Glossary

a	height of the observation cell, m
A	constant in the Arrhenius law, $m^2 s^{-1}$
D	diffusion coefficient, $m^2 s^{-1}$
e	optical path length, m
E	activation energy (Arrhenius law), J mol^{-1}
k	constant in eq 2
n	refractive index
N	number of fringes
R	ideal gas constant, J K^{-1} mol^{-1}
t	time, s
T	temperature, K
x	mass ratio of the solution, kg of solute/kg of water
x'	mass fraction of solute, kg of solute/kg of solution
λ	wavelength of laser light, m
θ	temperature, °C

Registry No. Ammonium perchlorate, 7790-98-9.

Literature Cited

(1) Onsager, L.; Fuoss, R. M. *J. Phys. Chem.* **1932**, *36*, 2689.
(2) Harned, H. S.; French, D. M. *Ann. N.Y. Acad. Sci.* **1945**, *46*, 267.
(3) Newman, J.; Chapman, T. W. *AIChE J.* **1973**, *19*, 343.
(4) Sanchez, V.; Oftadeh, H.; Durou, C.; Hot, J. P. *J. Chem. Eng. Data* **1977**, *22*, 123.
(5) Sanchez, V.; Clifton, M. J. *J. Chem. Eng. Data* **1978**, *23*, 209.
(6) Srinivasan, V. S. *Adv. Electrochem. Eng.* **1973**, *9*, 369.
(7) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1968.
(8) Hiquily, N.; Laguérie, C. *Propellants Explos. Pyrotech.* **1982**, *7*, 91.
(9) Ayerst, R. P.; Phillips, M. I. *J. Chem. Eng. Data* **1966**, *11*, 494.
(10) Ayerst, R. P.; Phillips, M. I. "Industrial Crystallization"; Proc. Symp. London, Instn. Chem. Engrs, 1969; p 56.

Received for review March 28, 1983. Revised manuscript received March 5, 1984. Accepted March 28, 1984.

Vapor Pressure Measurement of Tetralin at Reduced Pressures

Hirotake Katayama* and Yasuhiro Harada

Chemical Laboratory, College of Engineering, Hosei University, Koganei, Tokyo, Japan

The vapor pressure of Tetralin was measured over the pressure range of 0.40–32.5 kPa, i.e., the temperature range of 330.80–437.13 K. The results were fitted to Chebyshev polynomials and the Miller and Antoine equations, the percent root mean square deviations of which were estimated as 0.22, 0.29, and 0.33, respectively.

Introduction

To measure vapor–liquid equilibrium and vapor pressure at reduced pressure, we constructed a new equilibrium still. In this work the vapor pressure of Tetralin (1,2,3,4-tetrahydronaphthalene) has been measured at 0.40–32.5 kPa, because there have been only a few data on the vapor pressure at reduced pressures: the six values by Herz and Schuftan (*1*) in 1922, the three by Linder (*2*) in 1931, the three by Lagrange et al. (*3*) in 1971, the four by Nasir et al. (*4*) in 1980, and the four by Katayama and Watanabe (*5*) in 1980. Some of these are not precise.

Recently Tetralin has been employed as a reagent for the liquefaction of coal.

Experimental Section

Material. Commercial-grade Tetralin was distilled in a wetted wall column with 1-m length and 10-mm i.d. at 1.3 kPa. The intermediate distillate used for this work was monitored by measuring the change in the refractive indexes of each 10-mL distillate.

The purity of the Tetralin was estimated to be 99.8% by gas chromatography with Porapak-s as described in the previous paper (*5*). The refractive index and the density of the Tetralin at 25.0 °C have already been determined previously (*5*) as 1.5383, compared with the literature value 1.539 19 (*6*), and 963.6 kg/m^3, compared with the literature value 963.24 kg/m^3 (*7*).

Apparatus and Procedure. The experimental apparatus was set up as in Figure 1. The equilibrium still is made of Pyrex glass, and its cylinder is 400 mm high with a 70-mm i.d. The funnel of the Cottrell 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 funnel. The still is designed to decrease the pressure drop between the surface and the condenser sections.

The measurement and the control of pressure were carried out with a Multi-Range Model 157/100 pressure standard from Texas Instruments Inc. Its accuracy is ±0.002 kPa for the 35–10-kPa range and ±0.001 kPa for the 10–0.40-kPa range. The accuracy of pressure control on operation was found to be within ±0.000 03 kPa for the 35–1-kPa range, and within ±0.0004 kPa for the 1–0.40-kPa range. Since the pressure below 0.40 kPa could not be controlled well, the vapor pressures below this pressure were not measured.

Mercury thermometers with immersion lines marked 18 cm from the bulb end, which consisted of three sets of graduation from 40 to 100, 100 to 150, and 150 to 200 °C, were used. They have been calibrated in 10 °C intervals by Watanabe Keiki Seisakusho Co., Ltd., Tokyo. Their accuracies are within ±0.04 K.

The McLeod gage in Figure 1 was employed only when the zero counter (calibration) of the Bourdon capsule was to be determined.

About 120 mL of a sample was poured into the bottom of the still through the stopper 11. The circulation of vapor was carried out at the rate of 40 drops/min for 2 h. The outside wall of the still was held at 3 K below the boiling point. Since the Tetralin is polymerized by heating as described previously (*5*), a fresh sample was used after every three measurements.

Results and Discussion

The vapor pressure data of Tetralin are presented in Table I. The data are also plotted in Figure 2 including a comparison with values from the literature. The data are in good agreement with the literature in the pressure range between 32 and 5 kPa, but are somewhat smaller than quoted values below 5 kPa. The values of Nasir et al. (*4*) are larger than the others.

0021-9568/84/1729-0373$01.50/0

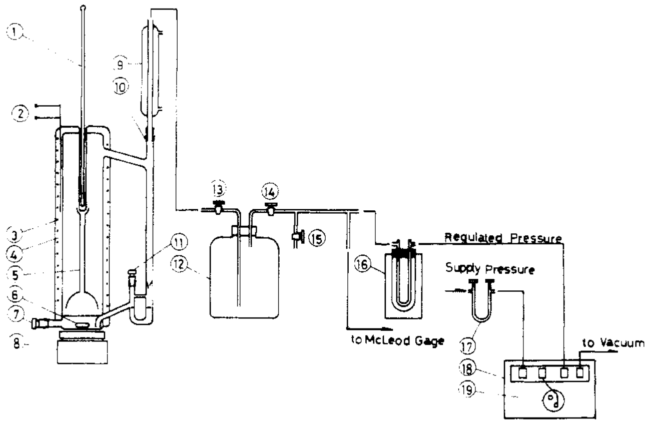

Figure 1. Experimental apparatus: (1) thermometer; (2) thermocouple; (3) nichrome heater; (4) asbestos; (5) Cottrell pump; (6) rotor; (7) greaseless stopper; (8) hot plate with magnetic stirrer; (9) condenser; (10) greaseless joint; (11) greaseless stopper; (12) buffer tank; (13–15) stopcocks; (16) cold trap; (17) molecular sieves; (18) pressure standard; (19) quartz Bourdon capsule.

Table I. Vapor Pressures of Tetralin

obsd		ϵ,[a] %	
T, K	p, kPa	Miller eq	Antoine eq
437.13	32.500	0.40	0.12
434.41	30.000	0.16	0.02
431.51	27.500	−0.10	−0.12
428.48	25.000	−0.62	−0.55
425.00	22.500	−0.58	−0.43
420.94	20.000	0.31	0.49
416.73	17.500	0.46	0.65
412.28	15.000	−0.26	−0.12
406.81	12.500	0.15	0.22
400.56	10.000	−0.04	−0.10
392.72	7.500	0.22	−0.01
382.42	5.000	0.06	−0.34
366.21	2.500	−0.06	−0.40
355.27	1.500	0.00	−0.06
347.22	1.000	−0.20	−0.04
345.20	0.900	−0.19	0.00
342.96	0.800	−0.07	0.14
340.53	0.700	−0.25	−0.04
339.15	0.650	−0.05	0.13
337.63	0.600	0.44	0.58
336.17	0.550	0.03	0.10
334.45	0.500	0.41	0.37
332.72	0.450	0.03	−0.17
330.80	0.400	−0.25	−0.69

	Miller eq	Antoine eq
mean dev[b]	0.22	0.25
max dev[a]	−0.62	−0.69

[a] ϵ = pressure deviation = $100(P_{\mathrm{exptl}} - P_{\mathrm{calcd}})/P_{\mathrm{exptl}}$. [b] $100\sum_i(|P_{\mathrm{exptl}} - P_{\mathrm{calcd}}|/P_{\mathrm{exptl}})_i/n$.

Chebyshev polynomials (*8*) and Miller (*9*) and Antoine equations of the following forms were used to fit the results:

Chebyshev polynomials

$$t \ln (p) = a_0/2 + \sum_{i=1}^{0} a_i E_i(x)$$

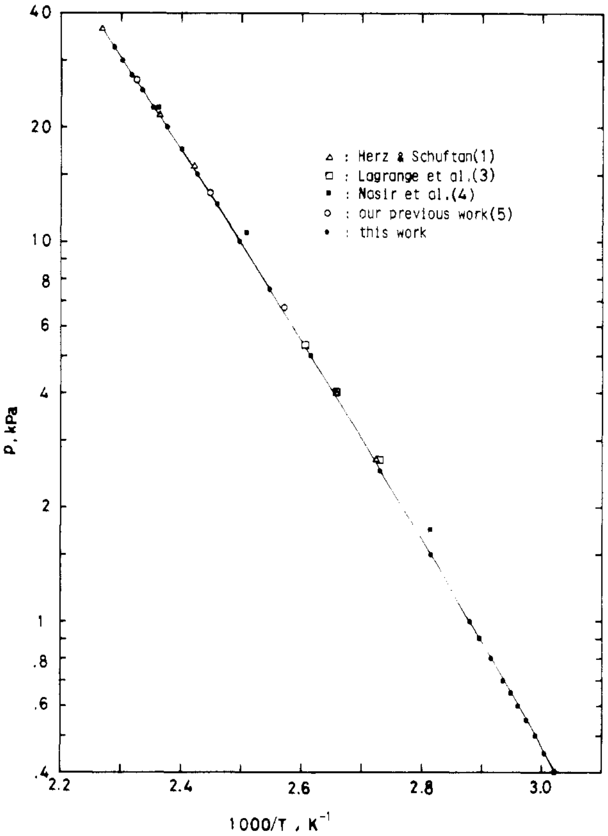

Figure 2. Vapor pressures of Tetralin vs. $1/T$.

where $t = T - 273.15$, $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_i(x) = 2xE_{i-1}(x) - E_{i-2}(x)$, and x is a function of temperature defined as

$$x = \frac{2T - (T_{\max} + T_{\min})}{T_{\max} - T_{\min}}$$

where $T_{\max}$ and $T_{\min}$ are 437.13 and 330.80 K, respectively

Miller equation

$$\ln (p) = A_{\mathrm{m}} + B_{\mathrm{m}}/t + C_{\mathrm{m}}t + D_{\mathrm{m}}t^2$$

or

$$t \ln (p) = A_{\mathrm{m}}t + B_{\mathrm{m}} + C_{\mathrm{m}}t^2 + D_{\mathrm{m}}t^3$$

Antoine equation

$$\ln (p) = A_{\mathrm{a}} - B_{\mathrm{a}}/(t + C_{\mathrm{a}})$$

or

$$t \ln (p) = A_{\mathrm{a}}t + D_{\mathrm{a}} - C_{\mathrm{a}} \ln (p)$$

where

$$D_{\mathrm{a}} = A_{\mathrm{a}}C_{\mathrm{a}} - B_{\mathrm{a}}$$

All the coefficients of the expressions were decided by the fits of $t \ln (p)$ as written in Table II.

Table II. Constants of Chebyshev Polynomials and Miller and Antoine Equations from Least-Squares Fit of $t \ln (p)$

Chebyshev constants				Miller constants		Antoine constants	
a_0	443.986	a_4	0.17822	A_{m}	−3.00640	A_{a}	13.64979
a_1	314.899	a_5	0.18306	B_{m}	−48.9855	B_{a}	3586.62
a_2	36.795	a_6	0.1374	C_{m}	0.562848×10^{-4}	C_{a}	188.697
a_3	−3.3684	a_7	0.1920	D_{m}	-0.910118×10^{-4}		

	Chebyshev polynomial	Miller eq	Antoine eq
prms[a]	0.22	0.29	0.33

[a] Percent root mean square deviation defined by $100[\sum_i((P_{\mathrm{exptl}} - P_{\mathrm{calcd}})/P_{\mathrm{exptl}})_i^2/n]^{1/2}$.

Table III. Temperature Difference between Experimental and Calculated Values against Vapor Pressure Using Miller and Antoine Equations

	ΔT,[a] K	
P, kPa	Miller eq	Antoine eq
32.500	−0.14	−0.04
30.000	−0.06	−0.01
27.500	0.03	0.04
25.000	0.21	0.18
22.500	0.19	0.14
20.000	−0.10	−0.16
17.500	−0.14	−0.20
15.000	0.08	0.03
12.500	−0.04	−0.06
10.000	0.01	0.03
7.500	−0.06	0.00
5.000	−0.01	0.08
2.500	0.01	0.09
1.500	0.00	0.01
1.000	0.04	0.01
0.900	0.04	0.00
0.800	0.01	−0.03
0.700	0.05	0.01
0.650	0.01	−0.02
0.600	−0.08	−0.10
0.550	0.00	−0.02
0.500	−0.07	−0.06
0.450	−0.01	0.03
0.400	0.04	0.12
	Miller eq	Antoine eq
mean dif,[b] K	0.06	0.06
max dif,[a] K	0.21	−0.20

[a] $T = T_{\mathrm{exptl}} - T_{\mathrm{calcd}}$. [b] $\sum_i |T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|_i / n$. n: number of data (=24).

Since the percent root mean square deviations of pressures (prms) using Chebyshev polynomials with the number of parameters from 3 to 10 were estimated as 2.70 at 3 parameters, 0.29 at 4 and 5, 0.26 at 6 and 7, 0.22 at 8–10, respectively, here 8 parameters are selected as written in Table II. The prms of the Miller and Antoine equations are listed as 0.29 and 0.33, respectively, in Table II. Percent pressure deviations and mean absolute deviations from the equations have also been presented in Table I.

Conversely, the temperatures were calculated by using the Miller and Antoine equations, and the differences between experimental and calculated values are shown in Table III. The mean differences of the temperatures obtained in both were equal to 0.06 K.

The Miller equation, having four constants, gave somewhat better correlations than the Antoine equation, having three constants, but the degrees of differences were very small.

Acknowledgment

We are deeply grateful to Professor Edwin F. Meyer, Department of Chemistry, DePaul University, Chicago, IL 60614, for his help and advice on the manuscript.

Glossary

p	pressure, kPa
T	temperature, K
t	$T - 273.15$ K

Greek Letters

ϵ	percent pressure deviation $(=100(P_{\mathrm{exptl}} - P_{\mathrm{calcd}})/P_{\mathrm{exptl}})$

Registry No. Tetralin, 119-64-2.

Literature Cited

(1) Herz, W.; Schuftan, P. *Z. Phys. Chem.* **1922**, *101*, 269.
(2) Linder, E. G. *J. Phys. Chem.* **1931**, *35*, 531.
(3) Lagrange, G.; Laurence, G.; Darmis, R. *Chim. Anal. (Paris)* **1971**, *53*, 107.
(4) Nasir, P.; Hwang, S. C.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 298.
(5) Katayama, H.; Watanabe, I. *J. Chem. Eng. Data* **1982**, *27*, 91.
(6) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950; Vol. 1, p 208.
(7) Dreisbach, R. R.; Martin, R. *Ind. Eng. Chem.* **1949**, *41*, 2875.
(8) Ambrose, D.; Counsell, J. F.; Davenport, A. J. *J. Chem. Thermodyn.* **1970**, *2*, 283.
(9) Miller, D. G. *Ind. Eng. Chem.* **1964**, *56*, 46.

Received for review June 8, 1983. Revised manuscript received February 23, 1984. Accepted March 30, 1984.

Investigation of Vapor Pressures and Enthalpies and Entropies of Vaporization of Xanthene at Elevated Temperatures

Alwarappa Sivaraman and Riki Kobayashi*

George R. Brown School of Engineering, Department of Chemical Engineering, Rice University, Houston, Texas 77251

Vapor pressures (6.35–817.29 mmHg) of xanthene, a polynuclear aromatic (three-ring) compound containing an oxygen group, over the temperature range 423–589 K, were measured. The measurements were performed in a high-temperature static apparatus. Chebyshev polynomials have been used to fit the experimental vapor pressure data. The results have been further processed to evaluate the enthalpies of vaporization and compared with the predicted enthalpy values, by a recently developed generalized correlation which incorporates the renormalization group theory with the corresponding states principle. The entropies of vaporization were also evaluated at their respective temperatures for xanthene.

Introduction

Vapor pressures and enthalpies and entropies of vaporization are a few of the important physical properties required in designing coal-liquid and shale oil processing and separation plants. The thermodynamic properties are virtually unknown at high temperatures for the three-ring heavy polynuclear hydrocarbons. We reported previously (*1–3*) the vapor pressures of various condensed aromatic compounds. In this work we continue the measurements of vapor pressures of a three-ring, oxygen-containing, coal-derived liquid, xanthene. The vapor pressures of xanthene are reported over a wide range of temperatures up to the onset of thermal decomposition. No experimental vapor pressures or enthalpies of vaporization are