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Vaporization Study of α-Bromonaphthalene

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Using two different molecular effusion techniques, we measured the vapor pressure of liquid α-bromonaphthalene in the temperature range 295–359 K. The pressure equation log P(kPa) = (6.9 ± 1.1) – (2950 ± 300)/T and the vaporization enthalpy ΔH°_{329} = 56 ± 6 kJ mol^{-1} were derived. Thermodynamic functions as free energy function, heat content, and entropy for gaseous and liquid phases were also evaluated.

Introduction

A large amount of experimental and theoretical work on the physical properties of α-bromonaphthalene is reported in literature.[1] Unfortunately, its vapor pressure is not well-known. The only data reported in literature are high-pressure data in the range 150–800 mmHg determined by comparative ebulliometry[2] and some other data that are very old and unreliable.[3,4]

As part of our program for the study of the vaporization of pure organic substances, vapor pressure values of α-bromonaphthalene were determined by using two different techniques based on molecular effusion.

Experimental Procedure and Results

The α-bromonaphthalene employed was supplied by Koch-Light (99.9% pure). The sample purity was tested by density measurements at 20 °C, d^{20} = 1.483 g cm^{-3} (1.482 g cm^{-3} [5]). The vaporization study of this compound was investigated by using the torsion-effusion and Knudsen-effusion technique.

The loading of the cells with the sample was always made in a drybox to avoid interaction with the atmosphere.

A. Torsion Effusion Technique

The equilibrium vapor pressure over α-bromonaphthalene was determined essentially by the torsion method. This technique and the experimental assembly have been described previously.[6,7] At each temperature, from the measurments of the torsion angle α of the effusion cell, the vapor pressure value was derived by using the well-known relation

$$p(\mathrm{kPa}) = 2K\alpha/(a_1l_1f_1 + a_2l_2f_2) = K^\circ\alpha \qquad (1)$$

where α is the cell deflection, a_1, a_2 and l_1, l_2 are the areas of the effusion orifices and their distances from the rotation axis, respectively, f_1 and f_2 are the Freeman and Searcy correction factors[8] for the orifice geometry, and K is the torsion constant of the suspension tungsten wire. In this study a particular cell (see Figure 1) with a geometrical constant K° = (5.94 ± 0.25) × 10^{-5} kPa deg^{-1} was employed. The temperatures were measured with a calibrated chromel–alumel thermocouple inserted in a second empty cell placed below the torsion cell. In order to test the temperature measurements and to test that thermodynamic equilibrium existed within the used cell, we measured the vapor pressure of sulfur. The corresponding heat of sublimation, ΔH°_{298}, derived by second- and third-law treatments of the data are in agreement with each other and with the values selected by Hultgren,[9] and this result has been considered proof that equilibrium conditions were obtained.

The vaporization of α-bromonaphthalene was studied in three runs over the temperature range 298–359 K. The results are reported in Table I and fitted in Figure 2. Because of the high vapor pressure of α-bromonaphthalene at room temperature, at the end of each run the sample was completely vaporized and the zero torsion angle was measured when the cell was empty. Consequently, the measured α values were appropriately corrected. The least-squares line through the vapor pressure points taken over the experimental temperature range covered is given by the equation

Table I. Vapor Pressures of α-Bromonaphthalene Measured by the Torsion Effusion Method

run	T, K	P, kPa	run	T, K	P, kPa
A.01	298	7.13 × 10^{-4}	A.02	323	8.33 × 10^{-3}
	301	9.50 × 10^{-4}		326	8.54 × 10^{-3}
	303	1.37 × 10^{-3}		328	1.04 × 10^{-2}
	306	1.31 × 10^{-3}		331	1.25 × 10^{-2}
	307	1.43 × 10^{-3}		331	1.17 × 10^{-2}
	313	2.85 × 10^{-3}		340	1.73 × 10^{-2}
	315	3.05 × 10^{-3}			
	318	3.62 × 10^{-3}	A.04	299	1.07 × 10^{-3}
	319	3.62 × 10^{-3}		307	1.72 × 10^{-3}
	320	4.16 × 10^{-3}		309	2.32 × 10^{-3}
	321	4.51 × 10^{-3}		311	2.61 × 10^{-3}
	322	4.75 × 10^{-3}		316	3.86 × 10^{-3}
	323	4.99 × 10^{-3}		323	6.18 × 10^{-3}
	325	5.82 × 10^{-3}		324	6.21 × 10^{-3}
	331	7.78 × 10^{-3}		328	7.00 × 10^{-3}
	334	8.94 × 10^{-3}		333	8.58 × 10^{-3}
	339	1.28 × 10^{-2}		336	1.03 × 10^{-2}
	347	2.02 × 10^{-2}		341	1.29 × 10^{-2}
	350	2.43 × 10^{-2}		343	1.75 × 10^{-2}
	359	4.20 × 10^{-2}		355	3.87 × 10^{-2}

$$\log p(\mathrm{kPa}) = (6.96 \pm 0.18) - (2980 \pm 57)/T \qquad (2)$$

where the errors are the standard deviations.

B. Knudsen Effusion Technique

A set of vapor pressure data in equilibrium with α-bromonaphthalene was determined by the Knudsen method.[10] The assembly used is reported in Figure 3. The temperatures of the cell were measured by a calibrated chromel–alumel thermocouple placed inside the thermostated copper block and in contact with the effusion cell. The assembly was heated by an oil bath.

The vapor pressures were evaluated by the mass loss of the sample by employing the relation

$$p(\mathrm{kPa}) = 2.29(m/\Delta t)(T/M)^{1/2}/SK' \qquad (3)$$

where m is the mass of the sample effused in time Δt at temperature T through the effusion hole of area S, M is the molar mass of the gas, and K' is the Clausing factor.[11] In each determination the vaporization time was evaluated by opening and closing the effusion hole with a movable pin (see Figure 3). The mass loss of the sample was determined by weighing the cell before and after each experiment. Here again, the test runs using pure substances performed with the different cells employed yielded vapor pressure values in good agreement with those selected in literature.[9]

In Table II and in Figure 2 are reported the vapor pressures of α-bromonaphthalene calculated by assuming that monomeric $BrC_{10}H_7$ is the only gaseous species in analogy with α-chloro-

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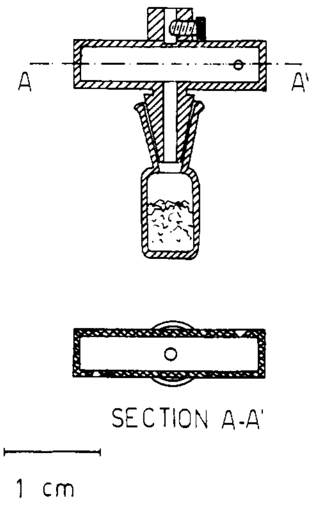

Figure 1. Schematic diagram of the torsion effusion cell.

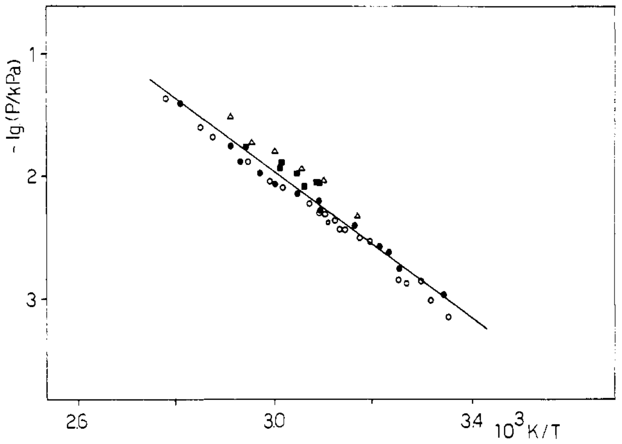

Figure 2. Experimental values of the vapor pressure of α-bromonaphthalene: torsion effusion technique (○, run A.01; ■, run A.02; ●, run A.04); Knudsen effusion technique (△).

Table II. Vapor Pressure of the α-Bromonaphthalene Measured by Different Knudsen Effusion Cells

cell	area of effusion hole, cm	T, K	no. of points	P, kPa
B.02	3.88×10^{-2}	315	4	4.95×10^{-3}
B.05	5.71×10^{-2}	322	4	9.26×10^{-3}
B.07	1.54×10^{-2}	323	1	8.97×10^{-3}
B.04	2.80×10^{-2}	327	4	1.16×10^{-2}
B.02	3.88×10^{-2}	333	1	1.61×10^{-2}
B.03	7.85×10^{-3}	338	2	1.84×10^{-2}
B.03	7.85×10^{-3}	343	2	2.83×10^{-2}

naphthalene.[12] The least-squares treatment of the data gave the following pressure–temperature equation:

$$\log p(\text{kPa}) = (6.33 \pm 0.33) - (2710 \pm 110)/T \qquad (4)$$

where the errors are the standard deviations. Of course, because of the relatively small temperature interval and the scarce experimental points, the overall errors could well be larger than those reported.

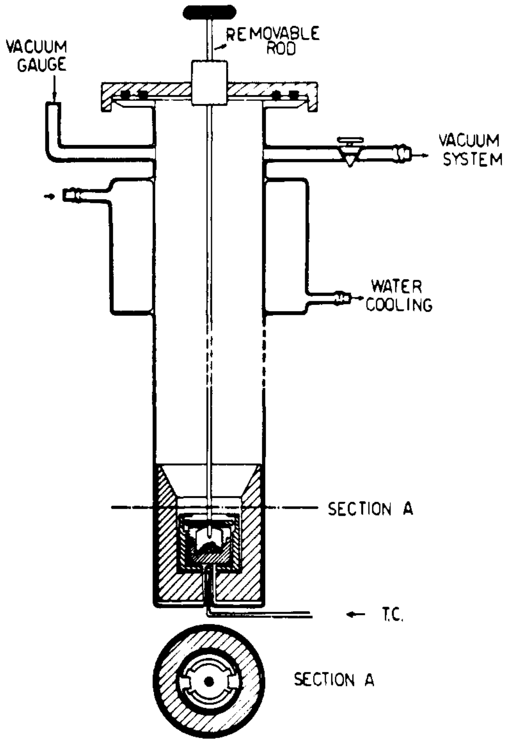

Figure 3. Knudsen effusion assembly.

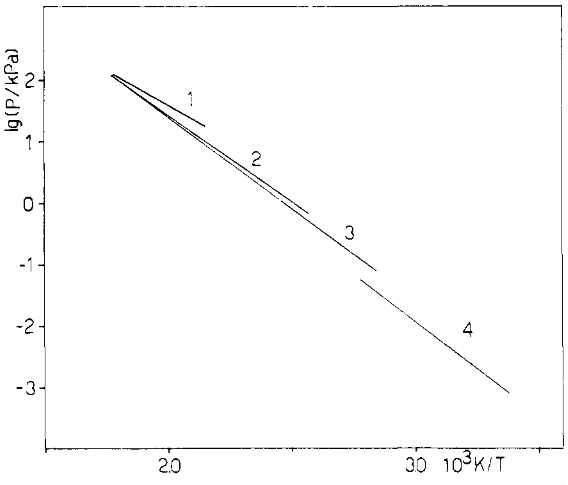

Figure 4. Vapor pressure of α-bromonaphthalene: 1, Hon et al.[2]; 2, Stull[4]; 3, Jordan[3]; 4, this work.

Conclusion

Considering the results obtained by the torsion and Knudsen effusion methods, we propose the following vapor pressure equation for α-bromonaphthalene:

$$\log p(\text{kPa}) = (6.9 \pm 1.1) - (2950 \pm 300)/T \qquad (5)$$

where the slope and intercept were evaluated by weighing the corresponding values obtained in each experiment. The associated errors were estimated by taking into account the errors in temperature measurements and in the calibration factors. In Figure 4 are reported vapor pressure–temperature dependence

Table III. Comparison of Vapor Pressure Equations and Vaporization Enthalpies of α-Bromonaphthalene

temp °C	no. of points	$\log p(\text{kPa}) = A - B/T$		ΔH°_T, kJ mol^{-1}	method	ref
		A	$10^{-3}B$			
80–290	22	7.40	3.88	74.2	selected data	3
84.2–281.1	10	7.40	2.96	56.6	selected data	4
196.27–285.93	14	6.10	2.23	42.6	ebulliometry	2
25–90	39	6.9 ± 1.1	2.95 ± 0.30	56 ± 6	torsion effus	this work
42–70	7				Knudsen effus	this work

Table IV. Thermodynamic Functions of α-Bromonaphthalene

	liquid[a]			gas		
T, K	$H°_T - H°_{298}$, kJ mol^{-1}	$S°_T$, J mol^{-1} K^{-1}	$-(G°_T - H°_{298})/T$, J mol^{-1} K^{-1}	$H°_T - H°_{298}$, kJ mol^{-1}	$S°_T$, J mol^{-1} K^{-1}	$-(G°_T - H°_{298})/T$, J mol^{-1} K^{-1}
298		283	283		376	376
300	0.3	284	283	0.3	377	376
320	3.9	294	283	3.4	387	376
340	7.7	304	284	6.8	397	377
360	11.7	314	285	10.3	407	379
380	15.9	324	287	14.0	417	380
400	20.4	334	289	17.8	427	383

[a] Values derived from the thermodynamic data of the gas phase (see text).

Table V. Vibrational Frequencies (cm^{-1}) of α-Bromonaphthalene

in gas[a]	in liquid[b]	assignt[c]	in gas[a]	in liquid[b]	assignt[c]	in gas[a]	in liquid[b]	assignt[c]
3103	3080	C-H	1362	1370	C-C	733	651	ring def op
3091	3059	C-H	1344	1339	C-H bend ip	700	731	C-H bend op
3066	3038	C-H	1260	1251	C-H bend ip	633	613	ring def ip
3060	3020	C-H	1207	1200	C-H bend ip	609	618	ring def ip
3020	3010	C-H	1158	1160	C-H bend ip	558	582	C-Br
3005	2990	C-H	1143	1140	C-H bend op	533	562	ring def ip
2951	2948	C-H	1130	1134	C-H bend op	520	531	ring def ip
1705	1682	C-C	1021	1022	C-H bend op	514	512	ring def ip
1622	1623	C-C	1062	1058	C-H bend op	473	471	ring def op
1582	1590	C-C	950	958	C-H bend ip	390	383	ring def op
1552	1560	C-C	942	949	C-H bend ip	344	320	ring def ip
1497	1500	C-C	913	899	C-H bend op	302	299	C-Br bend ip
1467	1455	C-C	855	857	C-H bend op	242	237	ring def op
1455	1454	C-C	819	790	ring def op	228	225	C-Br bend op
1432	1432	ring def ip	750	765	C-H bend op	185	175	ring def op
1370	1376	C-C	745	742	breathing	135	125	ring def op

[a] Argon (99.998% purity) was employed as matrix gas. [b] From Sharma et al.[15] [c] Legend: def, deformation; ip in-plane vibration; op, out-of-plane vibration. In-plane and out-of-plane normal modes are A′ and A″ vibrations, respectively, in the C_s group.

measured here and those reported by previous authors.[2-4] From the slope of eq 5, a second-law vaporization enthalpy $\Delta H°_{329} = 56 \pm 6$ kJ mol^{-1} was derived. In Table III are shown for comparison vapor pressure equations and enthalpies of vaporization along with similar values calculated from the data of previous investigations.

Considering that the mean experimental temperature, $T = 329$ K, is very close to 298 K, $\Delta H°_T \simeq \Delta H°_{298}$ was assumed and the free energy function, $-[(G°_T - H°_{298})/T]$, for the liquid phase was derived by using the equation

$$[(G°_T - H°_{298})/T]_l = R \ln p + \Delta H°_{298}/T + [(G°_T - H°_{298})/T]_g \quad (6)$$

The values so obtained are reported in Table IV. The free energy functions of α-bromonaphthalene in the ideal gas state were calculated by the statistical mechanic formulas by neglecting the electronic contribution and considering a planar configuration (C_s group and $\sigma = 1$) as hypothesized for α-bromonaphthalene by Chanh.[13] The bond lengths and the angles employed were those of α-bromonaphthalene. The necessary vibrational frequency values were experimentally determined by an infrared matrix isolation technique with a procedure similar to that described elsewhere.[14]

It is interesting to note that the found values agree with those derived by Sharma[15] in the liquid phase. They are reported in Table V.

In Table III are also reported the heat content functions for the liquid phase derived by a least-squares treatment of the free energy function according to the equation

$$\mathrm{d}[(G°_T - H°_{298})/T]/\mathrm{d}T = -(H°_T - H°_{298})/T^2 \quad (7)$$

and the absolute entropy values derived from the direct use of the Gibbs–Helmholtz equation. A value of $S°_{298} = 282 \pm 21$ J mol^{-1} K^{-1} for the liquid α-bromonaphthalene can be derived from the slope of the equation $R \ln P = \Delta S°_{298} - \Delta H°_{298}/T$ by considering the term $i = \int_{298}^{T}(\Delta Cp/T)\mathrm{d}T - (\int_{298}^{T}\Delta Cp\mathrm{d}T)/T \ll R \ln P$ and $S°_{298}(\mathrm{g}) = 376$ J mol^{-1} K^{-1}. The value is essentially identical with that found with the previous procedure ($S°_{298} = 283$ J mol^{-1} K^{-1}).

Furthermore, from the present vapor pressures and the well-known boiling point of α-bromonaphthalene,[3,4] the constants A and C of the Antoine equation, $\log p\,(\mathrm{kPa}) = A - B/(t + C)$ (t is the temperature in Celsius), were calculated. These values were determined according to a procedure suggested by Thomson[16] from the equation (8) obtained by least-squares

$$\log p(\mathrm{kPa}) = A - [(t_0 + C)(\log p - \log p_0)]/(t - t_0) \quad (8)$$

treatment of the data, where t_0 and p_0 represent the temperature and the pressure at the boiling point (281 °C, 101.3 kPa) and p is the pressure determined at the experimental temperature t (°C). From the A and C values, the average of B was derived, so that the Antoine constants $A = 7.02 \pm 0.36$, $B = 2523 \pm 80$, and $C = 222 \pm 20$ were evaluated. These values are higher than those reported by Hon et al.[2] ($A = 5.38175$, $B = 929.64$, $C = 91.06$) determined in the temperature range 196.27–285.93 °C. However, in the present case having considered the boiling point temperature and the experimental vapor pressures measured in the temperature range 25–86 °C, the temperature range utilized for deriving the Antoine constant results is larger and therefore their values should be more reliable.

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Vapor Pressures, Refractive Index at 20.0 °C, and Vapor–Liquid Equilibrium at 101.325 kPa in the Methyl *tert*-Butyl Ether–Methanol System

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The vapor pressures of methyl *tert*-butyl ether (MTBE) at roughly 3–55 °C and of methanol (MeOH) at roughly 26–65 °C were determined by comparative ebulliometry, the refractive index over the entire composition range of the MTBE–MeOH system was measured at 20.0 °C by dipping refractometry, and the isobaric vapor–liquid equilibrium in the system at 101.325 kPa was determined by dynamic method using a recirculation still. The estimated uncertainties in the measured temperature, pressure, refractive index, and compositions of the equilibrium phases are respectively ± 0.005 °C, $\pm 0.02\%$, $\pm 0.000\,03$ refractive index units, and ± 0.0005 to ± 0.005 in mole fraction. The vapor–liquid equilibrium data were fitted to the Wilson equation. At 101.325 kPa, the MTBE–MeOH system exhibits a minimum-boiling azeotrope of composition 68.5 mol % (85.7 wt %) MTBE at 51.27 °C.

Introduction

MTBE, well-known for its excellent antiknock quality, has been extensively tested as an octane booster for lead-free or low-leaded gasoline, and the use of pure MTBE (*1*, *2*) and of its mixtures with C_4 alcohols (*3*) for high-octane gasoline blending was recommended. Recently the use of MTBE as a gasoline component at concentrations of 7% or less by volume was approved by the Environmental Protection Agency (*4*). Produced by catalytic reaction of methanol with isobutylene, MTBE appears as a welcome outlet for isobutylene formed in C_4 streams of ethylene production plants as well as for the conventional refinery C_4 streams. It is also increasingly valued as a means of making pure isobutylene.

Although most of the processes of the abruptly growing MTBE production involve distillation at atmospheric pressure as a final stage, a search of the available literature failed to reveal reliable data on vapor–liquid equilibrium in the MTBE–MeOH system. For this system we report here the isobaric vapor–liquid equilibrium data at 101.325 kPa along with refractive indices at 20.0 °C useful for analysis. Vapor pressures of pure components were determined ebulliometrically over the approximate pressure range 15–100 kPa for comparison with the most accurate recent results for methanol obtained by Gibbard and Creek (*5*) using a static technique and with the data of Ambrose et al. (*6*) for MTBE.

Experimental Section

Materials. MTBE from two sources was used for the study. The first batch was the product of Chemische-Werke Hüls, FRG, with an indicated purity of at least 98%, and the second batch was synthesized in our laboratory from methanol and *tert*-butyl alcohol (both A.R. grade) in diluted sulfuric acid at ca. 52 °C by a procedure analogous to that described in literature (*7*, *8*) for the preparation of ethyl *tert*-butyl ether. In both cases, the MTBE product was repeatedly washed with water, shaken with the saturated potassium permanganate aqueous solution containing ca. 120 g/L potassium hydroxide (until the aqueous layer remained green), washed with water again, and twice rectified on a 60-plate bubble-cup column at 20:1 reflux ratio. The 40 and 60% heart-cut was taken at the first and second distillation stage, respectively. The MTBE was then dried by staying in contact with freshly cut metal sodium for several days and finally being distilled from sodium on a column (30 mm i.d., 65 cm length) packed with Pyrex-glass helices (3 mm diameter) at a reflux ratio of 7:1. The middle 50% fraction was used for the experiments.

A.R. grade methanol (Lachema, Brno, Czechoslovakia) was twice rectified in a 60-plate bubble-cup column at 20:1 reflux ratio, the middle 50% distillate portion being retained in both stages. It was then dried by the procedure of Lund and Bjerrum (*9*) which, briefly, involved a separate conversion of a portion (corresponding stoichiometrically to 5 g of magnesium/L) of the methanol batch to magnesium methoxide and refluxing the methanol with dissolved methoxide for 3 h. With the exclusion of moisture from the system, methanol was then given the final distillation in the packed column under the same conditions as described for MTBE.

The water used for pycnometric calibrations, refractometric adjustments, and indirect pressure determinations by means of the water boiling point was a sample redistilled on addition of potassium permanganate in a quartz apparatus and deareated by boiling off one-third of its volume.

No impurities in the MTBE and methanol employed for experiments were detected by gas chromatographic analysis. Karl

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