Double Azeotropy in the Benzene + Hexafluorobenzene System

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Vapor−liquid equilibrium was measured for the benzene (1) + hexafluorobenzene (2) system at 16 and 120 kPa. The system forms two azeotropes although its behavior is close to ideal. The compositions of the two azeotropes approach one another as the operating pressure is increased. The equilibrium data are thermodynamically consistent according to the point-to-point test of Fredenslund.

Introduction

The benzene (1) + hexafluorobenzene (2) system presents some unusual thermodynamic properties: (a) it is the only known case of an organic solution that forms two azeotropes at the experimental pressures and temperatures studied, although its behavior is close to ideal, (b) both components have very similar boiling points and freezing points and vapor pressures almost identical up to the critical point of the fluorocarbon, and (c) the solid−liquid phase diagram shows the formation of a 1:1 molecular complex with a congruent melting point of 297.21 K (Duncan and Swinton, 1966). Hexafluorobenzene forms complexes with benzene with incongruent melting points, indicating the presence of much weaker interactive forces.

The vapor−liquid equilibrium (VLE) diagram of the system has been determined by Gaw and Swinton (1968) at 303.15, 313.15, 323.15, 333.15, and 343.15 K, by Kogan and Morachevskii (1971) at 40, 66.7, and 101.3 kPa, and by Chinikamala et al. (1973) at 101.3 kPa. According to DECHEMA (Gmehling et al., 1980), the data of Chinikamala et al. at 101.3 kPa and of Kogan and Morachevskii at 40 kPa fail to pass the area test for thermodynamic consistency. The experimental data published indicate that the compositions of both azeotropes become more similar as the operating pressure increases. According to Gaw and Swinton (1968), the phenomenon of double azeotropy should persist to temperatures up to about 383 K. On the other hand, Ewing et al. (1981, 1984) measured dew and bubble pressures of benzene and hexafluorobenzene mixtures at constant composition and suggested that the two azeotropes disappear simultaneously at about 443 K.

In this work we have extended the vapor−liquid phase diagram to pressure levels higher and lower than those previously reported by Gaw and Swinton (1968), Kogan and Morachevskii (1972), Chinikamala et al. (1973).

Experimental Section

Chemicals. Hexafluorobenzene (99%) and benzene (99.9%, HPLC grade) were purchased from Aldrich. The purity was checked by gas chromatography: hexafluorobenzene, 99.84 mass %; benzene, 99.88 mass %. They were used without further purification. The experimental densities, refractive indexes, and normal boiling points are given in Table 1 and shown to be in good agreement with the corresponding values reported in the literature.

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Table 1. Properties of the Pure Compounds

component	d(293.15 K)/(g cm^{-3})		n(D, 293.15 K)		T_b(101.3 kPa)/K	
	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
benzene	0.878 58	0.879 00	1.4980	1.501 11	353.25	353.206
hexafluoro-benzene	1.618 01	1.617 68	1.3752	1.377 83	353.40	353.405

[a] TRC Thermodynamic Tables (1994).

Apparatus and Procedure. The equilibrium vessel used in this work was an all-glass, dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures P from 0.25 to 150 kPa, and temperatures T up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature-sensing element. The equilibrium temperature was measured with a digital Fisher thermometer with an accuracy of ±0.1 K, and the pressure with a digital manometer with an accuracy of ±0.01 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometer was calibrated against high-purity (>99.9 mass %) hexane vapor pressures.

The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. At this time, samples of the liquid and condensate were taken for analysis. The sample extraction was carried out with special syringes which allowed small-volume samples (0.1 mL) to be withdrawn in a system under partial vacuum.

Analysis. Compositions of the sampled liquid and condensed vapor phases were analyzed with a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated by using a Hewlett-Packard 3396 integrator. At least two analyses were made of each liquid and each vapor composition; the standard deviation of a composition analysis was usually less than 0.001 mole fraction.

Results and Discussion

The vapor pressure of hexafluorobenzene has been measured in the temperature range 307−362 K, and the experimental results are reported in Table 2 and Figure
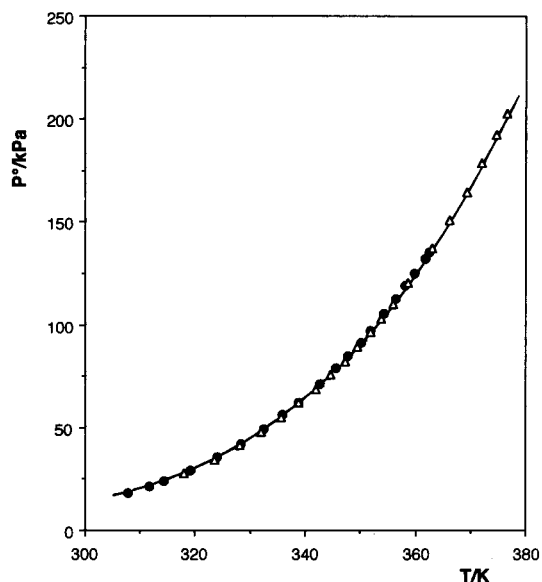
Figure 1. Variation of the vapor pressure of hexafluorobenzene with temperature: this work (●); data of Ambrose et al. (△).

Table 2. Vapor Pressure of Hexafluorobenzene as a Function of the Temperature

T/K	P°/kPa	T/K	P°/kPa
307.70	18.15	345.65	79.05
311.70	21.60	347.85	85.05
314.20	23.95	350.15	91.58
319.15	29.34	351.90	97.32
323.95	35.61	354.40	105.51
328.25	42.21	356.50	112.54
332.45	49.38	358.30	119.15
332.55	49.41	359.90	125.16
335.95	56.06	361.70	132.15
338.85	62.39	362.50	135.41
342.65	71.22		

1; the latter shows the excellent agreement of our measurements with those reported by Ambrose et al. (1990). The experimental data were adjusted to the Antoine equation

$$\ln(P_i^o/\text{kPa}) = A + \frac{B}{(T/\text{K}) + C} \qquad (1)$$

with $A = 14.2039$, $B = -2857.02$, and $C = -55.146$.

The vapor pressure of benzene was not measured because very good data are available in the literature (Ambrose et al., 1990). According to Ambrose et al. (1990), the Antoine constants for eq 1 are $A = 13.8564$, $B = -2772.133$, and $C = -53.165$. The VLE measurements were made at 16 and 120 kPa and are presented in Tables 3 and 4 and Figures 2 and 3.

The liquid-phase activity coefficients of the components in a nonideal mixture were calculated according to (Van Ness and Abbott, 1982)

$$y_i \phi_i P = x_i \gamma_i \phi_i^s P_i^o \exp[v_i(P - P_i^o)/RT] \qquad (2)$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, ϕ_i is the fugacity coefficient, P is the total pressure, γ_i is the activity coefficient, ϕ_i^s, is the pure component fugacity coefficient at saturation, P_i^o is the pure component vapor pressure, v_i is the liquid molar volume, R is the universal gas constant, and T is the absolute temperature.

The exponential term (Poynting factor) was considered to be unity for the experimental conditions of this work. Fugacity coefficients ϕ_i and ϕ_i^s, as calculated by means of

Table 3. Vapor−Liquid Equilibria for the System Benzene (1) + Hexafluorobenzene (2) at 120 kPa

x_1	y_1	T/K	γ_1	γ_2
0.0000	0.0000	358.70		
0.0638	0.0612	358.70	0.964	0.998
0.1034	0.0996	358.75	0.966	0.998
0.1156	0.1128	358.75	0.979	0.997
0.1494	0.1467	358.80	0.984	0.995
0.1526	0.1511	358.80	0.992	0.994
0.1950	0.1932	358.85	0.991	0.993
0.2198	0.2185	358.85	0.994	0.992
0.2336	0.2338	358.85	1.001	0.990
0.2610	0.2635	358.80	1.011	0.989
0.2655	0.2685	358.80	1.013	0.988
0.2771	0.2791	358.75	1.010	0.991
0.2959	0.2995	358.75	1.016	0.988
0.3174	0.3224	358.65	1.022	0.989
0.3417	0.3488	358.65	1.027	0.986
0.3828	0.3926	358.55	1.035	0.984
0.5169	0.5293	358.25	1.043	0.983
0.5600	0.5750	358.15	1.048	0.978
0.6246	0.6371	358.05	1.045	0.982
0.6783	0.6909	357.95	1.046	0.979
0.7274	0.7349	357.85	1.041	0.994
0.7487	0.7594	357.75	1.048	0.981
0.7594	0.7625	357.75	1.038	1.012
0.7700	0.7716	357.75	1.036	1.018
0.8051	0.8060	357.75	1.035	1.020
0.8466	0.8422	357.85	1.025	1.050
0.8809	0.8738	357.95	1.019	1.079
0.9089	0.9001	358.15	1.011	1.110
0.9315	0.9229	358.25	1.009	1.136
0.9494	0.9412	358.45	1.003	1.165
0.9600	0.9520	358.65	0.998	1.197
0.9785	0.9734	358.75	0.998	1.229
1.0000	1.0000	358.85		

Table 4. Vapor−Liquid Equilibria for the System Benzene (1) + Hexafluorobenzene (2) at 16 kPa

x_1	y_1	T/K	γ_1	γ_2
0.0000	0.0000	305.05		
0.1021	0.0976	305.05	0.884	1.009
0.1481	0.1452	305.05	0.907	1.007
0.1947	0.1944	305.05	0.924	1.004
0.1943	0.1943	305.05	0.925	1.003
0.2331	0.2375	305.05	0.943	0.998
0.2574	0.2677	305.05	0.962	0.990
0.3159	0.3312	304.95	0.974	0.986
0.3934	0.4173	304.75	0.994	0.977
0.4670	0.5015	304.45	1.020	0.965
0.5164	0.5558	304.25	1.031	0.956
0.5812	0.6237	303.95	1.042	0.948
0.6405	0.6852	303.65	1.053	0.937
0.6883	0.7298	303.35	1.057	0.941
0.7375	0.7709	303.15	1.051	0.956
0.7571	0.7900	303.05	1.054	0.951
0.7701	0.8016	302.95	1.056	0.954
0.8039	0.8291	302.85	1.051	0.968
0.8430	0.8610	302.75	1.046	0.988
0.8797	0.8892	302.65	1.040	1.033
0.9082	0.9142	302.55	1.040	1.052
0.9295	0.9315	302.50	1.038	1.097
0.9485	0.9489	302.55	1.033	1.118
0.9638	0.9628	302.65	1.027	1.151
0.9745	0.9737	302.75	1.023	1.151
1.0000	1.0000	303.25		

the virial equation of state, were found to be nearly unity. The liquid molar volumes as well as the equation and the parameters to calculate the second virial coefficients were taken from the literature (Daubert and Danner, 1994). If, in addition, the vapor phase is assumed to behave ideally then eq 2 simplifies to

$$\gamma_i = y_i P / x_i P_i^o \qquad (3)$$

The values of the activity coefficients calculated using eq 3 are reported in Tables 3 and 4 for the two pressure
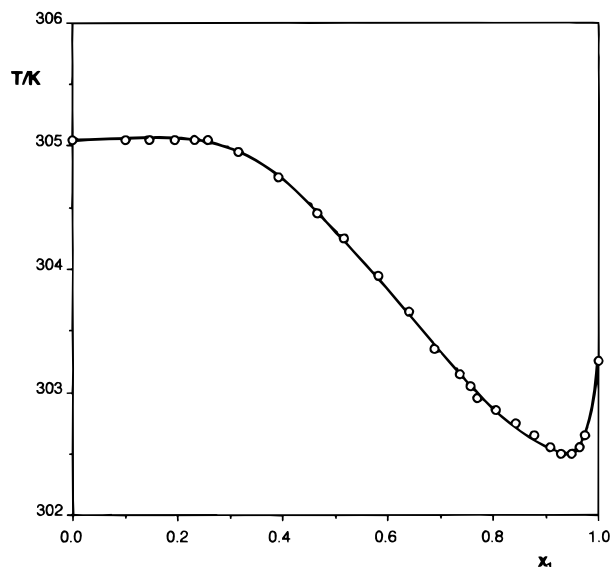
Figure 2. $T-x$ diagram for the benzene (1) + hexafluorobenzene (2) system at 16 kPa.
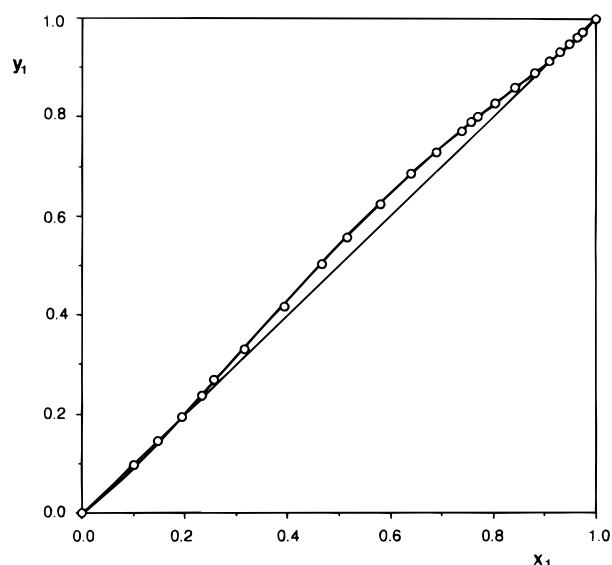

Figure 3. $y-x$ diagram for the benzene (1) + hexafluorobenzene (2) system at 16 kPa.

Table 5. Variation of the Azeotropic Composition with Pressure

low azeotrope		high azeotrope	
x_1	P/kPa	x_1	P/kPa
0.1237	33.59[b]	0.7657	101.33[c]
0.1638	14.17[a]	0.7969	101.33[b]
0.1685	22.26[a]	0.8072	120.00[d]
0.1736	33.79[a]	0.8298	74.34[a]
0.1885	16.00[d]	0.8500	66.66[b]
0.1905	71.27[a]	0.8770	52.65[a]
0.1998	49.76[a]	0.9037	36.37[a]
0.2088	40.00[b]	0.9180	40.00[b]
0.2175	66.66[b]	0.9201	36.31[b]
0.2256	120.00[d]	0.9363	24.42[a]
0.2322	101.33[b]	0.9529	16.00[d]
0.2483	101.33[c]	0.9606	15.92[a]

[a] Gaw and Swinton (1968). [b] Kogan and Morachevskii (1972). [c] Chinikamala et al. (1973). [d] This work.
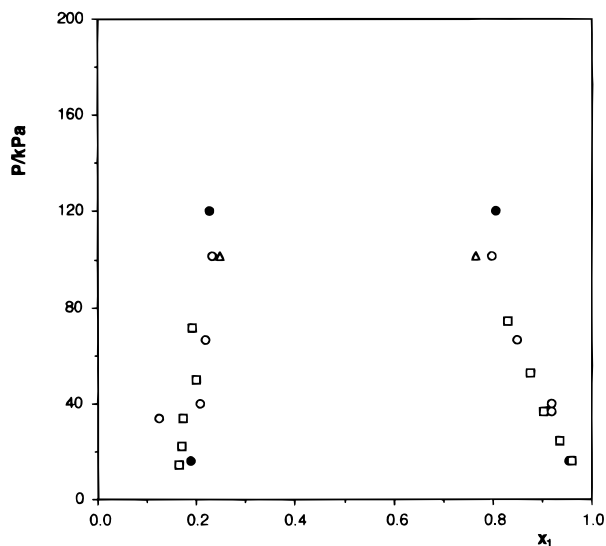

Figure 4. Variation of the vapor pressure of the azeotropes with their composition: (●) this work; data of Gaw et al. (□); data of Kogan (○); data of Chinikamala (△).

levels examined in this work. Inspection of the results given in these tables indicates that the system benzene + hexaflurobenzene behaves almost ideally, in spite of the fact that it has two azeotropic points. The calculated activity coefficients were tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977). A four-parameter Legendre polynomial was used for the excess Gibbs energy. According to Fredenslund et al. (1977), the $P-T-x-y$ data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, $\delta(y)$, is less than 0.01. The results of this test for the system in consideration are $\delta(y)$ = 0.0070 for 16 kPa and $\delta(y)$ = 0.0038 for 120 kPa. These results indicate that the experimental data are thermodynamically consistent.

Double Azeotrope Behavior. Composition and pressure values for both azeotropes are listed in Table 5. In this table, the values for different previously published data are also included. Azeotropic compositions have been obtained, in all cases, by determining x_1 values that make zero the best polynomial fit of the function $(x_1 - y_1)/x_1 = f(x_1)$. In the case of isothermal VLE data, azeotropic

pressures have been obtained from the best polynomial fit for $P = f(x_1)$, using the x_1 values previously determined.

Variation of azeotropic pressure with composition is shown in Figure 4 for all the data published in the literature, along with experimental data of this work. Inspection of Figure 4 shows that there is a moderate divergence among the different data. Nevertheless, it is clearly seen that the compositions of the two azeotropes approach each other with increasing pressure, as reported by Ewing et al (1984)

The tendency of the experimental azeotropic data plotted in Figure 4 indicates that the two azeotropes disappear together at about 5 atm (~415 K), while the estimated data by Ewing et al. (1984) show that this occurs at about 443 K (~8.8 atm).

Unfortunately, our experimental equipment (glass) does not allow us to work at pressures higher than the one reported in this work. It would be very interesting to obtain data at pressures higher than 4 atm to verify where this azeotropic boundary actually appears.

Acknowledgment

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