J. Chem. Eng. Data 1980, 25, 107-110

Isobaric Vapor–Liquid Equilibria of the *n*-Heptane–Toluene System at Subatmospheric Pressures

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The vapor–liquid equilibria of the *n*-hepatne–toluene system were measured at 50, 100, 200, 400, and 760 mmHg. The results could be successfully correlated at least down to 50 mmHg by the Wilson equation with the parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) of 1 atm pressure but could not be very satisfactorily done by its equation with the other parameters (Λ_{12} and Λ_{21}) of the pressure.

Knowledge of the effect of pressure on vapor–liquid equilibria is important for the designing of low-pressure distillation units. The vapor–liquid equilibria of the *n*-heptane–toluene system at 1 atm pressure were measured by many researchers (*3–5*, *7*, *9*), but there are no available data below this pressure.

In this report, isobaric data on this system are measured at 50, 100, 200, 400, and 760 mmHg, and the results could be predicted by the Wilson equation (*8*).

Experimental Section

Purity of Materials. Both *n*-heptane and toluene used in this work were analytical grade (99%) and were of commercial origin.

The purifications were carried out by wetted wall column with 1-m length and 10 mm i.d. at 100 mmHg, where each purity of distillate was checked by a refractive index; however, the purities of both reagents could not be improved.

The absence of the impurities for those reagents was also checked by gas chromatography, using a 1 m long by 3 mm i.d. column with Silicon DC 500 at 160 °C.

Compared with the literature values (*6*), the average errors of both vapor pressures in the range of 100–760 mmHg were ±0.17 °C. Those physical properties were summarized in Table I.

Apparatus. A Pyrex glass vapor recirculating equilibrium still with a Cottrell pump is shown in Figure 1. The funnel of the pump does not entirely cover the liquid surface so that discharged vapor can ascend not only through the Cottrell tube but also from the outside of the pump; that is, the pump is designed to decrease the pressure drop between the surface and the condensed sections. The bottom section of the still is a cylinder of 60 mm height by 50 mm i.d., its upper section is a double cylindrical column of 220 mm height by 40 and 80 mm i.d., and a powder of diatom earth is tightly packed between the two cylinders as insulating material.

Condensation and fractionation were prevented by holding the wall temperature of the outside cylinder at 10 °C above the boiling point. About 50 mL of the mixture was poured into the bottom of the still through a ball joint near the condenser and was agitated by a magnetic stirrer at about 300 rpm, Pressure was adjusted by a needle valve, and the vapor was circulated for 2 h.

Pressures were measured by a mercury manometer with 0.3 mmHg accuracy, and their reproducibilities were within 0.4 mmHg. Temperatures were measured with a standard mercury thermometer having an accuracy of 0.02 °C and were reproducible within 0.05 °C.

The liquid and vapor samples were taken out of the apparatus through their respective stopcocks after the vacuum pump was stopped and the pressure was recovered to the atmospheric pressure. By the above mentioned gas chromatography, those compositions were analyzed, and their precisions were estimated to be within 0.003 mole fractions.

Table I. Physical Properties of Chemicals

temp, °C	density, g/cm		refractive index, n_D		pressure, mmHg	bp, °C	
	exptl	lit. (*6*)	exptl	lit. (*6*)		exptl	lit. (*6*)
			n-Heptane				
20	0.6829	0.6835	1.3870	1.3877	124.54	46.70	46.929
					261.75	65.88	65.882
					402.39	77.84	78.169
					500.66	84.72	84.823
					757.40	98.40	98.30[a]
			Toluene				
20	0.8760	0.8670	1.4960	1.4969	124.67	57.11	57.293
					217.16	71.66	71.736
					402.43	89.49	89.667
					500.68	96.37	96.559
					760.00	110.67	110.623

[a] Interpolated.

Results

The experimental results are presented in Table II. The liquid-phase activity coefficients were calculated by the expression $\gamma_i = y_iP/x_ip_i$, where the vapor pressures of pure substances p_i were obtained from the Antoine equation given by Hala et al. (*1*).

The activity coefficient–composition diagrams are described in Figures 2–6. The results at atmospheric pressure are in fair agreement with Yerazunis et al. (*9*) in Figure 2, while those for other pressures cannot be compared due to lack of available data.

Furthermore, all the results are ensured to be thermodynamically consistent by the Herington test (*2*).

Discussion

The results are represented by the following Wilson equation (*8*).

$$\ln \gamma_i = -\ln (x_1\Lambda_{i1} + x_2\Lambda_{i2}) + 1 - \sum_{K=1}^{2} \frac{x_K\Lambda_{Ki}}{x_1\Lambda_{K1} + x_2\Lambda_{K2}} \tag{1}$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \tag{2}$$

$$i \neq j, \qquad i, j = 1 \text{ or } 2$$

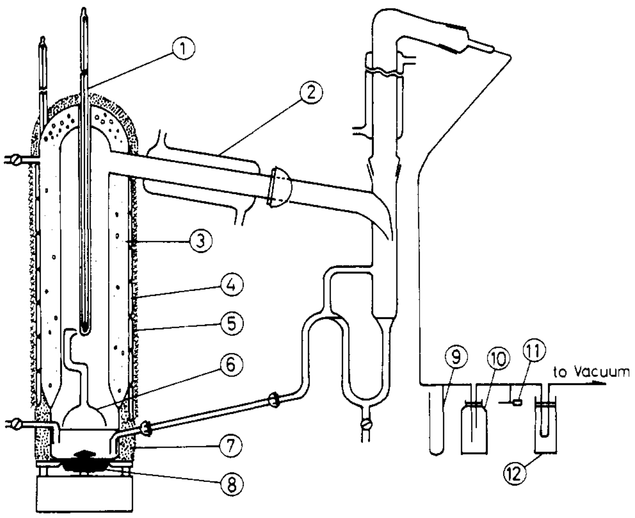
$$\Lambda_{11} = \Lambda_{22} = 1.0$$

The quantities of the Λ_{12} and Λ_{21} parameters were decided from the experimental results by the least-squares fit of the Q-function ($=g^E/RT$). Next, the quantities ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) were determined by eq 2, using the quantities of Λ_{12} and Λ_{21} and the mean temperatures of each pressure. Those appear in Table III.

0021-9568/80/1725-0107$01.00/0

Table II. Vapor-Liquid Equilibrium Data for the *n*-Heptane (1)-Toluene (2) System

p, mmHg	t, °C	x_1	y_1	γ_1	γ_2
760.0	110.7	0.000	0.000		
757.3	108.7	0.046	0.085	1.375	1.010
758.2	108.0	0.072	0.123	1.300	1.017
761.2	105.8	0.176	0.262	1.208	1.031
757.7	104.8	0.242	0.345	1.184	1.021
758.1	104.3	0.270	0.372	1.161	1.032
757.3	102.6	0.375	0.481	1.133	1.046
759.7	101.4	0.498	0.582	1.072	1.091
756.7	100.1	0.617	0.679	1.043	1.135
758.5	98.9	0.816	0.846	1.021	1.181
761.8	98.6	0.905	0.915	1.007	1.280
757.4	98.4	1.000	1.000		
400.0	89.5	0.000	0.000		
	88.5	0.024	0.053	1.579	0.997
	88.0	0.038	0.076	1.446	1.003
	86.9	0.075	0.144	1.422	1.004
	85.9	0.119	0.213	1.383	1.004
	85.6	0.127	0.228	1.389	1.002
	84.4	0.195	0.311	1.285	1.011
	84.1	0.210	0.330	1.283	1.011
	82.9	0.290	0.406	1.187	1.038
	81.4	0.409	0.516	1.124	1.073
	79.9	0.570	0.651	1.069	1.117
	79.4	0.645	0.707	1.040	1.151
	79.2	0.701	0.750	1.023	1.177
	78.7	0.771	0.807	1.018	1.205
	78.4	0.847	0.870	1.011	1.229
	78.1	0.958	0.964	0.998	1.260
	77.9	1.000	1.000		
200.0	69.5	0.000	0.000		
	68.8	0.014	0.034	1.671	1.004
	67.0	0.081	0.161	1.355	1.001
	66.9	0.086	0.171	1.459	1.002
	65.2	0.169	0.282	1.306	1.015
	64.5	0.193	0.326	1.356	1.008
	63.6	0.252	0.373	1.228	1.049
	62.9	0.317	0.446	1.196	1.041
	61.8	0.418	0.536	1.139	1.068
	60.7	0.548	0.632	1.069	1.139
	60.1	0.641	0.710	1.049	1.153
	59.9	0.671	0.732	1.041	1.175
	59.8	0.704	0.761	1.036	1.171
	59.5	0.809	0.837	1.005	1.249
	59.1	0.910	0.921	0.998	1.319
	58.7	1.000	1.000		
100.0	52.0	0.000	0.000		
	50.9	0.036	0.081	1.551	0.995
	49.6	0.080	0.160	1.432	1.008
	49.2	0.098	0.183	1.357	1.016
	48.0	0.155	0.262	1.300	1.036
	47.1	0.198	0.338	1.354	1.015
	46.8	0.215	0.346	1.300	1.036
	46.0	0.280	0.411	1.224	1.029
	45.1	0.343	0.471	1.190	1.083
	44.3	0.420	0.539	1.150	1.108
	43.6	0.547	0.637	1.076	1.147
	42.4	0.771	0.814	1.026	1.230
	42.0	0.879	0.901	1.014	1.262
	41.9	0.959	0.962	0.998	1.427
	41.7	1.000	1.000		
50.0	36.3	0.000	0.000		
	35.9	0.007	0.019	1.747	1.010
	35.7	0.039	0.087	1.519	1.027
	33.7	0.078	0.171	1.572	1.020
	32.9	0.177	0.235	1.499	1.024
	32.4	0.148	0.283	1.455	1.020
	31.0	0.257	0.396	1.254	1.052
	30.1	0.339	0.474	1.190	1.079
	29.2	0.458	0.577	1.122	1.109
	28.0	0.596	0.684	1.079	1.184
	27.9	0.650	0.716	1.044	1.224
	27.3	0.810	0.845	1.019	1.268
	27.1	0.813	0.845	.1.024	1.306
	27.0	0.840	0.863	1.017	1.361
	26.8	0.941	0.950	1.010	1.360
	26.7	1.000	1.000		



① Thermometer	② Condenser
③ Diatom Earth	④ Ribbon Heater
⑤ Glass Wool	⑥ Cottrell Pump
⑦ Asbestos	⑧ Magnetic Stirrer
⑨ Manometer	⑩ Buffer Tank
⑪ Needle Valve	⑫ Cold Trap

Figure 1. Experimental apparatus.

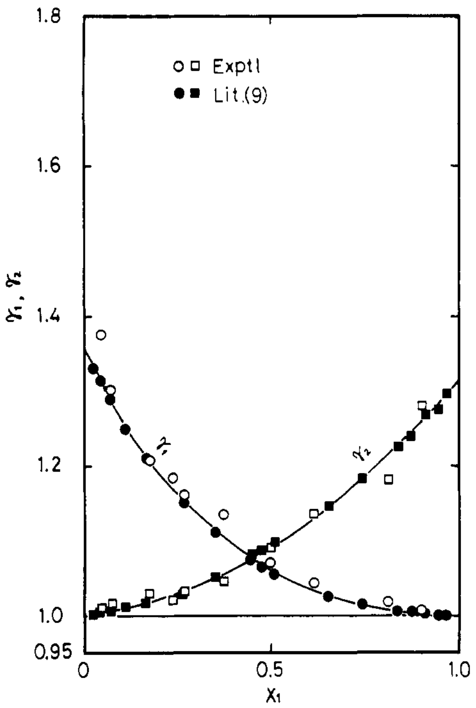


Figure 2. Activity coefficient for the *n*-heptane–toluene system at 760 mmHg. The solid line is calculated by the Wilson equation (1) with respective parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$).

Table III. Wilson Parameters for the *n*-Heptane-Toluene System

pressure, mmHg	$\lambda_{12} - \lambda_{11}$, cal/mol	$\lambda_{21} - \lambda_{22}$, cal/mol	Λ_{12}	Λ_{21}
760.0	29.8	220.1	0.6844	1.0474
400.0	87.1	208.0	0.6326	1.0421
200.0	196.1	126.9	0.5360	1.1515
100.0	181.2	152.6	0.5424	1.0906
50.0	341.0	66.1	0.4121	1.2386

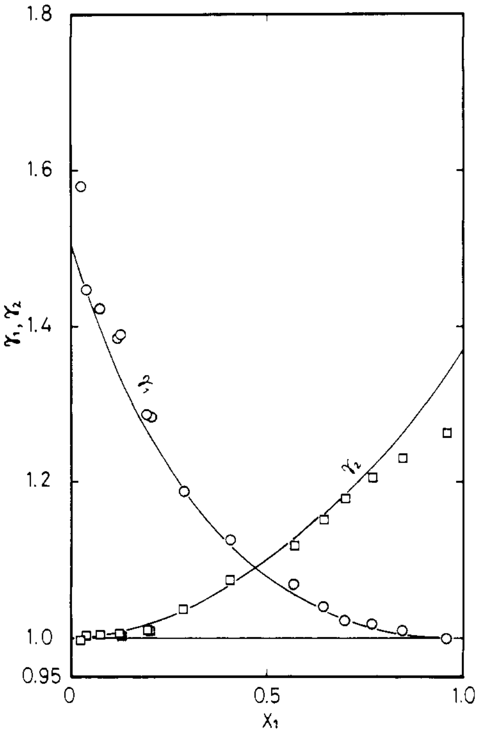


Figure 3. Activity coefficient for the *n*-heptane-toluene system at 400 mmHg.

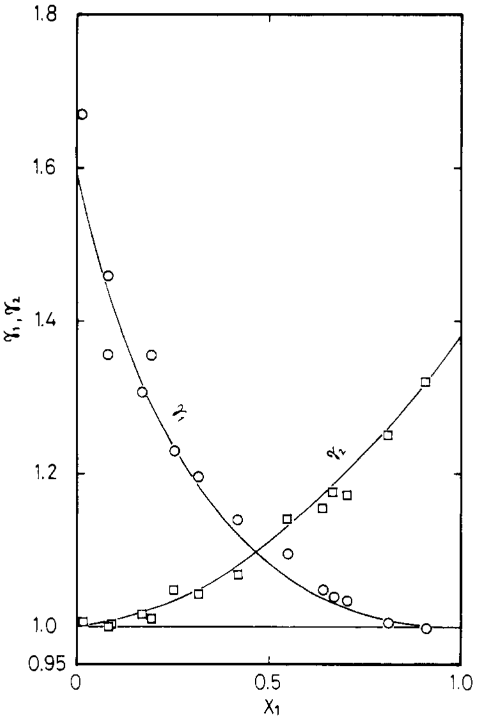


Figure 4. Activity coefficient for the *n*-heptane-toluene system at 200 mmHg.

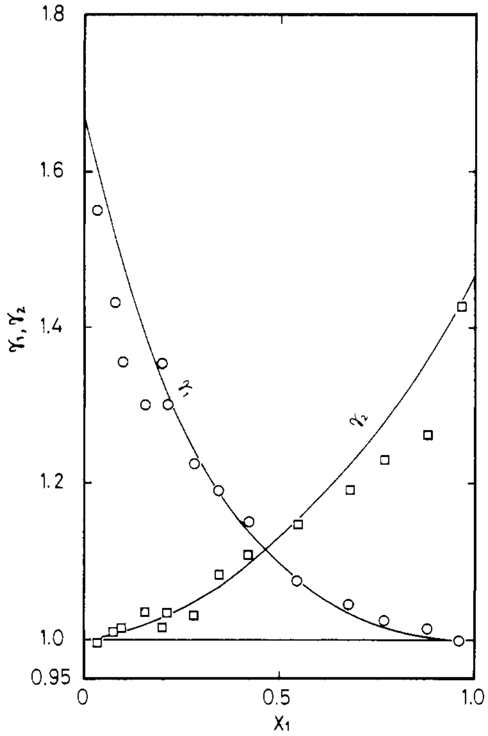


Figure 5. Activity coefficient for the *n*-heptane-toluene system at 100 mmHg.

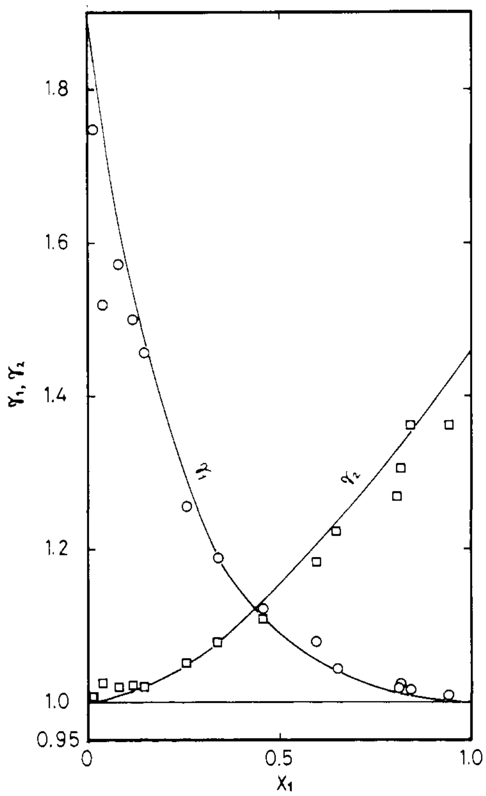


Figure 6. Activity coefficient for the *n*-heptane-toluene system at 50 mmHg.

The predictions of bubble points were made by using the following three pairs of Wilson parameters: employing the respective parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) to each pressure, applying also the atmospheric parameter ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) down to lower pressures, and adopting the other parameters Λ_{12} and Λ_{21} down to lower pressures as well. Namely those three pairs of parameters were used to obtain the vapor compositions and temperature at the given pressure and liquid compositions.

The differences between the predicted and experimental values of the vapor compositions and of their temperatures were taken, and their average differences are reported in Table IV. Both correlations of the respective parameters and those of atmospheric parameters are almost equal on the vapor compositions, but the atmospheric correlations of the latter are somewhat inferior to those of the former concerning temperature. Adopting the other atmospheric parameters of Λ_{12} and Λ_{21}, accuracies of both vapor compositions and their temperature decrease with reducing pressures.

Table IV. Average Deviations between the Predicted and Experimental Values by the Bubble Point Prediction

pressure, mmHg	$\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ at each pressure		$\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ of 1 atm pressure		Λ_{12}, Λ_{21} of 1 atm pressure	
	$\Delta y_1{}^a$	Δt^b	$\Delta y_1{}^a$	Δt^b	$\Delta y_1{}^a$	Δt^b
760.0	0.003	0.2	0.003	0.2	0.003	0.2
400.0	0.004	0.1	0.005	0.3	0.006	0.4
200.0	0.005	0.1	0.006	0.3	0.008	0.5
100.0	0.006	0.1	0.004	0.4	0.007	0.6
50.0	0.005	0.2	0.005	0.4	0.010	0.7

[a] $\Delta y_1 = \Sigma |y_{1,\text{calcd}} - y_{1,\text{exptl}}|/n$. [b] $\Delta t = \Sigma |t_{\text{calcd}} - t_{\text{exptl}}|/n$. n = number of data.

Glossary

g^E	molar excess Gibbs energy, cal/mol
P	total pressure, mmHg
p_i	vapor pressure of pure substance i, mmHg
Q	Q function ($=g^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$)
R	gas constant, cal/(mol K)
T, t	temperature, K, °C
v_i	molar liquid volume of pure i at temperature T, cm/mol
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases

Greek Letters

γ_i	i component activity coefficient of liquid phase
Λ_{12}, Λ_{21}	Wilson parameters defined by eq 2
$\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$	Wilson parameters, cal/mol

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Received for review April 30, 1979. Accepted September 20, 1979.

Thermodynamic Properties of the Molten Salt System Cesium Bromide–Cuprous Bromide

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Molar volumes, excess molar volumes, partial molar volumes, and molar volume expansion coefficients were calculated for the binary molten salt system cesium bromide–cuprous bromide.

The experimental procedures and density results obtained in the system cesium bromide–cuprous bromide have been described previously (**6**). The temperature coefficients of the densities were evaluated at nine mole fractions over the complete composition range and in the temperature range 507–950 °C, using the method of Archimedean displacement.

This paper reports on the calculation of molar volumes, excess molar volumes, partial molar volumes, and molar volume expansion coefficients in the system cesium bromide–cuprous bromide.

Density and Temperature Coefficients of the Density

The experimental density data (*6*) were fitted to equations of the form

$$\rho = a - bT \qquad (1)$$

where ρ is in grams per cubic centimeter and T in Kelvin, and are listed in Table I. Figure 1 gives an overview of the densities, calculated from the data in Table I, over the entire composition range at three chosen temperatures.

Table I. Least-Squares Fits for the Densities Fitted to Equation 1

mole % of CsBr	a, g cm^{-3}	10^3b, g cm^{-3} K^{-1}	std dev	temp range, K
100.000	4.244_9	1.223	a	a
85.097	4.283_4	1.323	0.0019	918–1226
74.239	4.451_0	1.326	0.0020	880–1223
58.763	4.586_4	1.377	0.0028	870–1222
40.543	4.617_3	1.231	0.0021	850–1226
30.000	4.932_2	1.400	0.0027	861–1223
19.961	5.021_7	1.300	0.0035	849–1227
10.467	5.085_8	1.141	0.0058	840–1224
0.000[b]	5.282_8	0.916	0.0067	780–1224

[a] See ref 4. [b] Pure CuBr.

Molar Volumes and Excess Molar Volumes

Calculated values for molar volumes, standard deviations in molar volumes, ideal molar volumes, and excess molar volumes at three chosen temperatures are listed in Table II. Molar volumes V_M, ideal molar volumes V_I, and excess molar volumes V_E were calculated from the equations

$$V_M = (1/\rho)\sum x_i M_i \qquad (2)$$

$$V_I = \sum (x_i M_i/\rho_i) \qquad (3)$$

$$V_E = (1/\rho)\sum x_i M_i - \sum (x_i M_i/\rho_i) \qquad (4)$$

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