1922 *J. Chem. Eng. Data* **2008,** *53,* 1922–1926

Vapor Pressures of Solid and Liquid Xanthene and Phenoxathiin from Effusion and Static Studies

Manuel J. S. Monte,[†],* Luís M. N. B. F. Santos,[†] Carlos A. D. Sousa,[†] and Michal Fulem[†],[‡]

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687 P-4169-007 Porto, Portugal

Vapor pressures of xanthene [CAS Registry No. 92-83-1] and phenoxathiin [CAS Registry No. 262-20-4] were measured in the temperature range from (318 to 382) K [(0.5 to 127) Pa] and from (318 to 373) K [(0.5 to 36) Pa], respectively, using a static method, in both crystalline and liquid phases. The vapor pressures of the crystalline phases of both compounds were also measured in the pressure range (0.1 to 1) Pa using the Knudsen effusion method. From the experimental results, the standard molar Gibbs energies and enthalpies of sublimation/vaporization, at $T = 298.15$ K, and the triple-point coordinates for these two compounds were derived. The enthalpies and temperatures of fusion were also determined using differential scanning calorimetry. To the best of our knowledge, vapor pressure data reported here are the first for crystalline phenoxathiin and for liquid xanthene.

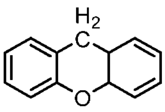
Introduction

We have been using the Knudsen effusion method for measuring vapor pressures of crystalline organic compounds under 1 Pa for more than two decades. At present, two effusion apparatuses are available in our laboratories: one (effusion apparatus I) enabling the simultaneous operation of three different effusion cells at the same temperatures[1] and another (effusion apparatus II) enabling the simultaneous operation of nine effusion cells at three different temperatures.[2] Results are usually in excellent agreement with measurements performed by other investigators and/or other techniques on the same compounds,[1–3] for both the derived enthalpies of sublimation and the measured vapor pressures. The derivation of empirical correlations between thermodynamic parameters of sublimation for several organic compounds[4–8] also attests to the accuracy of those effusion results. After measuring the vapor pressures of crystalline phenoxathiin (using the effusion apparatus I) and of xanthene (using the effusion apparatus II), a large uncertainty in the determination of vapor pressures was observed for xanthene. As shown in Table 2 and in Figure 1, the measured vapor pressures of xanthene are dependent on the size of the effusion orifices, decreasing significantly with the area of the orifices. A few measurements performed later on the same sample using the effusion apparatus I confirmed this trend. Even though phenoxathiin has a similar volatility and structure, the measured vapor pressures using three different effusion orifices were in mutual agreement, although a slight decrease of the measured pressure with increasing area of the effusion orifices was also observed. So we decided to examine two different situations occurring in the Knudsen effusion experiments for these two compounds—when the different effusion orifices yielded different vapor pressures and when the results were equal within the experimental uncertainty—measuring the vapor pressures of xanthene and phenoxathiin using another experimental apparatus based on a static method.[9] Moreover, we found only one data set on vapor pressure for each compound in the literature: for crystalline xanthene[10] and for liquid phenoxathiin at higher pressures.[11]

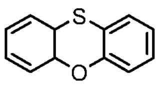
Table 1. Areas and Clausing Factors of the Effusion Orifices

	orifice	A_o/mm^2	w_o[a]
small orifices	A1	0.502	0.988
	A2	0.499	0.988
	A3	0.497	0.988
	A0	0.663	0.990
medium orifices	B4	0.774	0.991
	B5	0.783	0.991
	B6	0.773	0.991
	B0	0.785	0.991
large orifices	C7	1.116	0.992
	C8	1.125	0.992
	C9	1.150	0.992
	C0	0.996	0.992

[a] $w_o = \{1 + (3l/8r)\}^{-1}$, where l is the length of the effusion orifice ($l = 0.0125$ mm) and r is its radius.



xanthene ($C_{13}H_{10}O$)



phenoxathiin ($C_{12}H_8OS$)

Therefore, we it found useful to publish thermodynamic properties including vapor pressures of both crystalline and liquid phases, standard molar Gibbs energies and enthalpies of sublimation/vaporization, molar enthalpies of fusion, and the triple-point coordinates for these two compounds.

Experimental Section

Materials. Both compounds xanthene and phenoxathiin were obtained from Aldrich Chemical Co. with purity certificates of

---

* Corresponding author. E-mail: mjmonte@fc.up.pt. Tel.: +351 220402516. Fax: +351 220402659.

[†] University of Porto.

[‡] Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-162 53 Prague 6, Czech Republic.

10.1021/je800333q CCC: $40.75

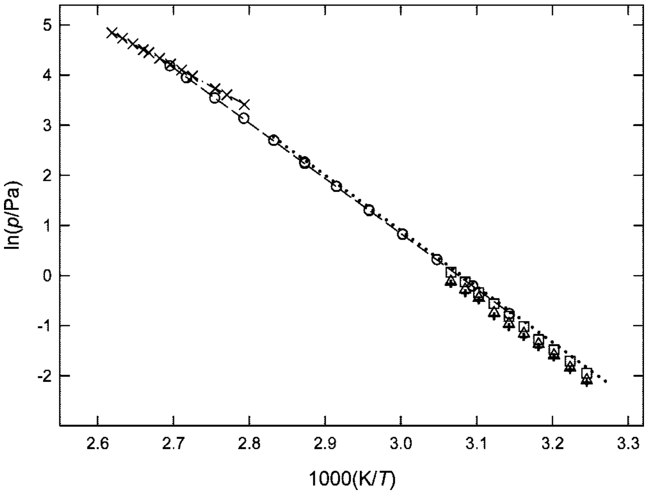


Figure 1. Vapor pressures of xanthene over the crystalline and liquid phases. ×, static liquid data; ○, static crystalline data; □, effusion data (small orifices); Δ, effusion data (medium orifices); +, effusion data (large orifices); •••••, Rordorf.[10]

Table 2. Effusion Results for the Crystalline Phase of the Studied Compounds[a]

				m/mg			p/Pa	
T/K	t/s	orifices	m_A	m_B	m_C	p_A	p_B	p_C
			Xanthene					
308.14	25046	A1-B4-C7	5.98	8.04	10.97	0.143	0.124	0.118
310.23	25046	A2-B5-C8	7.56	10.37	14.26	0.182	0.159	0.152
312.30	25046	A3-B6-C9	9.39	13.06	18.75	0.228	0.204	0.196
314.29	16499	A3-B6-C9	7.52	10.68	15.07	0.279	0.254	0.240
316.22	16499	A2-B5-C8	9.79	13.30	18.01	0.362	0.313	0.294
318.13	16499	A1-B4-C7	12.21	15.55	21.15			
318.29	10848	A3-B6-C9	7.67	10.68	15.03			
318.21	mean of the two previous results					0.443	0.380	0.358
320.20	10848	A2-B5-C8	10.08	13.17	17.83	0.570	0.474	0.446
322.28	10944	A3-B6-C9	12.56	17.56	25.15	0.711	0.637	0.612
324.14	10848	A1-B4-C7	15.27	19.62	26.30			
324.19	10944	A2-B5-C8	15.87	21.89	29.83			
324.16	mean of the two previous results					0.880	0.753	0.706
326.13	10944	A1-B4-C7	19.54	24.55	36.13			
326.13	10809	A1-B4-C7	18.19	23.64	31.40			
326.19	10809	A2-B5-C8	18.78	24.28	32.78			
326.15	mean of the three previous results					1.071	0.884	0.848
			Phenoxathiin					
308.14	20861	A0-B0-C0	7.57	8.84	11.07	0.157	0.154	0.152
310.12	16345	A0-B0-C0	7.42	8.55	10.86	0.197	0.191	0.191
312.15	16557	A0-B0-C0	9.60	11.15	14.03	0.252	0.247	0.245
314.16	16551	A0-B0-C0	11.87	13.86	17.47	0.313	0.308	0.306
316.14	12865	A0-B0-C0	11.49	13.48	16.83	0.390	0.387	0.380
318.15	11632	A0-B0-C0	13.09	15.46	19.45	0.494	0.492	0.488
320.17	8941	A0-B0-C0	12.86	15.03	18.79	0.634	0.624	0.615
321.88	10149	A0-B0-C0	17.42	20.36	25.57	0.758	0.743	0.739
324.14	9120	A0-B0-C0	20.06	23.41	29.55	0.975	0.959	0.954

[a] Results related to the small (A1, A2, A3, A0), medium (B4, B5, B6, B0), and large (C7, C8, C9, C0) effusion orifices are denoted, respectively, by the subscripts A, B, and C.

0.995 and 0.991, respectively. The samples were further purified by sublimation under reduced pressure, and final purities determined by gas chromatography (GC) were 0.9985 for xanthene and 0.9999 for phenoxathiin. GC analyses were performed using a Hewlett-Packard 4890 gas chromatograph equipped with column HP5 cross-linked 5 % PH ME Siloxane, length 30 m, film thickness 0.25 μm, i.d. 0.32 mm, and FID detector.

Differential scanning calorimetry was also performed to detect possible phase transitions in the crystalline phase and to determine the temperatures and enthalpies of fusion. The measurements were made in hermetically sealed steel crucibles using a Setaram DSC 141 calorimeter under a heating rate of $(3.33 \cdot 10^{-2})$ $\mathrm{K \cdot s^{-1}}$. The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high-purity reference materials:[12] naphthalene, benzoic acid, and indium. Its power scale was calibrated using high-purity indium ($x > 0.99999$). No crystalline transitions were detected between 298 K and the temperature of fusion for each of the studied compounds. Determined temperatures and enthalpies of fusion are given in Table 8.

Vapor Pressure Measuring Apparatus. All the used apparatuses for measuring vapor pressures, the Knudsen effusion apparatuses I[1] and II[2] and the static apparatus[9] were previously described in detail together with the measuring procedure. Therefore, only short descriptions are given here.

The Knudsen effusion apparatus I enables in each experiment the simultaneous use of three effusion cells contained in cylindrical holes inside three aluminum blocks. The crystalline samples contained in the effusion cells are assumed to be in thermal equilibrium with a thermostatically controlled silicone oil bath. The temperature of the bath is measured using Amarell-Precison liquid-in-glass mercury thermometers, with a scale graduation of 0.01 K, calibrated by Eichamt Wertheim (Germany) with an overall uncertainty of ± 0.01 K.

The Knudsen effusion apparatus II enables in each experiment the simultaneous use of nine effusion cells contained in cylindrical holes inside three aluminum blocks at three different temperatures. During an effusion experiment, each aluminum block is kept at a constant temperature, different from the other two blocks, and contains three effusion cells with effusion orifices of different areas: one "*small*" (series A), one "*medium*" (series B), and one "*large*" (series C). The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) previously calibrated by comparison with an SPRT (25 Ω; Tinsley, 5187A).

For the effusion experiments performed with each of the effusion apparatuses, the loss of mass Δm of the samples during a convenient effusion time period t is determined by weighing the effusion cells to ± 0.01 mg before and after the effusion period. For the temperature T, measured with an accuracy of ± 0.01 K in each of the effusion apparatuses, the vapor pressure p of the crystalline sample contained in each effusion cell is calculated using eq 1, where m is the sublimed mass during the effusion time period t; M is the molar mass of the effusing vapor; R is the gas constant; A_o is the area of the effusion orifice; and w_o is the respective transmission probability factor. The values of w_o and of the areas of the effusion orifices in platinum foil of 0.0125 mm thickness are given in Table 1.

$$p = (m/A_o w_o t)(2\pi RT/M)^{1/2} \quad (1)$$

The accuracy of the measured pressures is estimated to be better than ± 0.01 Pa.

The static apparatus is constructed of stainless steel tubing of internal diameter 17 mm with connections ConFlat DN 16 CF and includes all metal angle valves, VAT series 57 high-temperature range for UHV, operated pneumatically. The pressure is measured by a capacitance diaphragm absolute gage MKS Baratron 631A01TBEH. Its measuring upper limit is 133 Pa, and the uncertainty is 0.25 % of the reading pressure as stated by the manufacturer. The temperature of the pressure sensor is kept at $T = 423$ K by the self-controlling temperature system. The pressure gauge has been calibrated at 423 K by the manufacturer at seven equally spaced pressures from (0 to

Table 3. Parameters of Clarke and Glew Equation 2 Derived from Effusion Vapor Pressure Results for Crystalline Xanthene and Phenoxathiin at the Reference Temperatures θ and at the Standard Pressure $p^0 = 10^5$ Pa, Using the Constant Value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^0 = -19$ J·K^{-1}·mol^{-1} for Both Compounds

	ΔT	θ	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}G_{\mathrm{m}}^0$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^0$		
effusion orifices[a]	K	K	J·mol^{-1}	J·mol^{-1}	R^2	s[d]
			Xanthene			
S	308 to 326	298.15	36475 ± 50	94756 ± 809	0.9994	0.018
M			36700 ± 73	92618 ± 1168	0.9987	0.025
L			36818 ± 86	92424 ± 1376	0.9982	0.030
mean pressures[b]			36664 ± 56	93266 ± 905	0.9992	0.020
			Phenoxathiin			
S	308 to 324	298.15	36243 ± 36	95317 ± 622	0.9997	0.012
M		298.15	36311 ± 30	95779 ± 508	0.9998	0.009
L		298.15	36332 ± 29	95776 ± 494	0.9998	0.009
mean pressures[b]		298.15	36295 ± 30	95624 ± 506	0.9998	0.009
mean pressures[b]		327.02[c]	30576 ± 20	95076 ± 506	0.9998	0.009

[a] S, small orifices; M, medium orifices; L, large orifices. [b] Derived results considering the mean value of the pressures calculated for the different effusion orifices at each experimental temperature. [c] Calculated temperature of triple point using the effusion results for the crystalline phase and the static results for the liquid phase. [d] s is the standard deviation of the fit defined as $s = [\sum_{i=1}^{n} (\ln p - \ln p_{\mathrm{calcd}})_i^2 / n - m]^{1/2}$ where n is the number of experimental points used in the fit and m is the number of adjustable parameters of Clarke and Glew eq 2.

Table 4. Experimental Data on Vapor Pressure of Xanthene[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
				Crystalline Phase				
318.05	0.459	−0.009	342.97	5.855	−0.004	357.97	22.78	0.26
318.06	0.461	−0.007	342.95	5.854	0.006	362.94	34.17	−0.12
323.03	0.803	0.002	342.95	5.814	−0.034	362.94	34.09	−0.20
323.04	0.799	−0.002	347.94	9.220	−0.056	367.91	51.14	−0.47
328.01	1.351	0.004	347.95	9.480	0.195	367.94	51.37	−0.37
328.01	1.358	0.011	347.96	9.392	0.099	370.92	64.72	−1.03
332.98	2.254	0.025	352.98	14.62	0.04	370.92	64.71	−1.04
332.97	2.229	0.002	352.97	14.72	0.15			
332.97	2.236	0.009	352.95	14.66	0.12			
337.94	3.592	−0.037	352.99	14.66	0.07			
337.95	3.650	0.018	357.95	22.80	0.32			
				Liquid Phase				
357.97	30.44	0.00	368.93	60.48	0.13	375.90	91.02	0.04
357.98	30.42	−0.04	370.91	67.97	0.03	375.90	90.91	−0.07
360.96	36.80	−0.07	370.92	68.13	0.15	377.87	101.9	0.07
360.97	36.89	0.00	372.90	76.43	0.02	377.88	102.0	0.11
362.96	41.68	−0.14	372.90	76.64	0.22	379.86	114.0	0.05
362.96	41.86	0.04	372.92	76.57	0.06	379.87	114.1	0.08
366.93	53.55	0.09	374.90	85.67	−0.20	381.85	127.2	−0.13
366.94	53.55	0.06	374.90	85.55	−0.32	381.85	127.1	−0.23
368.93	60.43	0.08	374.91	85.78	−0.14			

[a] $\Delta p = p - p_{\mathrm{calcd}}$, where p_{calcd} is calculated from the Clarke and Glew eq 2 with parameters given in Table 6.

133) Pa with a maximum deviation of 0.23 %. This calibration is traceable to the National Institute of Standards and Technology (NIST).

The temperature of the sample is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection), which is in a good thermal contact with the sample. This thermometer was calibrated by comparison with an SPRT (25 Ω; Tinsley, 5187A). The uncertainty of the temperature measurements is estimated to be better than ± 0.01 K. All temperatures reported here are based on the international temperature scale ITS-90. The uncertainty in the pressure measurements is adequately described by the expression $\sigma(p/\mathrm{Pa}) = 0.01 + 0.0025(p/\mathrm{Pa})$.

Table 5. Experimental Data on Vapor Pressure of Phenoxathiin[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
				Crystalline Phase				
318.05	0.452	−0.004	323.02	0.802	0.002	326.99	1.233	−0.004
318.06	0.452	−0.005	323.06	0.807	0.004	326.99	1.239	0.002
320.04	0.571	−0.002	324.02	0.898	0.004	327.48	1.294	−0.010
320.05	0.572	−0.001	324.02	0.898	0.004	327.50	1.298	−0.009
321.04	0.643	0.002	324.96	0.998	0.007	327.51	1.295	−0.013
321.04	0.642	0.001	324.99	0.999	0.005	327.99	1.374	−0.004
322.02	0.719	0.003	325.99	1.115	0.006	328.00	1.368	−0.011
322.03	0.724	0.008	326.01	1.119	0.007			
				Liquid				
318.06	0.586	−0.012	337.94	3.204	0.027	352.94	9.728	0.030
318.07	0.588	−0.010	337.95	3.216	0.037	352.95	9.763	0.058
323.03	0.924	−0.004	337.97	3.217	0.033	352.95	9.740	0.035
323.04	0.927	−0.002	342.94	4.728	0.061	357.94	13.70	−0.03
327.99	1.410	−0.008	342.95	4.719	0.048	357.94	13.69	−0.04
328.00	1.405	−0.014	347.95	6.844	0.070	362.92	19.05	−0.14
329.98	1.680	0.006	347.95	6.838	0.064	362.93	19.06	−0.15
332.96	2.154	0.017	347.96	6.843	0.064	372.86	35.66	−0.64
332.96	2.151	0.014	352.94	9.729	0.031	372.87	35.67	−0.65

[a] $\Delta p = p - p_{\mathrm{calcd}}$, where p_{calcd} is calculated from the Clarke and Glew eq 2 with parameters given in Table 7.

Table 6. Parameters of Clarke and Glew Equation 2 Derived from Static Vapor Pressure Results for Crystalline and Liquid Xanthene at the Reference Temperatures θ and at the Standard Pressure $p^0 = 10^5$ Pa, Using the Constant Values $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^0 = -19$ J·K^{-1}·mol^{-1} and $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{p,\mathrm{m}}^0 = -74$ J·K^{-1}·mol^{-1}

	ΔT	θ	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}G_{\mathrm{m}}^0(\theta)$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^o(\theta)$		
phase	K	K	J·mol^{-1}	J·mol^{-1}	R^2	s[d]
crystalline	318 to 371	298.15	36206 ± 17	92608 ± 118	1.0000	0.0102
		344.5[b]	27503 ± 11	91727 ± 118		
		372.57[c]	22292 ± 11	91194 ± 118		
liquid[a]	358 to 382	298.15	31992 ± 11	73405 ± 55	1.0000	0.0017
		370[b]	22607 ± 1	68088 ± 55		
		372.57[c]	22292 ± 1	67898 ± 55		

[a] Including undercooled liquid. [b] Mean temperature. [c] Calculated temperature of the triple point using static data. [d] s is the standard deviation of the fit defined as $s = [\sum_{i=1}^{n} (\ln p - \ln p_{\mathrm{calcd}})_i^2/n - m]^{1/2}$ where n is the number of experimental points used in the fit and m is the number of adjustable parameters of Clarke and Glew eq 2.

Results and Discussion

The measurements of vapor pressures of crystalline xanthene and phenoxathiin using the Knudsen effusion method were performed in the temperature ranges (308 to 326) K and (308 to 324) K, respectively. Results are presented in Table 2. The measured vapor pressures of xanthene at each experimental temperature decrease with increasing size of the effusion orifices, while for phenoxatiin, although a slight similar trend is observed, the measured vapor pressures are not significantly dependent on the areas of the effusion orifices and are considered equal inside the experimental uncertainty (± 0.01 Pa). The vapor pressure measurements using the static method were performed above the crystalline as well as the liquid phase in the

Table 7. Parameters of Clarke and Glew Equation 2 Derived from Static Vapor Pressures Results for Crystalline and Liquid Phenoxathiin at the Reference Temperatures θ and at the Standard Pressure $p^0 = 10^5$ Pa, Using the Constant Values $\Delta_{cr}^{g}C_{p,m}^0 = -19$ J·K⁻¹·mol⁻¹ and $\Delta_{l}^{g}C_{p,m}^0 = -74$ J·K⁻¹·mol⁻¹

	ΔT	θ	$\Delta_{cr,l}^{g}G_m^0(\theta)$	$\Delta_{cr,l}^{g}H_m^0(\theta)$		
phase	K	K	J·mol⁻¹	J·mol⁻¹	R^2	s^e
crystalline	318 to 328	298.15	36533 ± 30	96865 ± 374	0.9997	0.0065
		323[b]	31524 ± 4	96392 ± 374		
		329.21[c]	30278 ± 7	96275 ± 374		
liquid[a]	318 to 373	298.15	34607 ± 17	77276 ± 127	0.9999	0.0104
		327.02[d]	30576 ± 8	75140 ± 127		
		329.21[c]	30278 ± 7	74977 ± 127		
		345.5[b]	28096 ± 6	73772 ± 127		

[a] Including undercooled liquid. [b] Mean temperature. [c] Calculated temperature of the triple point using static data for the crystalline phase. [d] Calculated temperature of the triple point using Knudsen effusion data for the crystalline phase. [e] s is the standard deviation of the fit defined as $s = [\sum_{i=1}^{n} (\ln p - \ln p_{calcd})_i^2/n - m]^{1/2}$ where n is the number of experimental points used in the fit and m is the number of adjustable parameters of Clarke and Glew eq 2.

temperature ranges of (318 to 382) K for xanthene and of (318 to 373) K for phenoxathiin. Xanthene and phenoxathiin readily supercool by more than 10 K allowing measurements on the crystalline and the liquid phase at the same temperature. These results are listed in Tables 4 and 5.

The experimental results of the vapor pressures were fitted by the Clarke and Glew eq 2[13]

$$R\cdot\ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_{cd}^{g}G_m^0(\theta)}{\theta} + \Delta_{cd}^{g}H_m^0(\theta)\left(\frac{1}{\theta}-\frac{1}{T}\right) + \Delta_{cd}^{g}C_{p,m}^0(\theta)\left[\left(\frac{\theta}{T}\right)-1+\ln\left(\frac{T}{\theta}\right)\right] \quad (2)$$

where p is the vapor pressure; p^0 is a selected reference pressure; θ is a selected reference temperature; R is the molar gas constant ($R = 8.31447$ J·K⁻¹·mol⁻¹); $\Delta_{cd}^{g}G_m^0$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phase) at the selected reference pressure (the gaseous phase is supposed to have characteristics of ideal gas at the pressure p^0); $\Delta_{cd}^{g}H_m^0$ is the difference in molar enthalpy between the gaseous and the condensed phase; and $\Delta_{cd}^{g}C_{p,m}^0$ is the difference between the heat capacities of the perfect gas and of the condensed phase. The parameters of the Clarke and Glew eq 2 are presented in Table 3 for the Knudsen effusion results for both xanthene and phenoxathiin and in Tables 6 and 7 for the static results derived for xanthene and for phenoxatiin. If the vapor pressures are not sufficiently accurate or the temperature interval of the measurement is too short, the correlation of only vapor pressures may result in unreasonable $\Delta_{cd}^{g}C_{p,m}^0$ (a good representation of the experimental vapor pressures may lead to incorrect derivatives of dp/dT and d^2p/dT^2). In such cases it is more convenient to insert values of $\Delta_{cd}^{g}C_{p,m}^0$ estimated or found in the literature to derive reliable standard molar enthalpies of sublimation/vaporization.

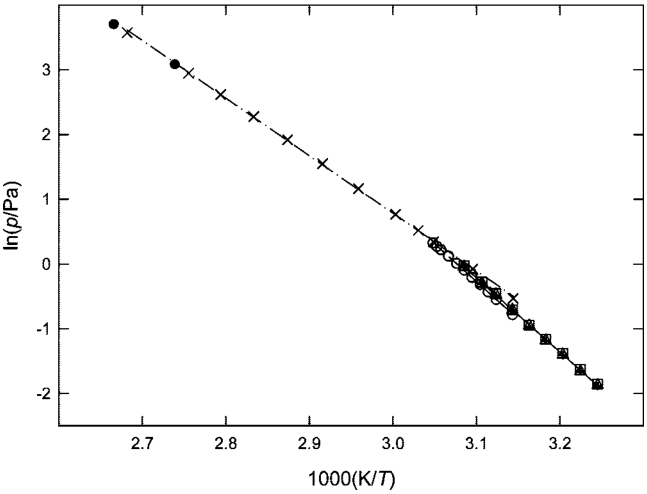


Figure 2. Vapor pressures of phenoxathiin over the crystalline and liquid phases. ×, static liquid data; ○, static crystalline data; □, effusion data (small orifices); Δ, effusion data (medium orifices); +, effusion data (large orifices); ●, Steele et al.[11]

The heat capacities of phenoxathiin and xanthene in the gas phase were calculated at 298.15 K using computational chemistry as $C_{p,m}^{o}(g) = 195.1$ J·K⁻¹·mol⁻¹ and $C_{p,m}^{o}(g) = 197.5$ J·K⁻¹·mol⁻¹, respectively. The geometry optimizations, as well as the fundamental vibrational frequency calculations, were performed for both compounds using density functional theory (DFT) with the hybrid exchange correlation functional B3LYP at the 6-311++G(d,p) level of theory. The frequencies were scaled using the scale factor of 0.9688.[14] The heat capacities at 298.15 K in the gaseous state were determined using the scaled vibrational frequency calculations. All theoretical calculations were performed using the Gaussian 03 software package.[15] For phenoxathiin, the values $\Delta_{cr}^{g}C_{p,m}^{o}(298.15\ K) = -19$ J·K⁻¹·mol⁻¹ and $\Delta_{l}^{g}C_{p,m}^{o}(298.15\ K) = -74$ J·K⁻¹·mol⁻¹ were calculated from the calculated gas phase results and from the condensed phase values $C_{p,m}^{o}(cr) = 213.8$ J·K⁻¹·mol⁻¹ and $C_{p,m}^{o}(l) = 269.2$ J·K⁻¹·mol⁻¹ calculated from the data presented by Steele et al.[11] As no heat capacity values in the condensed phases of xanthene were available and taking into account that the heat capacity values for the gas phase of xanthene and phenoxathiin are not significantly different, we estimated the same values for the heat capacity differences for xanthene.

Vapor pressures of crystalline xanthene determined in the present work using the static method are slightly lower than those presented by Rordorf[10] (see Figure 1). The value $\Delta_{cr}^{g}H_m^0(298.15\ K) = 93.0$ kJ·mol⁻¹ derived from Rordorf's

Table 8. Triple-Point Coordinates, Temperature, and Molar Enthalpy of Fusion of Xanthene and Phenoxathiin Determined in This Work and Found in the Literature

	T_{tp}	$T_{fus.}$	$\Delta_{cr}^{l}H_m^0(T)^a$	p_{tp}	
compound	K	K	kJ·mol⁻¹	Pa	method /reference
xanthene	–	374.56 ± 0.08	20.67 ± 0.33	–	DSC/this work
	372.57	–	23.30 ± 0.13	74.9	static/this work
	–	373.7	19.2	–	17
phenoxathiin	–	329.58 ± 0.13	19.43 ± 0.23	–	DSC/this work
	327.02	–	19.94 ± 0.52	1.31	Knudsen effusion and static[b]/this work
	329.21		21.30 ± 0.39	1.58	Static[c]/this work
	328.778	–	20.27	1.56	AC and IP[d]/11

[a] Temperature of fusion or temperature of the triple point. [b] Results derived from Knudsen effusion data for the crystalline phase and from static data for the liquid phase. [c] Results derived from static data. [d] AC (Adiabatic Calorimetry) and IP (Inclined Piston method).

data[10] and corrected using $\Delta_{\rm cr}^{\rm g}C_{p,\rm m}^{0} = -19\ {\rm J\cdot K^{-1}\cdot mol^{-1}}$ is in excellent agreement with the value $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{0}(298.15\ {\rm K}) = (92.6 \pm 0.1)\ {\rm kJ\cdot mol^{-1}}$determined in the present work. The vapor pressures of xanthene determined by the Knudsen effusion method are strongly dependent on the area of the effusion orifices (see Table 3). Results obtained through the smallest orifices are lower but close to the static results, although the derived value $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{0}(298.15\ {\rm K}) = (94.8 \pm 0.8)\ {\rm kJ\cdot mol^{-1}}$ is 2.2 $\rm kJ\cdot mol^{-1}$ higher than the result derived from the static data. The vapor pressures obtained through the other orifices are considerably lower. Explanations for the low values of the vapor pressures measured using the larger effusion orifices are probably connected to (i) a poor heat transport through the crystalline sample to the surface (self-cooling) and/or (ii) a low vaporization coefficient ("real" low vaporization coefficients of the samples are connected with kinetic slow steps in the vaporization process, but "apparent" low vaporization coefficients may arise from the above referred poor heat transfer).[16] Both effects would yield calculated pressures lower than the equilibrium vapor pressures especially for the larger effusion orifices. These effects are more important for the highest measured pressures yielding a decrease of the calculated enthalpies of sublimation with increasing areas of the effusion orifices.

Vapor pressure data of crystalline phenoxathiin obtained through the Knudsen effusion method does not depend significantly on the area of the effusion orifices, and the enthalpies of sublimation derived from the data obtained through the different effusion orifices are in excellent agreement (see Figure 2). The effusion vapor pressures are slightly higher than the results obtained through the static method which could only be measured through a narrow temperature range of 10 K due to the triple-point temperature and to the lower limit of sensibility of the pressure manometer (ca. 0.5 Pa). The liquid (including undercooled liquid) vapor pressures were measured through a temperature interval greater than 50 K. Considering the magnitude of the temperature range, we tried the regression of the data through the Clarke and Glew eq 2 with three adjustable thermodynamic parameters yielding the value $\Delta_{\rm l}^{\rm g}C_{p,\rm m}^{0} = -149\ {\rm J\cdot K^{-1}\cdot mol^{-1}}$. This result is considerably larger than the above-discussed value $\Delta_{\rm l}^{\rm g}C_{p,\rm m}^{\rm o}(298.15\ {\rm K}) = -74\ {\rm J\cdot K^{-1}\cdot mol^{-1}}$. So we decided to insert this last value in eq 2 allowing the adjustment of only the two other thermodynamic parameters. The derived enthalpy of vaporization $\Delta_{\rm l}^{\rm g}H_{\rm m}^{0}(298.15\ {\rm K}) = (77.3 \pm 0.1)\ {\rm kJ\cdot mol^{-1}}$ is only 1.5 $\rm kJ\cdot mol^{-1}$ higher than the value reported by Steele et al.[11] $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{0}(298.15\ {\rm K}) = (75.8 \pm 0.4)\ {\rm kJ\cdot mol^{-1}}$ determined from a much larger experimental range [(365.0 to 640.7) K] using inclined-piston gauge and ebuliometry. From our static results, the vapor pressure derived at 365 K using the Clarke and Glew eq 2 is $p = 22.0$ Pa, very close to the value $p = 21.6$ Pa reported by Steele et al. at this temperature.

Table 8 presents values of triple-point coordinates and enthalpies of fusion for the studied compounds. For xanthene, the enthalpy of fusion derived from the enthalpies of sublimation and of vaporization presented in Table 6 is somewhat higher than the result obtained using DSC and than the literature value.[17] For phenoxathiin, the enthalpy of fusion derived from the enthalpies of sublimation and of vaporization presented in Table 7 is in good agreement with the result obtained through DSC and the one reported by Steele et al.[11] The temperature of the triple point is also in reasonable agreement with DSC and Steele et al. results.

Literature Cited

(1) Ribeiro da Silva, M. A. V.; Monte, M. J. S. The Construction, Testing and Use of a New Knudsen Effusion Apparatus. *Thermochim. Acta* **1990**, *171*, 169–183.

(2) Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Santos, L. M. N. B. F. The design, construction and testing of a new Knudsen effusion apparatus. *J. Chem. Thermodyn.* **2006**, *38*, 778–787.

(3) Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Huinink, J. Vapour pressures and standard molar enthalpies of sublimation of seven crystalline copper(II) β-diketonates. The mean molar (Cu-O) bond-dissociation enthalpies. *J. Chem. Thermodyn.* **1995**, *27*, 175–190.

(4) Ribeiro da Silva, M. A. V.; Monte, M. J. S. Vapour Pressures and Enthalpies of Sublimation of Six Halogen Substituted 8-Hydroxyquinolines. *J. Chem. Thermodyn.* **1992**, *24*, 715–724.

(5) Monte, M. J. S.; Hillesheim, D. M. Vapour Pressures, Enthalpies and Entropies of Sublimation of trans-Cinnamic Acid and of Nine Methoxy and Dimethoxycinnamic Acids. *J. Chem. Thermodyn.* **1999**, *31*, 1443–1456.

(6) Monte, M. J. S.; Hillesheim, D. M. Thermodynamic Study on the Sublimation of Six Substituted Quinoxalines. *J. Chem. Eng. Data* **2000**, *45*, 1088–1092.

(7) Ribeiro da Silva, M. A. V.; Fonseca, J. M. S.; Carvalho, R. P. B. M.; Monte, M. J. S. Thermodynamic study of the sublimation of six halobenzoic acids. *J. Chem. Thermodyn.* **2005**, *37*, 275–283.

(8) Monte, M. J. S.; Sousa, C. A. D. Vapor Pressures and Phase Changes Enthalpy and Gibbs Energy of Three Crystalline Monomethyl Benzenedicarboxylates. *J. Chem. Eng. Data* **2005**, *50*, 2101–2105.

(9) Monte, M. J. S.; Santos, L. M. N. B. F.; Fulem, M.; Fonseca, J. M. S.; Sousa, C. A. D. New static apparatus and vapor pressure of reference materials: naphthalene, benzoic acid, benzophenone and ferrocene. *J. Chem. Eng. Data* **2006**, *51*, 757–766.

(10) Rordorf, B. F. Thermal-Properties of Dioxins, Furans and Related-Compounds. *Chemosphere* **1986**, *15* (9−12), 1325–1332.

(11) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. The Thermodynamic Properties of Thianthrene and Phenoxathiin. *J. Chem. Thermodyn.* **1993**, *25*, 965–992.

(12) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Planas Leitao, M. L.; Roux, M. V.; Torres, L. A. Reference materials for calorimetry and differential thermal analysis. *Thermochim. Acta* **1999**, *331*, 93–204.

(13) Clarke, E. C. W.; Glew, D. N. Evaluation of thermodynamic functions from equilibrium constants. *Trans. Faraday Soc.* **1966**, *62*, 539–547.

(14) Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factors. *J. Phys. Chem. A* **2007**, *111*, 11683–11700.

(15) Frisch, M. J. ; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N. ; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. ; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R. ; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03, Revision C.02*, Gaussian, Inc.: Wallingford CT, 2004.

(16) Cater, E. In The Effusion Method at Age 69: Current State of the Art. Hastie, J., Ed.; *10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases*; Nat. Bur. Stand. (U.S.), Spec. Publ. 561/l: WA, 1979; Vol I.

(17) Acree, W. E. Thermodynamic Properties of Organic-Compounds - Enthalpy of Fusion and Melting-Point Temperature Compilation. *Thermochim. Acta* **1991**, *189*, 37–56.

Received for review May 9, 2008. Accepted June 16, 2008. Thanks are due to the Fundação para a Ciência e Tecnologia (FCT) Lisbon, Portugal, for financial support given to Centro de Investigação em Química of University of Porto and to the Project POCTI/QUI/43144/2001 which was also financed through FEDER. M.F. is also grateful to the Fundação para a Ciência e Tecnologia for the postdoc grant SFRH/BPD/18065/2004.

JE800333Q