

CLXI.—*An Approximate Determination of the Molecular Depression of the Freezing Point for Bornyl Chloride; with a Note on the Recorded Values of the Same Constant for Camphor.*

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It is well known that if, during the reaction between α -pinene and hydrogen chloride, moisture or hydroxylic compounds are not rigorously excluded, some dipentene dihydrochloride is formed and prevents the solidification of the simultaneously formed bornyl chloride. This fact suggested that the molecular depression of freezing point for the latter substance might be large, and this expectation was strengthened by examination of the Tables of these

constants for organic solvents (Landolt-Börnstein-Roth, 5th Edn., II, p. 1427), which show that a high molecular depression of freezing point is often characteristic of compounds having a cyclic poly-methylene constitution, as indicated in the following comparative table.

Molecular Depressions of Freezing Point.

| | | | |
|------------------------------|-----|----------------------------|------|
| Phenol | 73 | <i>cyclo</i> Hexanol | 383 |
| Benzene | 51 | <i>cyclo</i> Hexane | 202 |
| Diphenyl..... | 80 | <i>Dicyclo</i> hexyl | 145 |
| <i>d</i> -Bromocamphor | 119 | Camphor | 498* |

* See later.

It seemed of interest, therefore, to make some rough measurements of *K* for bornyl chloride, because this substance would almost certainly be a better solvent for cryoscopic molecular-weight determinations on a micro-scale than is camphor (Rast, *Ber.*, 1922, **55**, 1051, 3727), since (1) it has a lower m. p., *viz.*, 119–120° instead of 179°, and (2) it is much less volatile. Camphor is often troublesome in the latter respect, and by volatilisation during experiments it leads to larger depressions than are correct for the actual concentrations of the solutions under investigation.

Accordingly, such determinations were performed with bornyl chloride as the solvent and certain pure substances as solutes. Observations were at first made following as far as possible Rast's micro-molecular weight technique (*loc. cit.*); later, however, it was considered advantageous to use larger quantities of materials.

The bornyl chloride used was prepared from pure fractionated α -pinene, b. p. 156°. After two crystallisations from alcohol it had an m. p. not higher than 123°. Redistillation of 90 g. and collection of only 20 g. of the middle fractions, b. p. 206–208°, gave a specimen with a sharp m. p. of 125.1°. Higher m. p.'s have been recorded (*viz.*, 131–132°, Riban, *Ann. Chim.*, 1875, **6**, 25, 481; 131°, Atterberg, *Ber.*, 1877, **10**, 1204, and Long, *J. Amer. Chem. Soc.*, 1899, **21**, 642; and 130–131°, Frankforter and Franz, *ibid.*, 1906, **28**, 1462), but as the essential measurement to be made—the depression of m. p.—is a difference, the slight contamination by (probably) *isobornyl* chloride, m. p. *ca.* 156°, was neglected.

Method.—The following procedure was employed in each case. Weighed quantities of bornyl chloride and solute were placed in a thin-walled hemispherical test-tube of fairly uniform wall thickness (a factor which seemed to affect reproducibility of successive observations), and the mixture was *just* melted in a glycerol bath (mechanically stirred). Very little volatilisation occurred. A thermometer and a thin helical glass stirrer were then introduced and the bath was allowed slowly to cool. The temperature at which a solid

crystalline structure first appeared was recorded; if, on reheating of the bath, this disappeared sharply at the *same temperature*, the latter was taken (compare Rast's method) as the m. p. The same operations were conducted on the pure solvent, and hence the depression of m. p. produced by a known amount of solute of known molecular weight in a given weight of solvent was obtained. From these data $K_{\text{bornyl chloride}}$ was calculated. The results are shown in Table I.

TABLE I.

| Substance. | M. | Wt. of solvent. | Wt. of solute. | δt . | K. |
|---|-----|-----------------|----------------|--------------|-------|
| Phenyl <i>p</i> -toluenesulphonate | 248 | 0.3788 | 0.3333 | 19.8° | 559 |
| Acenaphthene | 154 | 0.4010 | 0.0265 | 24.3 | 566 |
| Dibenzyl | 182 | 0.5287 | 0.0232 | 13.3 | 552 |
| Naphthalene | 128 | 0.3953 | 0.0483 | 50.3 | 524 |
| " | " | 0.2329 | 0.0145 | 23.0 | 473 |
| " | " | 4.6426 | 0.1642 | 12.8 | 463 |
| Benzoic acid..... | 122 | 0.4685 | 0.0302 | 12.3 | (233) |
| Cinnamic acid | 148 | 0.8787 | 0.0363 | 6.3 | (228) |
| Benzil | 210 | 0.6987 | 0.0288 | 10.0 | 509 |
| Ethyl 3-nitro-6-piperidino- benzoate | 278 | 0.7992 | 0.0307 | 7.8 | 564 |
| Phenyl 2-acetoxybenzoate | 256 | 0.6666 | 0.0312 | 10.1 | 552 |
| 3 : 3'-Dinitro-4 : 4'-dipiperidino- diphenylsulphone | 474 | 1.3254 | 0.0853 | 6.7 | 493 |

Mean value for K , omitting results in parentheses, 525.

The values for the molecular depression of m. p. (col. 6) are somewhat erratic, and great accuracy cannot be claimed for them. The visual method recommended by Rast (*loc. cit.*) for determination of m. p.'s of solutions in camphor is not so satisfactorily applicable to similar solutions in bornyl chloride because the appearance and disappearance of the "crystalline skeleton"—which is sharp and reproducible enough with camphor solutions—is, in the present case, less well defined at first and becomes increasingly vague with each repetition.

The constant, however, evidently lies in the neighbourhood of 500, and is therefore the largest known for any organic substance (some fused inorganic salts have larger, *e.g.*, barium chloride, about 1086). Cinnamic and benzoic acids are possibly dimeric in bornyl chloride solution, but this point was not further investigated.

Attempts to check the above results were made by measuring the m. p.'s of dilute solutions of naphthalene in bornyl chloride by the construction of cooling curves. The positions of the m. p.'s of such solutions were, however, too indefinite to justify precise calculations; the values for $K_{\text{bornyl chloride}}$ obtained from such results usually lay between 400 and 450, *i.e.*, considerably lower than those obtained above by using the modified Rast method.

Note on the Molecular Depression of Freezing Point of Camphor.

Rast (*Ber.*, 1922, **55**, 1051, 3727) suggested (without reference to the earlier work of Jouniaux, *Bull. Soc. chim.*, 1912, **11**, 546, 722) the use of camphor as a cryoscopic solvent, the novelty claimed being that the molecular depression of freezing point for this substance was so large that the ordinary m. p. apparatus could be adapted to a micro-method for the determination of molecular weight.

Rast adopted as the molecular depression constant for camphor the value 400, without discussion. This he calculated from m. p.'s of salol-camphor mixtures given in Landolt-Börnstein-Roth (4th Edn., p. 556) and determined by Caille (*Compt. rend.*, 1909, **148**, 1461). Jouniaux (*loc. cit.*) had previously obtained a higher value, *viz.*, 498, from a study of a number of cooling curves of pure substances in camphor solutions.

The latter value seems preferable to Rast's because (a) it is subject to an independent confirmation (Jouniaux, *Compt. rend.*, 1912, **154**, 1593) and (b) camphor is known frequently to combine with phenols (Leger, *Bull. Soc. chim.*, 1889, **4**, 725; Caille, *loc. cit.*; Wood and Scott, *J.*, 1910, **97**, 1573), thus making a value obtained with salol suspect *à priori*.

The shape of the salol-camphor fusion diagram given by Caille (*loc. cit.*) seemed open to question—no definite points were shown on this curve, which appeared to have been drawn from an insufficient number of observations. We accordingly attempted to repeat it.

Melting-point Curve for Mixtures of Salol and Camphor.—Ordinary pure specimens of the two components were used, m. p.'s 42.5° and 175° respectively. Observations were made in the usual way, but the best cooling curves—showing the clearest m. p.'s—were always obtained with mixtures freshly melted together. Attempts to repeat the determination with the same solution frequently failed owing to the excessive slowness of solidification of the liquid melt.

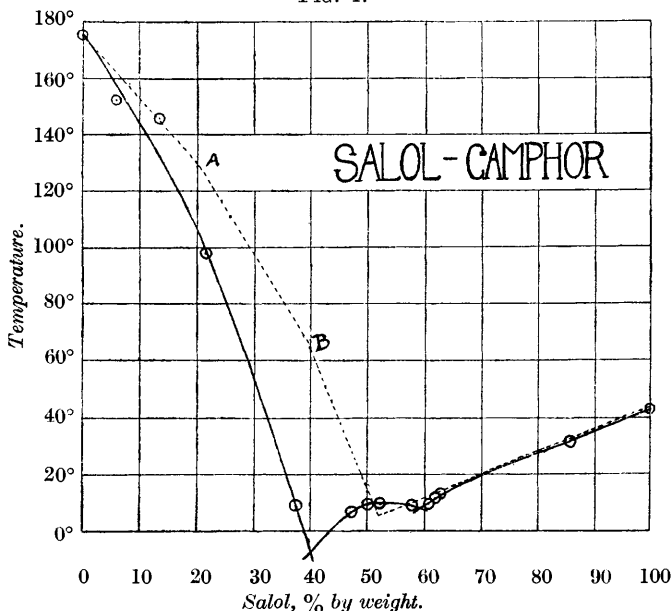
The results are set out in Table II and are plotted in Fig. 1 (unbroken line). For comparison, Caille's curve is superposed upon ours. As this author merely called his *x* axis "composition % des mélanges" and did not state whether molecular or weight percentages were employed, we have decided that the latter were intended and have therefore used these units throughout.

Considerable divergences from Caille's graph (Fig. 1, broken line) are found. Signs of compound formation are apparent, whilst the inclinations of the left-hand arms towards the temperature axis

TABLE II

| Wt. of salol. | Wt. of camphor. | Salol, %. | M. p. | Wt. of salol. | Wt. of camphor. | Salol, %. | M. p. |
|---------------|-----------------|-----------|-------|---------------|-----------------|-----------|-------|
| — | — | 0 | 175° | 9.4045 | 8.5082 | 52.5 | 8.8° |
| 0.7590 | 10.4994 | 7.0 | 147.0 | 6.0261 | 4.3740 | 57.8 | 8.75 |
| 2.1398 | 13.6920 | 13.5 | 145.4 | 11.1830 | 7.1820 | 60.9 | 9.0 |
| 2.1716 | 7.9932 | 21.4 | 98.0 | 7.9118 | 4.7953 | 61.75 | 11.0 |
| 6.3630 | 10.5226 | 37.7 | 8.6 | 5.9141 | 3.6104 | 62.10 | 12.40 |
| 6.0579 | 6.4699 | 47.8 | 6.9 | 17.4548 | 2.8789 | 85.80 | 30.8 |
| 9.3088 | 9.2792 | 50.1 | 8.6 | — | — | 100 | 42.5 |

FIG. 1.



The dotted curve is a copy of that given by Caille (*loc. cit.*) but redrawn on a slightly different scale. As a result, the artificial breaks at A and B which first aroused our suspicions are more clearly seen.

are markedly different in the two cases. The bearing of the latter fact upon the present enquiry is more clearly brought out by calculating K from data for solutions of the same concentration taken (1) from our curve and (2) from Caille's. Thus, for 5%, 10%, 15%, and 20% solutions of salol in camphor: (1) $K = 608, 597, 582,$ and $590,$ but (2) $K = 541, 462, 436,$ and $402.$ It was from this last figure for a 20% solution that Rast took his standard value of 400. [It is interesting to note that from the m. p.'s of ca. 5%, 10%, and 15% solutions of phenol in camphor (Wood and Scott, *loc. cit.*) K becomes 370, 424, and 451 respectively.]

In any case, until further determinations are made, the higher

value given by Jouniaux (*loc. cit.*), being the average of results obtained from 5 different substances in camphor solution, is preferable to that of Caille.

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