constant at 735 mm of Hg with a variation of ±2 mm of Hg. A standard mercury barometer was used to measure the atmospheric pressure to within ±0.1 mm of Hg. Temperatures were measured by means of calibrated 24-gage copper-constantan thermocouples in conjunction with an OSAW Vernier potentiometer with an accuracy of 0.00002 V and an OSAW spot-reflecting galvanometer having a sensitivity of 0.04 to 0.05 μA per mm of scale division. The accuracy of temperature measurements was of the order of ±0.1°C.

Table I. Physical Properties of 1,2-Dichloroethane

Molecular weight		98.97
Normal bp, °C	Exptl	83.47
	Lit	83.50 (*4*)
Refractive index, 30°C	Exptl	1.4402
	Lit	......
Density, 30°C	Exptl	1.2360
	Lit	......

Table II. Refractive Index–Composition Data at 30°C

1,2-Dichloroethane–ethylbenzene system		1,2-Dichloroethane–*p*-xylene system	
Mole fraction, 1,2-dichloroethane	Refractive index	Mole fraction, 1,2-dichloroethane	Refractive index
0.0000	1.4922	0.0000	1.4904
0.0751	1.4892	0.0788	1.4876
0.1487	1.4857	0.1488	1.4850
0.2607	1.4808	0.2130	1.4822
0.2764	1.4802	0.2807	1.4791
0.3430	1.4777	0.3454	1.4763
0.4000	1.4745	0.4036	1.4732
0.4584	1.4725	0.4579	1.4707
0.5094	1.4690	0.5019	1.4681
0.5582	1.4670	0.5615	1.4655
0.6049	1.4644	0.6053	1.4634
0.6489	1.4621	0.6569	1.4608
0.7005	1.4593	0.6950	1.4584
0.7453	1.4568	0.7459	1.4559
0.7839	1.4543	0.7952	1.4529
0.8194	1.4520	0.8262	1.4513
0.8605	1.4496	0.8574	1.4491
0.8966	1.4470	0.8978	1.4467
0.9330	1.4449	0.9332	1.4445
0.9678	1.4425	0.9742	1.4414
1.0000	1.4402	1.0000	1.4402

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