



Temperature and composition-dependent properties of the two-component system D- and L-camphor at 'ordinary' pressure

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ABSTRACT

The properties of dextrorotatory and racemic camphor have been investigated as a function of temperature and composition. A thorough literature survey has been undertaken for temperatures and enthalpies of all transitions and for structural information of the phases existing under ordinary pressure. The transition temperatures and enthalpies have been measured with differential scanning calorimetry. Cell parameters of all phases have been determined as a function of temperature up to the melt and the specific volume of liquid camphor has been determined. A temperature–composition phase diagram is presented containing all condensed-phase transitions, including an analysis of the melting transition. The melting point of racemic camphor is at least 2 K lower than the melting point of D- (and L-) camphor at 451 ± 2 K, whereas the melting enthalpy is the same within error. Below the melting point, mixtures of solid D- and L-camphor are solid solutions. Because the structures of the racemic compound near the melting point and the solid solution are equivalent for time and volume averaged measurements, they cannot be distinguished. One could call this a case of 'critical symmetry'.

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1. Introduction

1.1. General introduction

Phase behavior of binary mixtures has always received a lot of attention, not only to improve academic understanding but also for industrial applications, including in pharmacy. As for systems of optically active substances, a comprehensive treatise about their thermodynamic behavior appeared in 1981 written by Jacques et al. [1] Enantiomer mixtures behave different from pure substances, which can be demonstrated with temperature–composition (T – X) phase diagrams (X : composition in mole fraction).

Since camphor is known for centuries, its phase behavior was assumed to be well understood. However, after examination of its solid-state properties in the literature, basic data at 'ordinary' pressure surprisingly appeared to be either questionable or even lacking. The low-temperature binary phase diagram of camphor has received a fair amount of attention, in particular its solid–solid transitions [2–6]. Open questions are whether D-camphor and racemic DL-camphor have different melting points and different melting enthalpies. This would complete the phase diagram of the con-

densed phases presented by Mjojo and Schäfer and Wagner [3,6]. In addition, the evolution of the specific volume for D-camphor and for the racemic mixture have been studied from 100 K to their respective melting points and beyond into the melt. Although certain aspects of the low-temperature transition (phase III–phase II) of DL-camphor remain unclear [4,7,8], it falls outside the scope of this paper.

Finally, in this paper the word 'transition' is used in the sense of a reversible shift from one phase to another, hence while the two phases are in equilibrium. This has been done for the sake of brevity, even though the general meaning of the word (phase-) 'transition' also includes irreversible phase shifts.

1.2. Literature survey

1.2.1. The camphor molecule

The molecular formula of camphor was determined in 1833 but it took another 60 years before Julius Bredt proposed the correct structure in 1893 [9]. Camphor, a bicyclic monoterpene (1,7,7-trimethyl-bicyclo(2,2,1) heptan-2-one), exhibits two asymmetric carbon atoms (Fig. 1). Dextrorotatory camphor is made of molecules with the absolute configuration R, (1R,4R)-(+)-camphor (CAS No. 464-49-3), and levorotatory camphor is (1S,4S)-(-)-camphor (CAS No. 464-48-2). 4R and 4S are often omitted. Pure dextrorotatory camphor (D-camphor, $C_{10}H_{16}O$, $M = 152.2334$ g mol⁻¹) is produced naturally by the camphor tree and other plants and so is lev-

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Table 1
Crystallographic data from the literature for D- and DL-camphor.^a

Phase	Lattice parameters			Z	V (Å ³)	T (K)	Ref.
	a (Å)	b (Å)	c (Å)				
<i>D-Camphor</i>							
III, orthorhombic <i>P2₁2₁2₁</i>	8.9277	27.0359	7.3814	8	1781.64	100	[12]
II, hexagonal (OD)	7.14		11.72	2	517	295	[3,7]
I, face-centered cubic (OD)	10.1			4	1030	380	[3]
<i>DL-Camphor</i>							
III, orthorhombic <i>Cmcm</i>	6.8341	11.6584	11.5000	4	916	100	[8]
II, hexagonal (OD)	7.05		11.50	2	476	295	[3]

^a Z: number of molecules in unit cell, V: unit cell volume, T: measurement temperature, OD: orientationally disordered.

Table 2
Transition temperatures and enthalpy changes of D-camphor (in part based on Ref. [13]).

III → II		II → I		I → liquid		Ref.
T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	
245		370		450.8	6.0	[36]
		360.2	0.106			[10]
–	7.78 ± 0.08					[37]
		332 ± 28	0.4 ± 0.4 ^a	453 ± 25	6.5 ± 0.3 ^a	[33,38]
243	6.99 ± 0.15	374.2	0.234 ± 0.024	452	6.862	[24]
243.8 ± 0.1	6.99 ± 0.15					[5,6]
245.0	11.49					[38,39]
245				449		[40]
243	10.65					[41]
242 ± 1	16 ± 1 ^b					[42]
244	11.3 ± 0.8					[3]
				450	5.4 ± 0.4	[43]
				452.2		[44]
				447–448		[45]
				453.2		[46]
244.19	7.600 ^c	371.66	0.218 ^c			[4]
				462.3 ± 0.5	15.7 ± 0.6	[14,38]
				449.8–451.9	6.0 ± 0.2	[16]
				451.75		[13] ^d
				451.95		[13] ^d
				451.95		[13] ^d
				451.75		[15]
244 ± 1	10 ± 3	369 ± 6	0.19 ± 0.07	451 ± 2	6.2 ± 0.6	Average ^e

^a Calculated by fitting of sublimation and vaporization data, see also text.

^b Mjojo states that the enthalpy value is unreliable [3].

^c Estimates by Witusiewicz et al. [13] using heat capacity data of Nagumo et al. [4].

^d References found in Ref. [13] of which an original document could not be obtained: 451.75 K (Haller, 1882), 451.95 K (Louquinine, 1889), and 451.95 K (Fancone, 1912).

^e Data of De Wilde [24] not used for the average of the II-I transition and data of Donnelly et al. [14] not used for I-L average.

Table 3
Transition temperatures and enthalpies of DL-camphor.

III → II		II → I		I → liquid		Ref.
T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	
		367				[10]
210	0.84			440.6–446.1	5.6 ± 0.2	[16]
210 ± 1	0.84 ± 0.03			452	6.862	[5]
203.6	2.23					[39]
203.8	0.72	350	0.234 ± 0.024			[40]
						[6]
				451.6	6.82 ± 0.03	[38,47] ^a
206 ± 1	1.9 ^b			451.75		[15]
206						[3]
218.2	0.98 ^c			451		[41]
209.12	1.2 ^c	367 ^c	0.24 ^c			[4] Annealed
203.8		350		449		[4] Rapidly cooled
207 ± 3 ^d	1.2 ± 0.6	358 ± 10	0.237 ± 0.004	450 ± 4	6.4 ± 0.7	[48]
						Average

^a Frandsen [47] uses the phrase 'synthetic camphor', which implies DL-camphor, in the table in Ref. [13] it was grouped with D-camphor.

^b Mjojo [3] states that the enthalpy value is unreliable.

^c Values determined from data available in Ref. [4].

^d Average of unannealed samples.

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