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Enthalpy of Vaporization and Vapor Pressure of Benzene, Toluene, *p*-Xylene, and Tetralin between 1 and 16 bar

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This paper reports the vapor pressure and enthalpy of vaporization for benzene, toluene, *p*-xylene, and Tetralin between 1 and 16 bar measured by using an adiabatic flow calorimeter. The analysis of the results showed that the uncertainty of the data is within ±0.0099 bar for vapor pressure and ±15 J/mol for enthalpy of vaporization, ΔH_v.

Introduction

Vapor pressure and enthalpy of vaporization of pure substances and their mixtures are essential for both industrial design computations and the theoretical understanding of solutions and phase equilibria. The present study is a part of the experimental program initiated in this laboratory for the measurement of thermodynamic properties of pure substances and mixtures. The results presented in this paper are for benzene, toluene, *p*-xylene, and Tetralin for the vapor pressure and enthalpy of vaporization.

Vapor pressure data for benzene are available due to Bender, Furukawa, and Hyndman (*1*), Glanville and Sage (*2*), Gornowski, Amick, and Hixon (*3*), Kalafati, Rasskazov, and Petrov (*4*), and Zmaczynski (*5*) in the temperature range of 350 K to the critical point. Two sources due to Zmaczynski (*5*) and Krase and Goodman (*6*) were found for experimental vapor pressures of toluene up to 593.75 K. Practically no reliable data exist for *p*-xylene although some data exist for Tetralin, as reported by Lenoir et al. (*7*).

Very little information has been published on high-pressure enthalpies of vaporization for almost all pure substances and mixtures. The reasons for the lack of information are (i) the calorimetric experiments are inherently difficult to design and the apparatus must be carefully designed and (ii) the measurements are time-consuming. ΔH_v varies from about 30 000 to 45 000 J/mol at 1 bar to zero at the critical pressure. Therefore, it is necessary to have a knowledge of ΔH_v as a function of pressure. Among the work reported for benzene and toluene, the majority of data come from NBS laboratories. Todd, Hossenlopp, and Scott (*8*), Osborne and Ginnings (*9*), and Flock, Ginnings, and Holton (10) reported data on benzene in the pressure range 0.01267-2.33 bar. The only work available on toluene is that of Scott et al. (*11*) and it covers a pressure range 0.2533-2.0265 bar. In the case of Tetralin, Lenoir, Hayworth, and Hipkin (*7*) have reported ΔH_v in the temperature range of 320-620 K.

Experimental Section

The adiabatic flow calorimeter is similar in design and operation to the all-glass apparatus used by Viswanath and coworkers (*12-17*). The apparatus is designed for simultaneous measurement of vapor pressure and enthalpy of vaporization. The siphon vessel used to measure the evaporation rate enables one to collect data without disturbing the equilibrium of the system. Detailed descriptions of the apparatus are reported elsewhere (Natarajan (*18*); Natarajan and Viswanath (*19*)).

Following the suggestions of IUPAC (Herington (*20*)), benzene was used to standardize the calorimetric apparatus. Pressures were measured by using a high-precision Heise gauge, and it was calibrated by using an oil-lubricated Amthor dead-weight piston gauge, Model 460. The accuracy of pressure measurements is better than ±0.5 psi. As the pressures are reported in bar, three significant figures are maintained because of the conversion involved. Temperatures were measured by using NBS-certified thermometers and T-type copper-constantan thermocouples. The thermocouples used were calibrated in accordance with IPTS-68 requirements and indicated values were monitored by using digital electronic meters. These meters and all other electrical and electronic instruments were calibrated against Fluke standards. The accuracy of temperature measurement is ±10 mK. The volume of the siphon device was calibrated as a function of temperature in the range of 197.15-413.15 K by using mercury (impurity level less than 1 in 10^6) and the uncertainty assigned for siphon volume is ±0.0001 cm^3 for the range of experimental temperatures.

The materials employed for the present study were purified by using a 1 m long fractional distillation column and collecting the middle one-third fraction for the experiments. The chemicals were stored in amber-colored bottles and tested for purity from time to time. The physical methods used to test the purity were density, refractive index, and vapor pressure measurements. The measured properties compare well with the literature values and these results are shown in Table I. Capillary gas-liquid chromatograms and mass-spectral analysis were performed on benzene, toluene, *p*-xylene, and Tetralin and the results indicate that the purities of these compounds are better than the values shown in Table I. Tetralin could not be purified any further with the facilities available at the present time.

Analysis

Enthalpy is a derived quantity and therefore it becomes necessary to compute this property by using related measurable parameters. In this experiment a small nichrome heater, wound on a Teflon bobbin and kept immersed in the calorimeter liquid, supplies the heat necessary to vaporize the liquid. Hence, the energy supplied through the heater (at the boiling points) is a measure of enthalpy of vaporization. The energy imparted by the heater is estimated by the measured quantities of emf and current. These quantities along with the measured evaporation rate (time taken for the condensed vapor to fill the precalibrated siphon vessel) can be used to compute ΔH_v by employing the relation

$$(\Delta H_v)P = 10^{-3}EItM/\rho_s V \qquad (1)$$

The available saturated-liquid density data for benzene (*24-28*), toluene (*24, 25, 28, 29*), *p*-xylene (*25, 28, 29*), and Tetralin (*30-32*) were fitted to the modified Rackett equation

$$1/\rho_s = xZ_R^{[1+(1-T_r)^{2/7}]} \qquad (2)$$

and the ρ_s values calculated by eq 2 were used in eq 1. The constants x and Z_R are listed in Table II for use with eq 2. The calculated ρ_s values for all four compounds were found to agree with the experimental values with a maximum deviation of 0.5 × 10^{-6} mol/cm^3. The values of molecular weight used in eq

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Table I. Specification of Materials

material	supplier	purity^d/%	n_D (305.15 K) exptl	n_D (305.15 K) lit.	ρ(303.15 K)/(g/cm^3) exptl	ρ(303.15 K)/(g/cm^3) lit.
benzene	Mallinckrodt	99.994	1.4952	1.4954^c	0.8679	0.8680^c
toluene	Mallinckrodt	99.907	1.4923	1.4922^a	0.8574	0.8573^c
p-xylene	Alfa Chemicals	99.942	1.4903	1.4904^a	0.8523	0.8524^a
Tetralin	Aldrich	94.792	1.5410	1.5392^b	0.9656	0.9662^b

[a] Dreisbach (*21*). [b] Mair and Streiff (*22*). [c] Sumer and Thompson (*23*). [d] After purification.

Table II. Constants for Eq 2

compd	x	Z_R	T_c/K
benzene	12.218621	0.26967	562.15
toluene	13.000756	0.26455	591.82
p-xylene	13.750171	0.25888	616.26
Tetralin	13.723651	0.245135	720.15

Table III. Vapor Pressure of Toluene

temp/K	$p°$/bar^a exptl	$p°$/bar^a calcd	dev/%	$p°$/(bar^a) ref *5*	$p°$/(bar^a) ref *6*
379.63	0.965	0.969	−0.42	0.900	0.892
380.63	1.000	0.991	0.86	0.926	0.918
388.13	1.177	1.188	−0.94	1.145	1.142
393.26	1.356	1.355	0.11	1.317	1.322
402.56	1.738	1.731	0.41	1.680	1.715
408.77	2.044	2.036	0.37	1.963	2.028
417.50	2.537	2.541	−0.15	2.421	2.543
424.85	3.025	3.033	−0.29	2.866	3.046
432.03	3.567	3.572	−0.14	3.357	3.602
440.72	4.301	4.296	0.10		4.361
445.27	4.718	4.706	0.23		4.794
458.30	5.981	6.001	−0.34		6.168
470.39	7.399	7.383	0.20		7.615
498.96	11.711	11.744	0.23		11.817
504.50	12.818	12.854	−0.28		12.833
521.13	16.837	16.830	0.04		16.743

[a] 1 bar = 14.50377 psia.

Table IV. Vapor Pressure of *p*-Xylene

temp/K	$p°$/bar exptl	$p°$/bar calcd	dev/%	$p°$(ref *34*)/bar
411.49	1.023	1.026	0.35	1.022
418.42	1.209	1.205	0.37	1.197
422.71	1.337	1.334	0.28	1.320
426.40	1.452	1.457	−0.35	1.437
431.81	1.663	1.660	0.18	1.626
435.60	1.831	1.820	0.61	1.772
440.16	2.030	2.033	−0.12	1.964
447.01	2.389	2.399	−0.45	2.287
452.26	2.702	2.720	−0.68	2.545
483.58	5.441	5.395	0.84	4.854
509.27	8.323	8.311	0.14	7.623
526.29	10.239	10.377	−1.35	10.000
540.20	12.440	12.307	1.06	12.379
557.25	16.203	16.236	−0.21	16.214

Table V. Vapor Pressure of Tetralin

temp/K	$p°$/bar exptl	$p°$/bar calcd	dev/%	$p°$(ref *7*)/bar
498.33	1.499	1.499	−0.02	1.427
551.82	4.284	4.268	0.37	3.981
567.46	5.378	5.420	−0.78	5.192
584.73	7.000	5.962	0.54	6.820
604.52	9.273	9.285	−0.13	9.056

Table VI. Parameters of Eq 4

	benzene	toluene	*p*-xylene	Tetralin
A_0	−4.1256	−17.5322	11.0915	5.6178
A_1	22.8275	185.829	−95.3637	−32.4467
A_2	−49.699	−774.550	289.530	55.5490
A_3	31.8597	1546.29	−396.188	−39.639
A_4	−6.7767	−1518.14	192.428	
A_5		581.874		
δ_m	0.73	−0.95	−1.24	−0.78
$\bar{\delta}$	0.28	0.32	0.64	0.37
χ	0.02	0.01	0.04	0.03

1 are 78.114, 92.141, 106.168, and 132.206, respectively, for the compounds benzene, toluene, *p*-xylene, and Tetralin. The maximum error, introduced by our instrumentation network, evaluated by using the relation

$$\frac{\Delta(\Delta H_v)_P}{(\Delta H_v)_P} = \left\{\frac{\Delta E}{E} + \frac{\Delta I}{I} + \frac{\Delta t}{t} + \frac{\Delta \rho_s}{\rho_s} + \frac{\Delta V}{V}\right\} \qquad (3)$$

was found to be less than ±3 J/mol.

Experimental Results

Vapor Pressure. The pure-component vapor pressure data for toluene, *p*-xylene, and Tetralin are presented in Tables III–V. The data on benzene are reported in an earlier paper (*19*). The data were fitted to the equation

$$\ln\{p^\circ/P_c\} = \sum_{i=0}^{n} A_i\{(T_c/T) - 1\}^{i/2} \qquad (4)$$

and the values of the constants A_i are listed in Table VI. The critical constants used are the values suggested by Kudchadker, Alani, and Zwolinski (*33*).

Numerous values of $p°$ are available for benzene with which comparison could be made. While most of these data are smoothed values, Kalafati, Rasskazov, and Petrov (*4*) data appear to be more reliable. They agree within 0.1% with values from eq 4. The comparison of the vapor pressures for benzene is discussed in ref *19*. In the case of toluene, only the Krase and Goodman (*6*) data cover the pressure range used in this work. Table III shows that their data agree with the present data within 1.0%. The data reported by Zmaczynski (*5*) up to 3.35 bar show a deviation of 0.3% from our values. The data of Glaser and Ruland (*34*) for *p*-xylene are smoothed data and the accuracy of their work is not known. Their temperature measurement was reported to be ±1 K. The comparison of the data is shown in Table IV. Only a few data are reported for Tetralin in the pressure range of 1.499–9.273 bar because of the purity of Tetralin. Lenoir, Hayworth, and Hipkin (*7*) reported five data points and these values were fitted to eq 4. The calculated values from this fit are less than the present experimental values for $p°$. Lenoir et al. (*7*) did not report the purity of Tetralin that was used. Also, their reported physical properties, refractive index (20 °C) and density (60 and 75 °F in Table I of their paper), do not agree with the accurate values of Mair and Streiff (*22*).

Enthalpy of Vaporization. The enthalpy of vaporization data for benzene are available at only a few temperatures and those values are due to Todd, Hossenlopp, and Scott (*8*), Storvick and Smith (*35*), and Flock, Ginnings, and Holton (*10*). Organick and Studhalter (*36*) have reported calculated values derived from *PVT* measurements. A comparison of the experimental values with the literature values is presented in an earlier paper (*19*). In order to make the comparison possible, the experimental

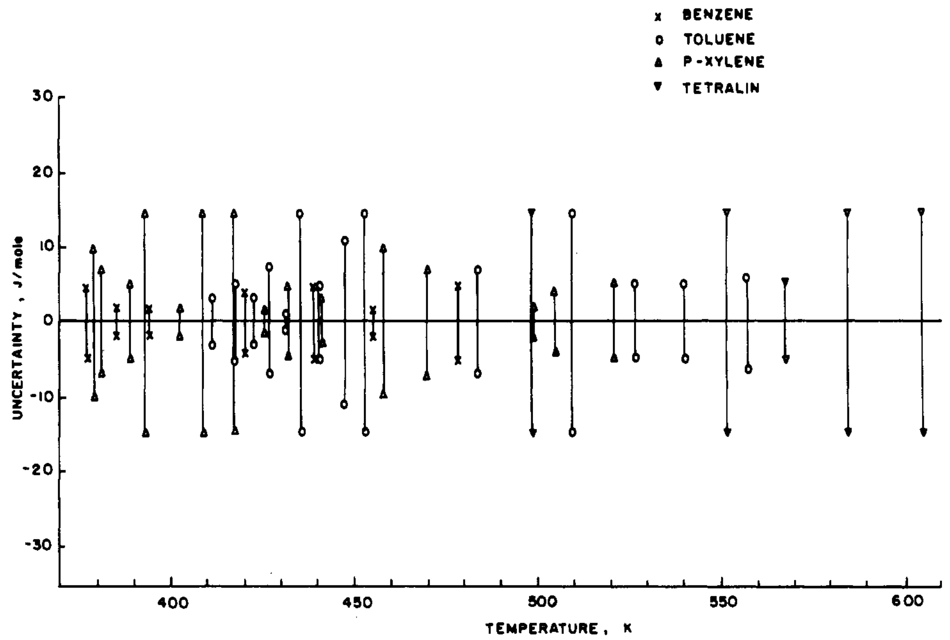

Figure 1. Uncertainty in experimental data: (*x* axis) temperature, K; (*y* axis) uncertainty, J/mol.

Table VII. Parameters of Eq 5

	benzene	toluene	p-xylene	Tetralin
B_0	0.98407	3.2986	0.8926	-82.918
B_1	7.8169	1.7140	12.545	228.334
B_2	-7.1807	-1.6193	-10.668	-199.141
B_3	1.8050	0.1285	2.6316	57.395
δ_m	0.64	0.35	-0.29	-0.31
$\bar{\delta}$	0.22	0.15	0.09	0.14
χ	0.08	0.05	0.04	0.06

data were fitted to the equation of the type suggested by Todd and co-workers (*8*)

$$\ln\left[(\Delta H_v)_P\right] = \sum_{i=0}^{n} B_i\left[\ln\left\{T_c/(T_c - T)\right\}\right]^{i/3} \qquad (5)$$

by least-squares regression technique. The calculated $(\Delta H_v)_P$ values, using the constants listed in Table VII (and T_c = 563.09), were also presented earlier (*19*). From the values listed in ref *19*, it can be concluded that the values reported by Todd and co-workers (*8*) agree with the present data within 0.57% and the values reported by Flock, Ginnings, and Holten (*10*) within 0.52%. Hence, the agreement between the present data and the best data reported from NBS is very good. At elevated pressures, comparison was possible only with derived or calculated values. Storvick and Smith (*35*) reported data on saturated-liquid and vapor enthalpy at eight different temperatures between 433.15 K and the critical temperature. Their experimental method involves the measurement of the energy transferred from the substance flowing through a double-jacketed calorimeter to boiling Freon 11. This method of measuring the energy transfer through a wall between the two energy transferring liquids is less accurate compared to the present method. (The same observations can be made with respect to the experimental work of Lenoir et al. (*7*)). Analysis of their $(\Delta H_v)_P$ values shows that they deviate from the present values by as much as 3.8%. The calculated $(\Delta H_v)_P$ values of Organick and Studhalter (*36*) were fitted to eq 5 and the calculated ΔH_v values at the experimental temperatures were evaluated. The comparison of these values with the experimental values shows that *PVT* predictions of $(\Delta H_v)_P$ are remarkably good. These results on benzene are presented in ref *19*.

The regression results of the least-squares fit to eq 5 of the experimental data for benzene also demonstrate the internal consistency of the data (average absolute percent deviation is 0.22 and standard deviation is 0.08 bar). Each individual experimental datum presented for benzene was obtained as an average of at least three different run values. Thus, the re-

Table VIII. Experimental $(\Delta H_v)_P$ for Toluene[a]

temp/ K	$(\Delta H_v)_P$/(kJ/mol)		dev/ %
	exptl	calcd	
379.63	33.471	33.512	−0.12
380.63	33.405	33.452	−0.14
388.13	33.112	32.995	0.35
393.26	32.689	32.676	0.04
402.56	32.121	32.083	0.12
408.77	31.585	31.677	−0.29
417.50	31.062	31.092	−0.10
424.85	30.620	30.585	0.11
432.03	30.110	30.077	0.11
440.72	29.383	29.443	−0.20
445.27	29.155	29.102	0.18
458.30	28.096	28.092	0.01
470.39	27.067	27.101	−0.12
498.96	24.469	24.508	−0.16
504.50	24.021	23.955	0.28
521.13	22.146	22.161	−0.07

[a] Literature values, Scott et al. (*11*): 33.192 at 383.77 K and 31.539 at 410.11 K.

Table IX. Experimental $(\Delta H_v)_P$ of p-Xylene[a]

temp/ K	$(\Delta H_v)_P$/(kJ mol)		dev/ %
	exptl	calcd	
411.49	36.001	36.002	0.00
418.27	35.588	35.593	−0.01
422.71	35.294	35.314	−0.06
426.40	35.051	35.076	−0.07
431.81	34.697	34.717	−0.05
435.60	34.478	34.457	0.06
440.16	34.159	34.137	0.06
447.01	33.677	33.639	0.11
452.26	33.298	33.243	0.16
483.58	30.544	30.633	−0.29
509.27	28.137	28.154	−0.06
526.29	36.370	26.326	0.20
540.20	24.698	24.704	−0.02
557.25	22.523	22.529	−0.03

[a] Literature values, Osborne and Ginnings (*9*): 42.373 at 298.15 K.

Table X. Experimental $(\Delta H_v)_P$ for Tetralin

temp/ K	$(\Delta H_v)_P$/(kJ/mol) exptl	$(\Delta H_v)_P$/(kJ/mol) calcd	dev/%	$(\Delta H_v)_P{}^{\text{ref 7}}$/ (kJ/mol)
498.33	41.314	41.318	−0.00	41.163
551.82	37.653	37.593	0.16	35.934
567.46	35.709	35.820	0.31	34.803
584.73	33.933	33.866	−0.20	33.378
604.52	31.989	32.002	0.04	31.101

producibility of the data was checked all the time. Figure 1 shows the uncertainty of the experimental data as a function of temperature for benzene and the other three substances.

Tables VIII–X present the experimental data and the few published literature values for other compounds. The B_i values estimated by least-squares analysis are listed in Table VII along with their statistics. The $(\Delta H_v)_P$ values calculated by using eq 5 are shown in the respective Tables VIII–X.

Conclusion

The vapor pressure and enthalpy of vaporization for benzene, toluene, *p*-xylene, and Tetralin in the pressure range of 1–16 bar were measured by using an adiabatic flow calorimeter. The recommendations of IUPAC (*20*) were followed in standardizing the apparatus. Our estimate of uncertainties on ΔH_v is ±15 J/mol and that on vapor pressure is within 0.0099 bar. The data were compared with literature values and the comparison supports the present estimate of uncertainty.

A significant feature of the apparatus is its use for the simultaneous measurement of the vapor pressures and the enthalpies of vaporization. Such data, when used in testing a theory or a model unequivocally eliminate the inconsistencies associated with different data sets collected in different laboratories. The present work on benzene, toluene, *p*-xylene, and Tetralin will add to the knowledge of the effect of one- and two-ring compounds and of methyl substitution.

Glossary

A_i	constant in eq 4
B_i	constant in eq 5
E	emf, V
$(\Delta H_v)_P$	enthalpy of vaporization at high pressures, kJ/mol
I	current, A
i	integer exponents in eq 4 and 5
M	molecular weight
n	integer exponent in eq 4 and 5
P	pressure, bar
p°	vapor pressure, bar
T	temperature, K
V	volume
x	constant in eq 2
Z_R	compressibility in eq 2

Subscripts

c	at critical point
r	reduced property
s	at conditions of saturation

Greek Letters

Δ	difference in eq 3
ρ	density, g cm^{-3}
δ_m	maximum percent deviation
$\bar{\delta}$	average absolute percent deviation
χ	standard deviation

Registry No. Benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; Tetralin, 119-64-2.

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