Integral Isobaric Heats of Vaporization of Benzene–Chloroethane Systems

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Integral isobaric heats of vaporization of benzene–1,1,1-trichloroethane and benzene–1,1,2,2-tetrachloroethane systems were measured at pressures of 684 and 760 mmHg. The experimental results for these systems and the benzene–1,2-dichloroethane system are compared with values calculated using the experimental data on heats of mixing and vapor–liquid equilibria. The experimental values agree with the calculated values with a maximum deviation of 0.8% and an average absolute deviation of 0.2%.

This paper is a continuation of the work on the experimental determination of latent heats of vaporization of binary mixtures reported from this laboratory (*4*, *8*). We give here the experimental results of the heats of vaporization of benzene–1,1,1-trichloroethane and benzene–1,1,2,2-tetrachloroethane. These values as well as those of the benzene–1,2-dichloroethane system reported earlier (*4*) are compared with the values calculated from the experimental values of heats of mixing and vapor–liquid equilibrium data (*6*).

Experimental Section

Materials. "Pro analysis" grade benzene supplied by Sarabhai Merck Limited, India, purified as described earlier (*4*) was used.

Laboratory reagent grade 1,1,1-trichloroethane, supplied by M/s. British Drug House, Poole, England, was purified before use by first washing with concentrated hydrochloric acid and subsequently with a 10% solution of potassium carbonate and finally with a 10% solution of sodium chloride. The product was dried over calcium chloride and distilled twice; 0.02% by weight of phenol was added to the feed as a stabilizer (*7*) during distillation.

Commercial grade 1,1,2,2-tetrachloroethane, supplied by M/s. Calico Chemicals and Plastics Division, Bombay, India, was purified and used. Concentrated sulfuric acid (25 cm^3) was added to about 200 cm^3 of the tetrachloroethane. The mixture was stirred and maintained at 80 °C for 10 min. The impure acid layer was separated and fresh acid (25 cm^3) was added. Washing with acid was continued till no color appeared in the acid layer. It was then washed with distilled water, steam distilled, and dried over potassium carbonate; 0.02% by weight of phenol was added as a stabilizer during steam distillation.

The substances thus purified were checked for purity by measuring their physical properties. The important physical properties measured (useful in the analysis of the mixtures as well) compare well with the data available in literature as shown in Table I.

Analysis of Mixtures. Refractive index was used as the basis for determining the composition of the benzene–1,1,1-trichloroethane mixtures as the differences in refractive indices of pure substances were found to be sufficiently apart. The refractive indices of synthetic mixtures of benzene–1,1,1-trichloroethane determined at 30 °C using a Pulfrich refractometer with a monochromatic (sodium D line) light source fitted the relation with mole fraction of benzene as

$$x_1 = -95.8961 + 115.8997\eta_D - 34.1705\eta_D^2 \qquad (1)$$

with an average absolute deviation of 0.4% and a maximum deviation of −1.3%. Equation 1 was used to determine the compositions of the required mixtures from a measurement of their refractive indices.

As the refractive indices of benzene and 1,1,2,2-tetrachloroethane are very close, refractive index could not be used as the criterion to determine the compositions of their mixtures. Therefore density at 30 °C was used as the criterion for analyzing these mixtures. Measurements of density for synthetic mixtures (employing a pycnometer having a total volume of 8.0128 cm^3 at 30 °C) were found to fit the relation with mole fraction of benzene as

$$x_1 = 1.732\,31 - 0.538\,21\rho - 0.353\,71\rho^2 \qquad (2)$$

with an average absolute deviation of 0.2% and a maximum deviation of 0.7%. Experimental observations of density at 30 °C were used in conjunction with eq 2 to determine the compositions of the required mixtures.

Apparatus and Procedure. A brief description of the apparatus used and experimental procedure, the details of which appeared earlier (*4*, *8*), is given in this paper.

A schematic diagram of the apparatus is given in Figure 1. It consists of: (a) preheater, (b) calorimeter, (c) liquid meter, and (d) pressurizing unit. The preheater used is a 3-l. flask provided with a stirrer introduced through a mercury seal and is heated by an external heater. The liquid from the preheater flows by gravity into the calorimeter and also into the flask surrounding it. The calorimeter, enclosed in a jacket evacuated to 10^{-4} mmHg in the annular space and provided with nichrome wire fused to tungsten leads, evaporates the contents without loss of energy to the surroundings. The liquid meter totally collects the vapors condensed and siphons out to the preheater as soon as it is filled permitting a closed cycle of operation. This arrangement enables one to determine the enthalpy change in vaporizing a known quantity of liquid at its bubble point to the dew point.

About 1.5 l. of the liquid mixture of known composition is charged to the preheater and heated to about 2 °C less than its bubble point. The calorimeter heater is then switched on and the current adjusted to a constant value. On attainment of steady state in about 4 h indicated by constant composition of the condensate, the time required to fill the liquid between two constant marks in the liquid meter is noted. The current as well as the potential drop across the calorimeter are also noted. As the volume between the two fixed marks in the liquid meter is known by prior calibration, the latent heat of vaporization can be determined.

Method of Calculation

As the P–V–T data of the systems are not available, rigorous methods of calculations of heat of vaporization of mixtures suggested by Strickland-Constable (*11*) and Stein and Martin (*10*) cannot be used. However, employing a few assumptions as suggested by Gambill (*3*) an expression for heat of vaporization of the mixture can be derived in the form

Table I. Physical Properties of Purified Components[a]

Component	Normal boiling point, °C		Refractive index at 30 °C		Density at 30 °C (g cm^{-3})	
	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.
Benzene	80.1	80.1 (*1*)	1.4947	1.4947 (*1*)	0.8684	0.8684 (*1*)
1,1,1-Trichloroethane	74.0	74.1 (*2*)	1.4317	1.4320 (*2*)	1.3206	1.3209 (*7*)
1,1,2,2-Tetrachloroethane	146.1	146.2 (*7*)	1.4889	1.4884 (*7*)	1.5783	1.5786 (*7*)

[a] Numbers in the parentheses indicate references to literature data.

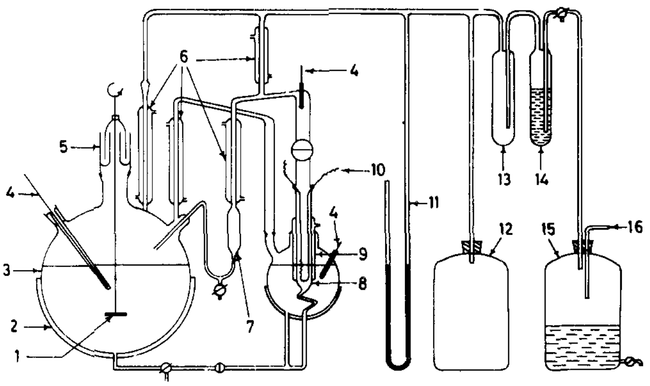

Figure 1. Schematic diagram of the heat of vaporization apparatus: 1, stirrer; 2, heater; 3, preheater; 4, thermometer; 5, liquid seal; 6, condensers; 7, liquid meter; 8, calorimeter; 9, calorimeter jacket; 10, calorimeter heater leads; 11, manometer; 12, surge tank; 13, CCl_2 bubbler; 14, H_2SO_4 bubbler; 15, pressurizing unit; 16, constant head water supply.

$$L = \sum_i x_i L_{i,T_b} + \Delta H_m + \sum_i \int_{T_b}^{T_d} y_i C_{P,i}\, dT \qquad (3)$$

When the difference between the bubble point and dew point temperature is small, $C_{P,i}$ can be assumed to be constant and eq 3 integrated to give

$$L = x_1 L_1 + x_2 L_2 + \Delta H_m + (T_d - T_b)(y_1 C_{P,1} + y_2 C_{P,2}) \qquad (4)$$

Equation 4 is useful for the calculation of heats of vaporization of benzene–1,2-dichloroethane, and benzene–1,1,1-trichloroethane systems as the bubble point and dew point for the systems are very close. In the case of the benzene–1,1,2,2-tetrachloroethane system the difference between the bubble point and dew point is considerable and therefore eq 3 along with the following ideal gas C_P equations (*5, 9*) were used for the saturated vapor:

$$C_{P,1} = -0.409 + 77.621T \times 10^{-3} - 26.429T^2 \times 10^{-6} \text{ (benzene)}$$

$$C_{P,2} = 9.09 + 6.3524T \times 10^{-2} - 4.7637T^2 \times 10^{-5} + 1.2865T^3 \times 10^{-8} \text{ (1,1,2,2-tetrachloroethane)}$$

Experimental data on heats of mixing and vapor–liquid equilibrium for the systems obtained in this laboratory (*6*) were used in the calculations. Some typical values of heats of mixing determined at 35 °C for these systems are shown below.

System	Mole fraction of benzene	Heats of mixing (J g^{-1} mol^{-1})
Benzene–1,2-dichloroethane	0.30	65
Benzene–1,1,1-trichloroethane	0.36	48
Benzene–1,1,2,2-tetrachloroethane	0.58	−584

Table II. Ideal Gas Heat Capacities of the Systems

System	Mean temp, K	$C_{P,1}$[a] cal g mol^{-1}	$C_{P,2}$[b] K^{-1}
Benzene–1,2-dichloroethane	351.5	23.61	20.62
Benzene–1,1,1-trichloroethane	346.9	23.33	23.94

[a] Values from ref 9. [b] Values from ref 5. Cal = 4.186 J.

Table III. Latent Heats of Benzene–1,1,1-Trichloroethane Mixtures

	Pressure 684 mmHg		Pressure 760 mmHg	
Mole fraction of benzene	Boiling point (°C)	Latent heat of vaporization (cal g^{-1} mol^{-1})	Boiling point (°C)	Latent heat of vaporization (cal g^{-1} mol^{-1})
0.00	70.9	7748	74.0	7700 (7692)[a]
0.1650	71.8	7705	74.9	7653
0.2950	72.5	7666	75.7	7608
0.4868	73.6	7606	76.8	7560
0.6000	74.2	7569	77.5	7520
0.6975	74.8	7538	78.1	7487
0.8160	75.5	7475	79.3	7430
1.00	76.7	7407 (7393)[a]	80.1	7357 (7360)[a]

[a] Values from ref 1 and 7.

Table IV. Latent Heat of Vaporization of Benzene–1,1,2,2-Tetrachloroethane Mixtures

	Pressure 684 mmHg		Pressure 760 mmHg	
Mole fraction of benzene	Boiling point (°C)	Latent heat of vaporization (cal g^{-1} mol^{-1})	Boiling point (°C)	Latent heat of vaporization (cal g^{-1} mol^{-1})
0.000	142.6	9316	146.2	9250 (9240)[a]
0.253	119.0	9120	122.6	9058
0.463	102.1	8903	105.5	8845
0.635	90.3	8602	93.7	8546
0.809	82.4	8241	85.8	8187
0.910	79.0	7860	82.4	7810
1.000	76.7	7407	80.1	7357

[a] Value from ref 7.

In the absence of experimental information on heats of mixing at other temperatures, values obtained at 35 °C for various compositions were used for calculating the values at all temperatures. When eq 4 was employed the heat capacities were calculated at the mean temperature of the system. The values of ideal gas C_P for saturated vapor used in the calculation are given in Table II.

Results and Discussion

Experiments were conducted to determine the heats of vaporization of benzene–1,1,1-trichloroethane and benzene–1,1,2,2-tetrachloroethane systems at 684 mmHg (prevailing in the laboratory) and 760 mmHg pressure. The results tabulated in Tables III and IV are the averages of the experimental results

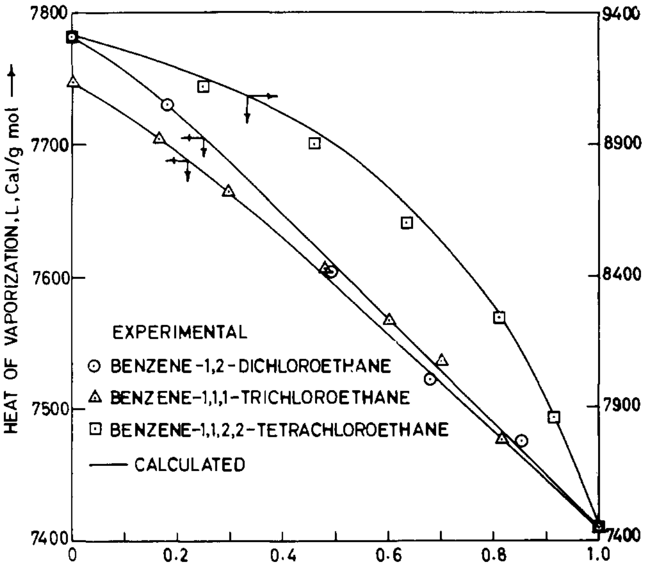

Figure 2. Comparison of the calculated and experimental heats of vaporization of benzene–chloroethane systems at 684 mmHg.

of four runs under similar conditions and the maximum deviation among different values for a particular composition was not more than 0.3%. These values and the data for the benzene–1,2-dichloroethane system reported earlier (*4*) are compared with the values calculated employing the method described above. The results given in Figure 2 show that the calculated and experimental values for all the systems are in good agreement (maximum deviation = 0.8%, overall average absolute deviation = 0.2%). The data on benzene–1,2-dichloroethane and benzene–1,1,1-trichloroethane systems follow a linear combination whereas the data on benzene–1,1,2,2-tetrachloroethane deviates as much as 10–30% from the linear rule ($L = x_1L_1 + x_2L_2$). However, Figure 2, which seems to indicate deviation from linearity in the case of the systems benzene–1,2 dichloroethane and benzene–1,1,1-trichloroethane, has a maximum deviation of 0.15%. Thus, it can be taken that these two systems follow a linear latent heat rule with composition. The good agreement between the calculated and experimental data presented in this paper implies that (i) data on heats of vaporization, heats of mixing, and vapor–liquid equilibrium collected for this purpose are self-consistent, (ii) benzene–1,2-dichloroethane and benzene–1,1,1-trichloroethane systems are nearly ideal, while (iii) benzene–1,1,2,2-tetrachloroethane is highly nonideal. Experimental results on systems studied extensively (not reported in this paper) agreed with other investigators' data within ±0.4% deviation indicating that the results obtained by this apparatus and method are accurate.

Glossary

$C_{P,i}$	ideal gas heat capacity of component *i* at pressure *P*, cal g^{-1} mol^{-1} $^\circ K^{-1}$
ΔH_m	heat of mixing of the mixture, cal g^{-1} mol^{-1}
L	isobaric integral heat of vaporization, cal g^{-1} mol^{-1}
T	temperature, °K
T_b	bubble point of the mixture, °K
T_d	dew point of the mixture, °K
x	mole fraction
x_i	mole fraction of component *i* in the liquid
y_i	mole fraction of component *i* in vapor

Greek letters

ρ	density at 30 °C, g cm^{-3}
η_D	refractive index for sodium D line at 30 °C

Subscripts

1	benzene
2	chloroethane
i	component *i*
b	bubble point
d	dew point
m	mixture

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