Vapor Pressure Measurements of Diphenylmethane, Thianaphthene, and Bicyclohexyl at Elevated Temperatures

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In this paper we present the values of vapor pressure at elevated temperature for diphenylmethane (424.64–648.25 K), thianaphthene (424.40–630.60 K), and bicyclohexyl (424.25–577.25 K). A high-temperature static apparatus has been used for the measurements. The experimental data of vapor pressures have been fitted to Chebyshev polynomials. The values of d*p*/d*T* over the temperature ranges investigated are reported.

Introduction

The relationship between temperature and vapor pressure has interested scientists for many years. The present investigations were undertaken for heavier molecules, for which thermodynamic properties are virtually unknown, especially at high temperatures. One of the most important basic properties of a compound is its vapor pressure. This investigation was undertaken to obtain data on the vapor pressures of diphenylmethane, thianaphthene, and bicyclohexyl over a wide range of temperatures up to their conditions of initial thermal decomposition. Presently only a few experimental data of vapor pressures exist for diphenylmethane. In this work, the vapor pressures and dp/dT can be directly applied for the calculation of their enthalpies of vaporization at higher temperatures.

Experimental Section

***Materials*.** All compounds studied were purchased from Aldrich Chemical Co. with the following reported purities: diphenylmethane, 99%; thianaphthene, 97%; and bicyclohexyl, 97%. The substances were purified by the following number of successive crystallization operations: diphenylmethane, 5; thianaphthene, 7; and bicyclohexyl, 11. The purity was checked by the freezing-point method of Rossini et al. (*5*). The purities determined in this way were the following: diphenylmethane, 99.90 ± 0.05%; thianaphthene, 99.90 ± 0.05%; and bicyclohexyl, 99.95 ± 0.05%.

***Methods*.** The measurement of vapor pressure was carried out with the apparatus that was described earlier (*8*). Some modifications were made to the apparatus and in the experimental procedure to achieve higher temperatures and to improve the accuracy of measurements. Among the modifications were to replace valves in crucial positions with bellows valves, to complete isolation of the upper portion of the differential pressure indicator from the fluid under study, and to insert provisions to minimize the sublimation of the bath fluid components.

Since the upper temperature limit of the bath fluid (Monsanto Therminol 66) used in the previous study (*8*) was ca. 570 K, it was replaced by Monsanto's Therminol 88, which can be used from ca. 424 K (the melting point of the bath fluid) to 650 K.

Before ~50 cm^3 of degassed sample was charged into the equilibrium cell (EC) (liquid flowing under gravity), the system between valves 1, 4, 6, and 7 (see Figure 1) was thoroughly evacuated to a vacuum of ~10^{-3} mmHg. After the sample was charged, complete degassing was checked as discussed earlier (*8*).

The temperature of the bath was then increased to the required value, the space between valves 2 and 4 and 4, 9, and 11 evacuated, the pressure on both sides of the diaphragm equalized (valves 2, 3, and 11 closed and 4 and 9 open), and the null position of the differential pressure null indicator adjusted. This procedure was repeated for each vapor pressure measurement.

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.

The measurement of pressure was carried out with a high temperature Ruska differential pressure null detector and a gas lubricated dead weight gauge Model 2465.

The overall accuracy of the pressure measurement is estimated to be 0.015% of the measured value.

Results and Discussion

Because the vapor pressures of compounds were measured at high temperatures, at which most of these substances are unstable, we took special care to establish when thermal instability began. The procedure used in these measurements applied the fact that the vapor pressure of pure compounds is a function of temperature only and must be reproduced if decomposition does not occur. In the initial series of measurements the vapor pressures were measured up to the temperature at which the probability of thermal decomposition would take place, the temperature was lowered, and the vapor pressure was measured to detect any excess pressure in order to check for stability. If the values of vapor pressures were reproducible to the range of accuracy stated above, the measurements were continued to higher temperatures until the first symptoms of thermal instability appeared as detected on large-scale plots of the data. If decomposition occurred, it was necessary to discard the sample, insert a new charge, and repeat all of the steps, resulting ultimately in a vapor pressure measurement at some lower temperature at which it could be confirmed that thermal decomposition had not begun.

The measurements of vapor pressures were made at ca. 6–8 K intervals in following temperature ranges: diphenylmethane; 424.64–648.25 K; thianaphthene; 424.40–630.60 K; and bicyclohexyyl; 424.25–577.25 K. Duplicate runs of measurements were made for each substance. The values of experimental vapor pressures of diphenylmethane, thianaphthene, and bicyclohexyl are reported in Tables I, II and III, respectively.

After examining most of the existing vapor pressure equations, we chose to fit the vapor pressure obtained in this work to Chebyshev polynomials (as suggested by Ambrose et al.) (*1*) which assume the form

$$T \log p = a_0/2 + a_1E_1(x) + a_2E_2(x) + \ldots + a_sE_s(x) + \ldots + A_nE_n(x)$$

where $E_s(x)$ is the Chebyshev polynomial in x of degree s and x is a function of temperature defined as

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

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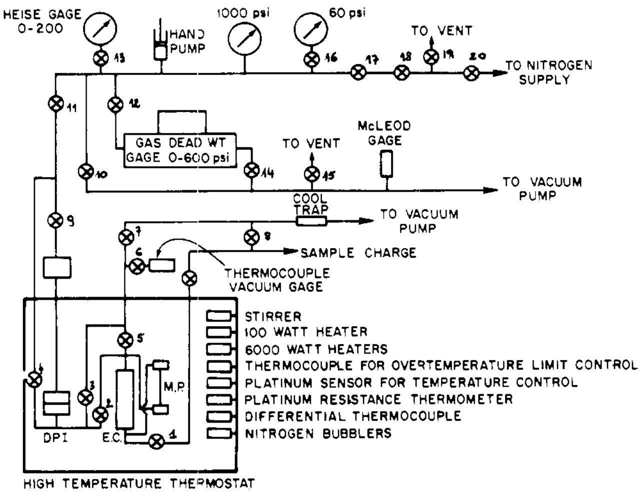

Figure 1. High-temperature, vapor pressure apparatus.

Table I. Vapor Pressures and dp/dT of Diphenylmethane

T, K	p, mmHg	dp/dT, mmHg/K	T, K	p, mmHg	dp/dT, mmHg/K
424.64[a]	29.28	1.12	528.38	626.31	13.83
424.91	29.47	1.13	536.94[a]	750.22	16.02
431.21	37.07	1.38	537.51	757.10	16.18
437.21	46.37	1.67	545.44	894.59	18.43
443.46	58.50	2.00	553.39[b]	1033.73	20.89
449.40	71.16	2.37	553.43	1033.11	20.90
455.47	86.16	2.81	561.15	1215.29	23.50
462.72	107.10	3.40	569.12	1398.59	26.40
469.16	130.77	4.00	577.03	1640.69	29.50
475.84	160.08	4.70	584.60[a]	1898.33	32.69
482.85[a]	198.29	5.54	593.78	2235.38	36.86
490.31[a]	242.88	6.55	609.47	2782.78	44.79
499.14	307.80	7.90	622.38	3441.98	52.14
505.82	365.53	9.05	630.23	3851.44	56.99
513.48	441.28	10.52	637.57	4326.03	61.81
520.94	528.79	12.09	647.25	5027.14	68.62

[a] Measurements made at second run. [b] Measurements made after raising temperature to 593.78 K.

Table II. Vapor Pressures and dp/dT of Thianaphthene

T, K	p, mmHg	dp/dT, mmHg/K	T, K	p, mmHg	dp/dT, mmHg/K
424.40	115.34	3.71	527.96	1519.87	29.68
430.78	140.02	4.38	537.01	1810.04	34.01
430.80[a]	140.02	4.38	537.02[a]	1810.14	34.02
437.38	172.17	5.16	544.57	2090.85	37.95
443.21	204.54	5.94	552.81	2421.68	42.60
448.94	241.64	6.79	561.31	2810.35	47.80
455.10	286.55	7.79	568.43	3167.19	52.47
462.63	350.34	9.17	576.18	3590.64	57.89
468.85	412.51	10.43	583.15	4008.26	63.08
475.40	486.41	11.90	593.10	4672.09	70.99
482.97	579.39	13.78	593.19[a]	4672.58	71.06
497.77	813.57	18.06	601.76[a]	5330.80	78.36
505.63	959.40	20.70	610.05[a]	6004.69	85.83
513.00	1124.14	23.41	621.59[a]	7043.70	96.89
520.48	1318.25	26.41	630.60[a]	7947.30	106.04

[a] Measurements made during the second run.

where T_{max} and T_{min} are temperatures, respectively, just above and just below the extreme temperature of the measured values. The first few Chebyshev polynomials are

$$E_0(x) = 1 \qquad E_1(x) = x \qquad E_2(x) = 2x^2 - 1$$

$$E_3(x) = 4x^3 - 3x$$

and they are calculated from the relation

$$E_{s+1}(x) - 2xE_s(x) + E_{s-1}(x) = 0$$

Table III. Vapor Pressures and dp/dT of Bicyclohexyl

T, K	p, mmHg	dp/dT, mmHg/K	T, K	p, mmHg	dp/dT. mmHg/K
424.25	71.94	2.49	499.28	583.03	13.28
431.09	90.44	3.01	506.33	693.09	15.00
436.98	109.48	3.52	513.21	799.18	16.83
443.44[a]	134.11	4.15	521.41[a]	943.92	19.20
449.48[a]	161.73	4.80	528.67[a]	1086.32	21.48
455.32	190.56	5.50	537.04[a]	1279.21	24.34
462.56[a]	233.44	6.47	545.22[a]	1488.73	27.39
462.57	233.48	6.47	553.18[a]	1720.58	30.60
469.18	282.05	7.45	561.36[a]	1989.63	34.17
475.82	335.51	8.54	568.79[a]	2258.14	37.67
483.15	401.42	9.87	577.25[a]	2600.82	41.96
490.74	483.66	11.39			

[a] Measurements made during the second run.

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

order	diphenyl-methane 7	thia-naphthene 7	bicyclo-hexyl 6
a_0	3041.313	3344.965	2772.710
a_1	883.393	791.720	590.578
a_2	−13.591	−5.042	−7.164
a_3	2.152	1.000	1.436
a_4	1.406	−0.644	0.544
a_5	0.280	0.133	−0.108
a_6	0.575	0.259	−0.201
a_7	1.688	−0.525	
T_{max}/K	647.26	630.61	577.26
T_{min}/K	424.63	424.39	424.24
prms[a]	0.78	0.19	0.34

[a] $\text{prms} = \left[\frac{\{[\Sigma(p - p_{calcd})/p](100)\}^2}{n}\right]^{1/2}$.

Table V. Estimated Critical Parameters Used (*6*, *7*)

	T_c, K	p_c, atm
diphenylmethane	770.2	28.2
thianaphthene	752.0	38.3
bicyclohexyl	731.4	25.3

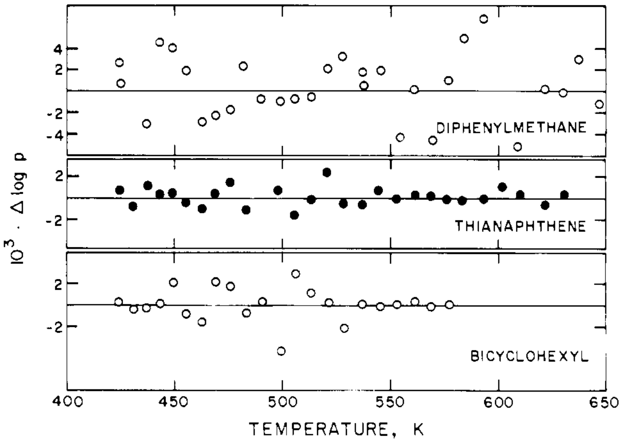

Figure 2. Residuals in log p (i.e., $\Delta \log p = \log p - \log p_{calcd}$, for diphenylmethane, thianaphthene, and bicyclohexyl.

The values of $T \log p$ were fitted by Chebyshev polynomials up to order 7; the output included residuals $p - p_{calcd}$, the sum of squares of residuals, and dp/dT. The coefficients for the polynomials which cover the temperature range investigated whose limits are represented by T_{max} and T_{min} are given in Table IV. For diphenylmethane and thianaphthene, a good fit was obtained by using the 7th-order polynomial, and percent root mean square (rms) deviations 0.78 and 0.19, respectively, were obtained. For bicyclohexyl, a 6th-order polynomial was chosen

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

	diphenylmethane	thianaphthene	bicyclohexyl
a_0	3991.790	4259.691	3937.652
a_1	1350.165	1242.321	1167.051
a_2	−16.583	−11.818	−7.344
a_3	8.278	−0.366	6.467
a_4	0.543	−1.674	−0.953
T_{max}/K	770.50	752.20	731.50
T_{min}/K	424.63	424.39	424.24
prms	0.99	0.32	0.39

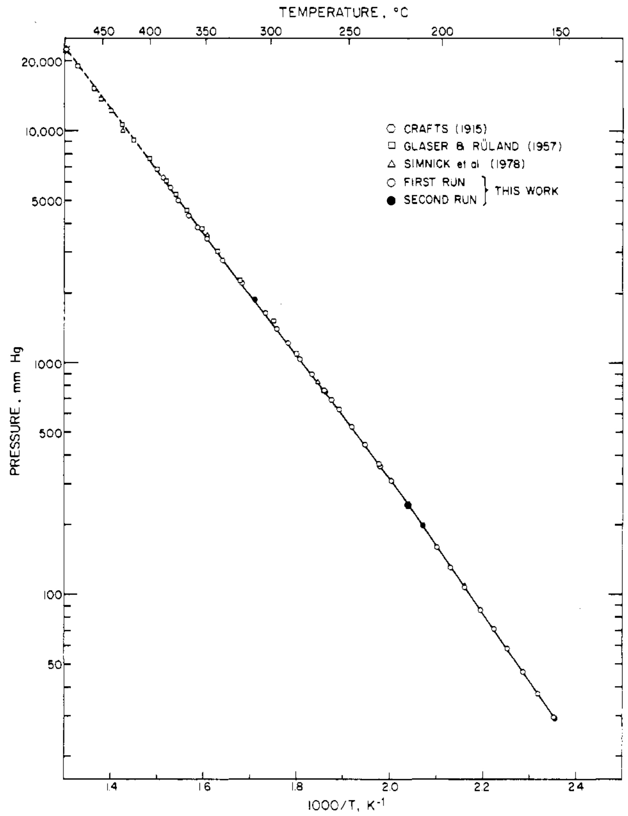

Figure 3. Vapor pressures of diphenylmethane.

to give a 0.34% rms deviation. In Figure 2 the residuals $\Delta \log p = \log p - \log p_{calcd}$ for the investigated compounds are shown.

Because diphenylmethane, thianaphthene, and bicyclohexyl are unstable in the higher temperature range, the measurement of the vapor pressures up to the critical point is not possible. In order to ensure that the curve-fitting technique used here did not lead to spurious results between the temperature limit of the data and the critical temperature, we used estimated critical-point values in making the final fit of the Chebyshev polynomials whose coefficients are given in Table VI. Although the resulting 4th-order polynomial did not fit the data of this study quite as well, its behavior up to the critical point is now reasonable. They are shown by dashed lines in Figures 3, 4, and 5 for diphenylmethane, thianaphthene, and bicyclohexyl, respectively.

The values of dp/dT at the investigated range of temperature calculated from the 4th-order Chebyshev polynomial (coefficients from Table VI) are reported in Tables I, II, and III for diphenylmethane, thianaphthene, and bicyclohexyl, respectively.

Comparison with Existing Data

In Figure 3 the comparison of vapor pressures of diphenylmethane obtained in this work was made with available data from the literature. Crafts (*2*) measured the vapor pressure of diphenylmethane at temperature ranges between 265 and 496 °C. They reported correlated data. The values obtained in this work are somewhat lower, especially at higher ranges of temperature.

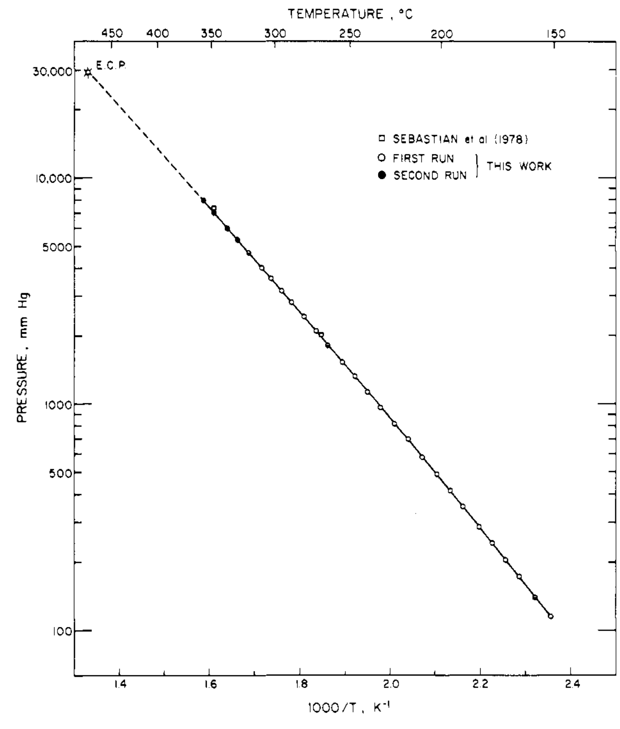

Figure 4. Vapor pressure of thianaphthene.

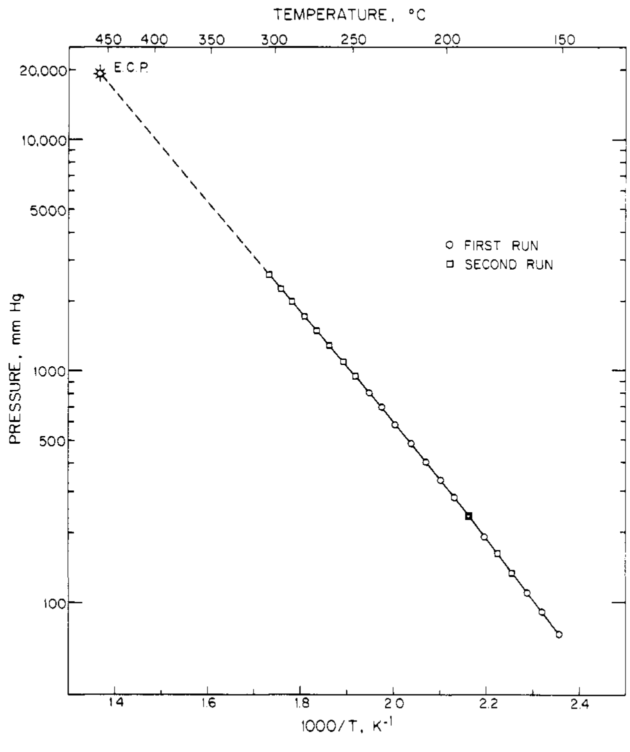

Figure 5. Vapor pressure of bicyclohexyl.

The recent values of vapor pressures are reported by Simnick et al., (*7*) for four temperatures: 189, 268.7, 348.6, and 428.5 °C. Good agreement was obtained for the first two temperatures, but for 348.6 °C the values obtained in this work are ~5% lower.

Sebastian et al. (*6*) reported the values of vapor pressures of thianaphthene for two temperatures, 267.9 and 348.0 °C, which are somewhat higher than ours. The comparison is shown in Figure 4.

J. Chem. Eng. Data **1980**, *25*, 305-307

Dobry and Keller reported the vapor pressures of bicyclohexyl represented by the Clapeyron equation at the temperature range up to 240 °C, but values calculated from this equation are in serious disagreement with ours.

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X-ray Diffraction Data for Some Amine Salts of Long-Chain Fatty Acids and Related Compounds

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X-ray long and short spacings of 48 amine salts of long-chain fatty acids and of some related compounds and mixtures are presented. Included are data on four homologous series of amine salts, those of piperazine, morpholine, cyclohexylamine, and tris(hydroxyethyl)aminomethane. The long-spacing data are used to calculate the angles of tilt for these four series. Studies on the polymorphic forms of palmitamide are presented, along with a calculation of the angle of tilt of long-chain fatty amides from data derived mainly from the literature. X-ray long and short spacings of four methyl ketones (2-tridecanone, 2-pentadecanone, 2-heptadecanone, and 2-nonadecanone) are presented, along with a calculation of the angle of tilt of these compounds.

Introduction

During our investigations of the solid-liquid phase relations between long-chain fatty acid derivatives, many highly pure crystalline compounds were prepared and characterized. The present report deals with the X-ray diffraction measurements of the "long" and "short" spacings for a few homologous series of amine salts, for a number of individual amine salts, amides, and N-substituted amides of long-chain saturated and unsaturated fatty acids, and for a few related compounds.

Experimental Section

Unless otherwise indicated, the compounds were prepared and purified by the procedures previously described for the amine salts (*1*), the acid-free amides (*2*), the N-substituted amides (*3*), the octadecenoic acids (*4*), and the various aminopyridine salts (*5,6*). The A form of palmitamide was obtained by recrystallization of the B form from a dilute methanol solution. The mixture of morpholine stearate and cyclohexylamine palmitate was prepared from equimolar amounts of the pure salts. The mixture was melted and the melt was allowed to cool slowly until it crystallized.

The X-ray long- and short-spacing measurements were made by the powder method of O'Connor et al. (*7*). A General Electric XRD-5 diffractometer or a Phillips Electronics diffractometer was used to obtain X-ray diffraction patterns by the direct-measurement technique with a chart recorder. The instrument was equipped with a copper-target X-ray tube and a 0.018-mm nickel filter. Divergence and antiscattering slits were used. The X-rays were generated at 30 kVp and 15 mA from 0 to 12.5°, 2θ, and 36 kVp and 16 mA from 12.5 to 50°, 2θ.

Results and Discussion

Table I shows X-ray long and short spacings on 48 amine salts of long-chain fatty acids and on some related compounds and mixtures, including four homologous series of amine salts. The long spacings, L, for each of these homologous series show a linear relationship to n, the number of carbon atoms in the fatty acid molecule. This relationship can be represented by eq 1, where m is the number of long-chain molecules contributing

$$L = (md)n + k \qquad (1)$$

to the length of the repeating unit, d is the increase in long spacing per additional carbon atom per molecule measured along a line perpendicular to the 001 planes of the crystal lattice, n is the number of carbons in the acid residue, and k is a constant.

The method of least squares was used to determine the equation of the best straight line through the L vs. n data for each of the homologous series. A digital computer gave the values for md and k of the equation, as well as the standard error of estimate of the individual values of L.

The equation for the piperazine salts, items 1-7 in Table I, was

$$L = 2.270n + 5.022 \qquad (2)$$

with an average deviation of 0.02 Å. The calculated angle of tilt is therefore $\sin^{-1} 2.270/2.54 = 63° 20'$ (*8*). The angles of tilt for the other three homologous series, calculated in a similar manner, were the following: for the morpholine salts, items 8-11, 74° 41′; for the cyclohexylamine salts, items 12-20, 42° 39′; and for the tris(hydroxyethyl)aminomethane salts, items 22-26, 47° 23′.

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