Table II. Dissociation Constants for Commercial-Grade and Pure DIPA in 1.00 M Potassium Chloride Solution[a]

	10^9K, mol/L			
T, K	293	303	313	323
DIPA commercial grade	0.456	0.846	1.47	2.35
	0.453	0.838	1.42	2.28
	0.454		1.40	2.34
DIPA pure	0.480	0.851	1.42	2.34
	0.450	0.841	1.42	2.43
	0.451			2.62
				2.35

[a] See footnote of Table I.

strength the dissociation constants of DIPA and DEA are essentially equal. The deviations of the dissociation constants of DEA and DIPA, due to nonideality of the solutions, will also be essentially the same because of the structural similarity of the molecules.

Therefore it can be concluded that, at zero ionic strength, the dissociation constants of DIPA are given by the equation which describes the dissociation constants of DEA (*4*):

$$\log K_{I=0} = (-1.82 \times 10^3)/T - 4.10 + (4.44 \times 10^{-3})T$$

The second series of experiments gives the dissociation constants for commercial-grade and pure DIPA at 293, 303, 313, and 323 K (Table II). These results show that the presence of small amounts of MIPA have no effect on the dissociation constant of DIPA.

The standard deviation of the results is 5% of the K values (0.02 pK units) for each of both series of experiments (Tables I and II). The larger difference (10-20% in K values, 0.04-0.08 pK units) between the results for commercial-grade DIPA shown in Tables I and II is due to the separate calibration procedures of the electrode since for each of these series new calibration solutions were prepared. The estimated accuracy for our calibration solutions for $\mathrm{pH} > 10$ is ±0.05 pH unit.

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Literature Cited

(1) Bos, M. *Anal. Chim. Acta* **1977**, *90*, 61.
(2) Klein, J. P. *Oil Gas Int.* **1970**, *10*, 109.
(3) Kohl, A. L.; Riesenfeld, F. C. "Gas Purification"; Gulf Publishing Co.: Houston, TX, 1974.
(4) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965.
(5) Saha, N. C.; Jain, S. K.; Dua, R. K. *Chromatographia* **1977**, *10*, 368.
(6) Sharma, M. M. *Trans. Faraday Soc.* **1965**, *61*, 681.

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Vapor-Pressure Measurements of 1-Methylnaphthalene, 2-Methylnaphthalene, and 9,10-Dihydrophenanthrene at Elevated Temperatures

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Vapor pressures of three polynuclear aromatic compounds were measured over the following elevated temperature ranges: (1) 1-methylnaphthalene, 424.43-593.38 K; (2) 2-methylnaphthalene, 424.41-638.93 K; and (3) 9,10-dihydrophenanthrene, 437.28-552.61 K. The measurements were carried out with a high-temperature static apparatus. The experimental vapor-pressure data have been fitted to Chebyshev polynomials. The values of dp/dT over the temperatures investigated for 1-methylnaphthalene and 2-methylnaphthalene are reported.

Introduction

In a previous paper (*1*) we reported the vapor pressures of three polynuclear aromatic compounds, diphenylmethane, thianaphthene, and bicyclohexyl. In this work we continue the measurements of vapor pressures of compounds which appear in oils associated with the liquefaction of coal. We report the vapor pressures of 1-methylnaphthalene, 2-methylnaphthalene, and 9,10-dihydrophenanthrene over a wide range of temperatures up to their respective conditions of measurable initial thermal decomposition.

No experimental vapor-pressure values are reported in the literature in the range of the present investigation for 9,10-dihydrophenanthrene. The data of Camin and Rossini (*2*) for 1-methylnaphthalene and 2-methylnaphthalene cover the temperature range up to their boiling points.

Materials

The samples of 1-methylnaphthalene, 2-methylnaphthalene, and 9,10-dihydrophenanthrene were purchased from Aldrich Chemical Co. with reported purities of 97, 99, and 97%, respectively. 1-Methylnaphthalene was purified in a low temperature zone refiner (for substances with melting points above room temperature); 32 and 48 passes were made, respectively. The purities were checked by the freezing-point method of Rossini et al. (*3*), and the results were as follows: 1-methylnaphthalene, 99.95%; 2-methylnaphthalene, 99.98%; and 9,10-dihydrophenanthrene, 99.95%.

Apparatus and Procedure

The measurements of vapor pressures were carried out with a high-temperature static apparatus described elsewhere (*1*, *4*). Some modifications were made to the apparatus to control the sublimation of the bath fluid. Monsanto Therminol 88 was replaced by a commercial mixture of inorganic salts (Draw Temp 275 manufactured by E. F. Houghton Co.).

The temperature near the equilibrium cell was measured in IPTS-68 with an accuracy of ±0.01 K by means of a Leeds and Northrup platinum resistance thermometer with a calibration traceable to the National Bureau of Standards and checked in

Table I. Vapor Pressures and dp/dT of 1-Methylnaphthalene

T, K	P, mmHg	dp/dT, mmHg/K	T, K	P, mmHg	dp/dT, mmHg/K
424.43	57.91	2.03	513.41	690.93	15.47
431.94	74.47	2.51	516.42	739.71	16.32
439.57	96.10	3.09	517.75	762.28	16.71
448.55	127.28	3.90	527.82	946.82	19.85
455.65	157.69	4.64	536.84	1138.70	22.99
462.66	193.05	5.48	544.85	1334.47	26.03
469.18	231.70	6.36	552.88	1555.54	29.31
475.50	274.79	7.31	561.18	1813.56	32.93
483.33	336.82	8.63	568.49	2067.68	36.28
490.85	406.91	10.07	576.84	2388.31	40.27
499.08	497.39	11.84	584.38	2711.08	43.97
506.97	597.92	13.75	593.38	3116.01	48.45

Table II. Vapor Pressures and dp/dT of 2-Methylnaphthalene

T, K	P, mmHg	dp/dT, mmHg/K	T, K	P, mmHg	dp/dT, mmHg/K
424.41	64.72	2.22	527.84	1012.52	21.02
431.87	82.45	2.74	536.39	1204.14	24.13
437.49	98.88	3.18	544.44	14.11.30	27.32
443.04	117.12	3.68	552.96	1658.96	30.97
448.98	140.68	4.27	560.97	1914.08	34.65
454.99	169.14	4.94	568.66	2195.29	38.39
462.33	208.89	5.86	576.95	2530.98	42.61
469.35	253.61	6.86	584.96	2891.38	46.85
475.19	296.56	7.79	593.44	3314.34	51.45
482.64	360.08	9.11	600.68	3713.04	55.40
490.15	434.84	10.61	608.35	4174.54	59.56
498.49	530.66	12.48	620.26	4897.69	65.74
505.62	626.35	14.25	629.32	5521.06	70.04
512.26	727.50	16.09	638.93	6161.04	73.98
520.05	861.56	18.44			

Table III. Vapor Pressures of 9,10-Dihydrophenanthrene

T, K	P, mmHg	T, K	P, mmHg
437.28	12.06	498.61	90.68
443.10	15.42	505.51	110.14
448.97	19.02	512.91	134.88
454.93	23.85	520.18	163.66
462.30	30.52	527.84	199.15
469.11	37.85	536.65	248.21
474.87	45.05	544.40	297.86
482.49	56.72	552.61	360.46
490.02	71.00		

this laboratory at the triple-point temperature of water.

The pressure measurements were made with a high-temperature Ruska differential pressure null detector and a Ruska gas-lubricated dead weight gauge Model 2465. The procedure concerning estimation of initial thermal decomposition was the same as described previously.

Results and Discussion

Similar to our previous measurements of vapor pressures (*1*), special care was taken to establish where thermal instability began. Thus, at least two series of measurements were made for each compound investigated. The measurements were made at ~7-9 K intervals in the temperature ranges 424.43-593.38 K for 1-methylnaphthalene, 424.41-638.93 K for 2-methylnaphthalene, and 437.28-552.61 K for 9,10-dihydrophenanthrene. The values of experimental vapor pressures of 1-methylnaphthalene, 2-methylnaphthalene, and 9,10-dihydrophenanthrene are listed in Tables I-III, respectively.

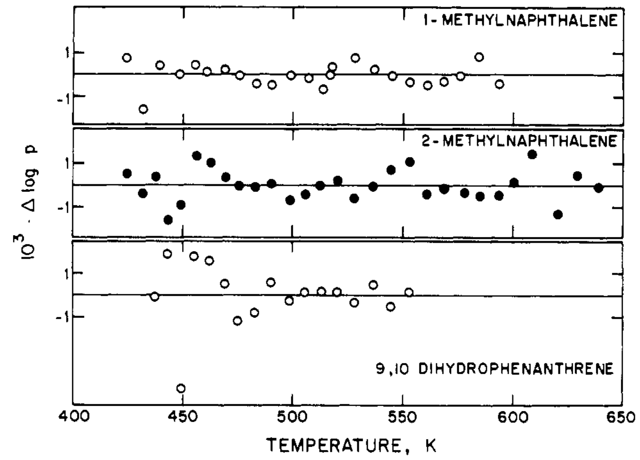

Figure 1. Residuals in log p for 1-methylnaphthalene, 2-methylnaphthalene, and 9,10-dihydrophenanthrene.

Chebyshev polynomials of the following form are used to fit the vapor pressure obtained in this work:

$$T \log p = a_0/2 + \sum_{i=1}^{n} a_i E_i(x)$$

where $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_3(x) = 4x^3 - 3x$, and $E_{i+1}(x) = 2xE_i(x) - E_{i-1}(x)$; x is a function of temperatures defined as

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

where $T_{\max}$ and $T_{\min}$ are temperatures, respectively, just above and just below the extreme temperatures of the measured values.

The values of $T \log P$ were fitted by Chebyshev polynomials up to the fifth order. The coefficients of the polynomials cover the ranges of temperature bounded by $T_{\max}$ and $T_{\min}$ given in Table IV. For 1-methylnaphthalene, the fourth-order polynomial was chosen to give a 0.13% root mean square deviation. For 2-methylnaphthalene and 9,10-dihydrophenanthrene, a good fit was obtained by using the fifth-order polynomials giving percent root mean square deviations of 0.16 and 0.31, respectively. In Figure 1 the residuals, $\Delta \log P = \log p - \log p_{\text{calcd}}$ for the compounds investigated are presented.

Because the polynuclear aromatic compounds investigated in this work are thermally unstable below their critical temperatures, and in the case of 9,10-dihydrophenanthrene even

Table IV. Constants of Chebyshev Polynomials for $T \log p$

	1-methylnaphthalene	2-methylnaphthalene		9,10-dihydrophenanthrene
order	4	5	4	5
a_0	2834.199	3213.244	3213.125	1893.261
a_1	662.835	828.965	829.113	468.280
a_2	−6.1730	−10.6236	−10.6894	−1.8573
a_3	0.2501	−1.2058	−0.8815	1.7818
a_4	−0.4421	−1.0996	−1.0178	−1.9200
a_5		−1.1727		−0.6466
$T_{\max}$/K	593.40	638.95	638.95	552.70
$T_{\min}$/K	424.40	424.40	424.40	437.20
% rms	0.13	0.16	0.40	0.31

Table V. Estimated Critical Parameters Used

	T_c, K	P_c, atm
1-methylnaphthalene	772	35.2
2-methylnaphthalene	761	34.6
9,10-dihydrophenanthrene	774	12.97
estimated bp	587.26	

Table VI. Constants of Chebyshev Polynomials for $T \log p$

	1-methylnaphthalene	2-methylnaphthalene	9,10-dihydrophenanthrene
a	4138.000	4134.410	2171.397
a	1383.112	1283.869	606.468
a	−6.1503	−8.9977	−2.3576
a	8.2009	12.1703	1.5415
a	1.2376	7.5364	−1.1510
a		3.0921	−1.9399
T_{max}/K	772.10	761.10	587.30
T_{min}/K	415.20	424.40	437.20
% rms	0.19	0.48	0.30

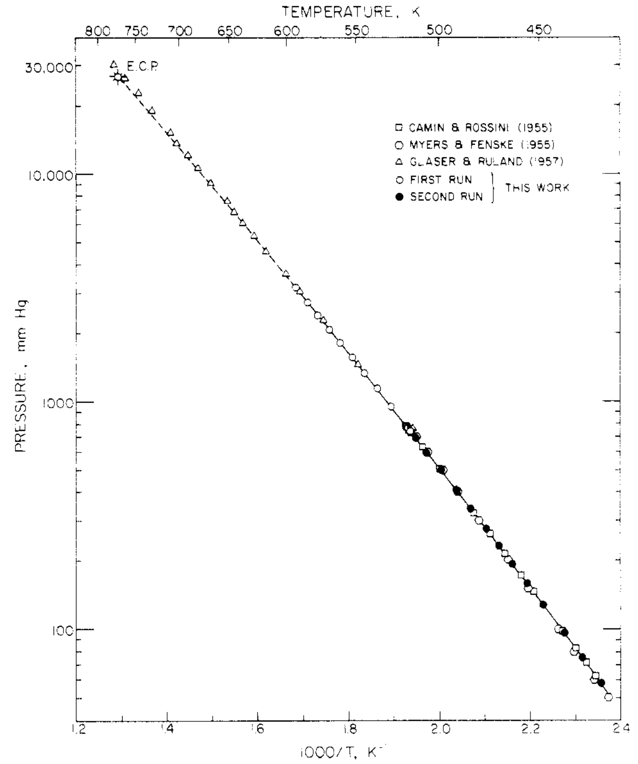

Figure 2. Vapor pressures of 1-methylnaphthalene vs. 1/T.

below its normal boiling point, to estimate the vapor pressure in this temperature range between investigated T_{max} and estimated critical temperature (Table V), we fitted the experimental vapor-pressure data over an extended range of temperatures including the estimated critical temperature for 1-methylnaphthalene and 2-methylnaphthalene and up to the estimated boiling point for 9,10-dihydrophenanthrene. The Chebyshev coefficients along with temperature range and percent root mean square deviation for this exercise are given in Table VI.

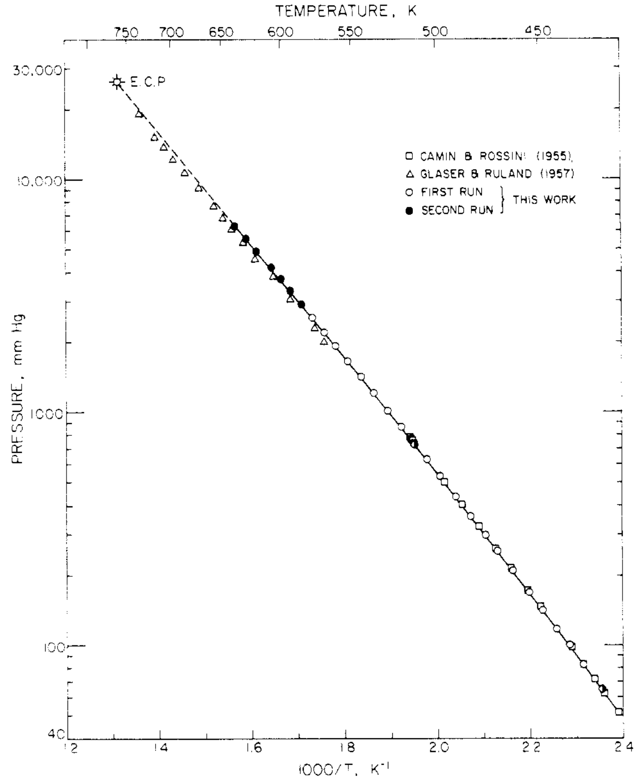

Figure 3. Vapor pressures of 2-methylnaphthalene vs. 1/T.

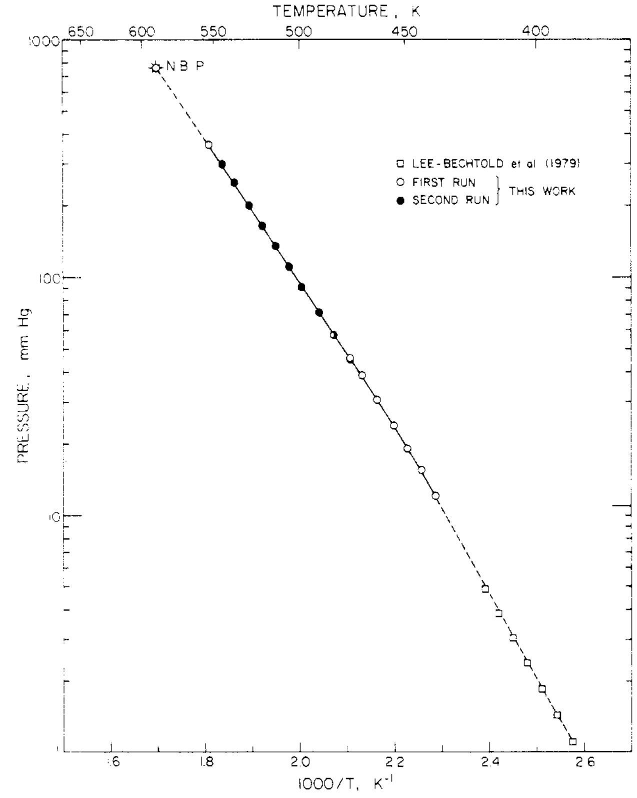

Figure 4. Vapor pressures of 9,10-dihydrophenanthrene vs. 1/T.

The values of dp/dT for the range of temperature investigated calculated from fourth-order Chebyshev polynomial with coefficients from Table IV, for 1-methylnaphthalene and 2-methylnaphthalene, are given in Tables I and II, respectively. We do not report the values of dp/dT for 9,10-dihydrophenanthrene because of the restricted range of the data and the questionable behavior of the calculated heats of vaporization therefrom. The reason for that behavior is that measured values of the vapor pressure of 9,10-dihydrophenanthrene at lower temperature ranges are small, between 12 and 50 mmHg, leading to an even further reduction of the vapor-pressure values that would yield reliable experimental points.

Comparison with Existing Data

In Figure 2 the comparison of vapor pressures of 1-methylnaphthalene obtained during this investigation was made with data available from the literature. Camin and Rossini (*2*) measured the vapor pressure of 1-methylnaphthalene between 415.29 and 518.48 K. Our data are in very good agreement with their results. Myers and Fenske (*5*) reported the smoothed data for 1-methylnaphthalene between 325.45 and 516.15 K. Their values at lower ranges of investigated temperature are slightly smaller than both ours and the data of Camin and Rossini (*2*). Smoothed data of vapor pressures of 1-methylnaphthalene reported by Glaser and Ruland (*6*) at the temperature range between 515.15 and 778.15 K are in serious disagreement with our results, their data being rather higher than ours.

In Figure 3, comparison of vapor-pressure data for 2-methylnaphthalene are shown. Similarly, for 2-methylnaphthalene, good agreement with the data of Camin and Rossini (*2*) at temperature ranges between 412.34 and 514.81 K is evident, while serious discrepancies with smoothed data of Glaser and Ruland (*6*) between 515.15 and 735.15 K are noted.

For 9,10-dihydrophenanthrene, only the data of Lee-Bechtold et al. (*7*) are available, covering the temperature range from 353.15 to 418.15 K which does not overlap ours. In Figure 4 our data from higher temperatures are shown. An extrapolated line from our data to lower temperatures appears to merge with the line through their data.

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Literature Cited

(1) Wieczorek, S. A.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 302.
(2) Camin, D. L; Rossini, F. D. *J. Phys. Chem.* **1955**, *59*, 1173.
(3) Glasgow, A. R.; Streiff, A. J.; Rossini, F. D. *J. Res. Natl. Bur. Stand (U.S.)* **1945**, *35*, 355.
(4) Nasir, P.; Hwang, S. C.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 298.
(5) Myers, H. S.; Fenske, M. R. *Ind. Eng. Chem.* **1955**, *47*, 1652.
(6) Glaser, F.; Ruland, H. *Chem.-Ing.-Tech.* **1957**, *29*, 772.
(7) Lee-Bechtold, S. H.; Horsenloop, I. A.; Scott, D. W.; Osborn, A. G.; Good, W. D. *J. Chem. Thermodyn.* **1979**, *11*, 469.

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Heats of Vaporization of Five Polynuclear Aromatic Compounds at Elevated Temperatures

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Heats of vaporization of five polynuclear aromatic compounds, thianaphthene, 1-methylnaphthalene, 2-methylnaphthalene, bicyclohexyl, and diphenylmethane over a wide range of elevated temperatures have been calculated from the Clausius–Clapeyron equation by using acentric factors and vapor pressures recently measured by the authors. The values of d*p*/d*T* calculated from Chebyshev polynomials were used. Compressibility factors of saturated vapor and liquid were estimated from three-parameter corresponding-states correlation using acentric factors determined from new vapor-pressure data.

Introduction

In previous papers (*3*, *4*) the vapor pressures of polynuclear aromatic compounds over a wide range of elevated temperatures were reported. The experimental data of vapor pressures were fitted to Chebyshev polynomials, and values of dp/dT were calculated.

No literature measurements of heats of vaporization over the range of temperatures were found for these compounds. In view of the importance of thermal data in coal liquefaction technology, such data are urgently needed.

In the present work we report calculated values of heats of vaporization based on our own data over a range of temperatures which were covered in the vapor-pressure measurements. The heats of vaporization were calculated by using the Clausius–Clapeyron relation and the three-parameter corresponding-states correlation of Pitzer (*1*) to evaluate the compressibility factor of saturated vapor and liquid.

Table I. Estimated Critical Parameters

		T_c, K	p_c, atm	ω
thianaphthene	C_8H_6S	752.0	38.3	0.294
1-methylnaphthalene	$C_{11}H_{10}$	772.0[a]	35.2[a]	0.340
1-methylnaphthalene	$C_{11}H_{10}$	761.0[a]	34.6[a]	0.371
bicyclohexyl	$C_{12}H_{22}$	731.4	25.3	0.394
diphenylmethane	$C_{13}H_{12}$	770.2	28.2	0.438

[a] Taken from ref *2*.

Results and Discussion

The heats of vaporization of five polynuclear aromatic compounds, thianaphthene, 1-methylnaphthalene, 2-methylnaphthalene, bicyclohexyl, and diphenylmethane, were calculated from the Clausius–Clapeyron equation:

$$dp/dT = \Delta Hv/(RT^2/p)\Delta Z \tag{1}$$

or

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta Hv}{R\Delta Z} \tag{2}$$

where

$$\Delta Z = Z_s^{v} - Z_s^{L}$$

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