CCXXXI.—*The Molecular Lowering of Freezing Point for Camphor.*

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Two widely divergent values for the molecular lowering of freezing point of camphor, *viz.*, 400 (Rast, *Ber.*, 1922, **55**, 1051, 3727) and 498 (Jouniaux, *Bull. Soc. chim.*, 1912, **11**, 722), have coexisted in the literature for some years. As the former value was deduced from a m. p. diagram (salol–camphor, Caille, *Compt. rend.*, 1909, **148**, 1458) which Le Fèvre and Webb (this vol., p. 1211) have shown to be inaccurate, the opinion was expressed by these authors that the apparently carefully determined value of Jouniaux was the more correct.

Jouniaux plotted cooling curves both for pure camphor and for a number of solutions of substances in this solvent, and from the resulting depressions of m. p. obtained the following very consistent values for the molecular-depression constant of camphor :

Solute.	K.	Solute.	K.
Naphthalene	494	Pyrogallol	500
α-Nitronaphthalene	505	Benzoic acid	492
β-Naphthylamine	499		

This author further pointed out that the value 498 received an independent confirmation from the coincidence of the latent heat of fusion (*viz.*, 8·24 cals.) calculated either from van 't Hoff's equation, $K = 0·02T^2/L$, or from Clapeyron's formula

$$L = T/E \cdot (v_l - v_s) \cdot dp/dT$$

(using data given by Ramsay and Young, *Phil. Trans.*, 1884, **175**, 45; Allen, J., 1900, **77**, 413; and Vanstone, J., 1910, **97**, 429).

However, in view of the fact that, by taking $K_{camphor} = 400$, satisfactory molecular-weight determinations are frequently performed cryoscopically in camphor, the correctness of Jouniaux's

figure seemed suspect. Our original intention was, therefore, to verify and extend his experimental results quoted above.

Freezing Points of Various Dilute Solutions in Camphor.—The camphor used throughout the following experiments was commercial " pure camphor." Its f. p., found in the apparatus used below, was 178·7°. Since the highest recorded value for the m. p. is 178·5—179° (corr.) (Kempf, *J. pr. Chem.*, 1908, **78**, 259), whilst Foerster (*Ber.*, 1890, **23**, 2983) observed a solidification point of 178·7° (corr.), further purification of our specimen was considered unnecessary.

The f. p.'s of the solutions referred to in Table I were ascertained from cooling curves constructed from half-minute temperature readings. In each case the melt was contained in a closed boiling tube, fitted with a glass stirrer and a thermometer graduated in 0·2° but easily readable to 0·1°, and surrounded by a wide glycerol-filled jacket of such a size that when the whole was immersed in a 1·5-litre glycerol bath the rate of cooling (between 150° and 200°) did not greatly exceed 1° in 2 minutes. No attempts were made to obtain absolute f. p.'s, since only a difference of two temperatures was required in each case; the thermometer was therefore not standardised before use nor were any exposed stem corrections applied to the observations made with it. Very little supercooling was noticed even when the melts were not stirred. The temperatures at which the first changes of direction of the cooling curves occurred were identical with those when first separation of solid was observable.

The data so obtained and the values for $K_{camphor}$ calculated therefrom are given in Table I.

The mean value for $K_{camphor}$ is thus found to be 396, which differs greatly from that obtained by Jouniaux (*Bull. Soc. chim.*, 1912, **11**, 546). It is difficult to reconcile our figure with that of this worker. The apparently convincing mathematical verification advanced by him (*ibid.*, p. 993) contains arithmetical errors, and has been shown elsewhere (Le Fèvre and Tideman, *Nature*, 1931, **127**, 972) to be useless as evidence in support of his experimental work.

The System Camphor–Salicylic Acid.—From Table I it will be observed that as the concentration of salicylic acid increases so does the magnitude of K. Examination of the literature relating to these two substances showed that Léger (*Compt. rend.*, 1890, **111**, 110; *Bull. Soc. chim.*, 1890, **4**, 726) had described a compound, m. p. *ca.* 60°, the composition of which was represented by the formula " $C^{14}H^6O^6,2C^{20}H^{16}O^2$." No definite physicochemical evidence was offered in support of its existence, but the above result with salicylic acid (see Table I) would suggest that the steeper arm of the fusion point–composition curve for this system should be

TABLE I.

Solute.	Wt. of solute.	Wt. of solvent.	Depression of f. p.	M.	K.
Naphthalene	0·3936	8·6013	14·3°	128	400
α-Nitronaphthalene	0·3233	9·9811	7·4	173	395
,, ...	0·2663	8·8157	7·1	,,	407
β-Naphthylamine	0·3086	8·5036	9·9	143	390
Pyrogallol	0·4623	9·8610	14·1	126	379
,, ...	0·3256	10·2013	9·7	,,	383
Benzoic acid	0·2475	8·7870	9·0	122	390
,, ...	0·2811	8·9901	10·2	,,	398
Salicylic acid	0·1641	8·9821	5·2	138	393
,, ...	0·2414	9·9288	7·1	,,	403
,, ...	0·3957	9·1005	13·3	,,	(422)
,, ...	1·0001	8·9948	35·3	,,	(438)
Quinol	0·3706	9·9810	13·2	110	391
,, ...	0·2815	10·0110	10·1	,,	395
Acenaphthene	0·3257	8·7758	9·8	154	407
,, ...	0·3950	9·1010	11·3	,,	401
p-Nitrophenol	0·4246	9·6871	12·3	139	390
Picric acid	0·4643	9·1360	9·1	229	410
3 : 3′-Dinitro-4 : 4′-di-piperidinodiphenyl-sulphone	0·5243	6·9011	6·3	474	393
Ethyl 3-nitro-6-piperidino-benzoate	0·7496	9·9810	10·7	278	396

Mean value for K, results in parentheses being omitted, = 396.

that which inclines towards the 100% camphor axis rather than towards the 100% salicylic acid axis.

We have therefore carried out a series of f. p. determinations of mixtures of salicylic acid and camphor; details are given in Table II, and from these the freezing point–composition curve shown in Fig. 1 is plotted. The thermometer employed for these experiments coincided with a standard instrument between 0° and 100° but from 100° to 180° its readings became lower than the correct figures. The correction at 180° was + 0·8°. The fourth column (Table II) contains uncorrected f. p.'s, however, since the accuracy of the higher f. p.'s is not very material.

TABLE II.

Freezing Points of Mixtures of Salicylic Acid and Camphor.

Camphor, g.	Salicylic acid, g.	Salicylic acid, mols.%.	F. p.	Camphor, g.	Salicylic acid, g.	Salicylic acid, mols.%.	F. p.
—	—	0	178·0°	7·4265	2·8095	29·4	55·3°
8·9821	0·1641	1·6	173·2	7·2798	2·7661	29·5	55·2
9·9288	0·2414	2·6	171·0	7·2920	2·9000	30·5	54·3
9·1005	0·3957	4·6	165·0	7·1019	2·9008	31·0	54·1
9·5644	0·5891	6·4	158·0	7·1605	3·0620	32·0	55·1
8·9948	1·0005	10·9	143·0	6·1382	4·1151	42·5	92·0
8·5139	1·5937	17·1	117·0	5·0936	5·0814	52·4	110·9
8·1162	2·1652	22·7	88·0	4·1049	6·1407	62·2	126·0
7·7951	2·3032	24·6	75·0	3·0700	7·4174	72·7	136·3
7·5754	2·5770	27·3	56·0	2·0964	8·3828	81·3	143·1
7·4206	2·5682	27·6	55·0	1·1189	9·0534	89·9	148·0
7·4663	2·6783	28·3	53·3	—	—	100·0	157·3

The curve shown in Fig. 1 definitely indicates the existence of a compound, $2C_{10}H_{16}O,C_7H_6O_3$, m. p. 56°. The melts containing the two constituents in about the proportion required for this compound crystallised well on cooling, forming at first feathery crystals

FIG. 1.

Salicylic acid, mols. %.
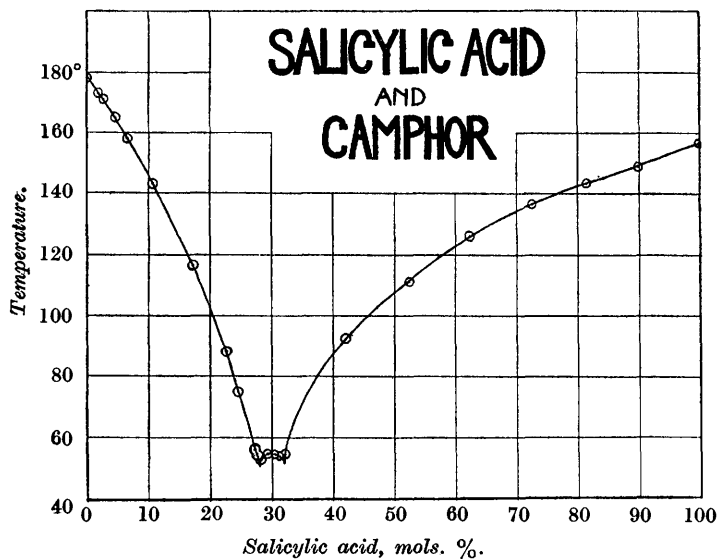
throughout the mass and then solidifying to a white cake with the appearance and feel of soap. This is in complete accordance with the description given by Léger (*Compt. rend.*, 1890, **111**, 109).

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