

31. *Depression of the Melting Point of r-isoBorneol, l-Borneol, and d-Camphoroxime by Various Substances.*

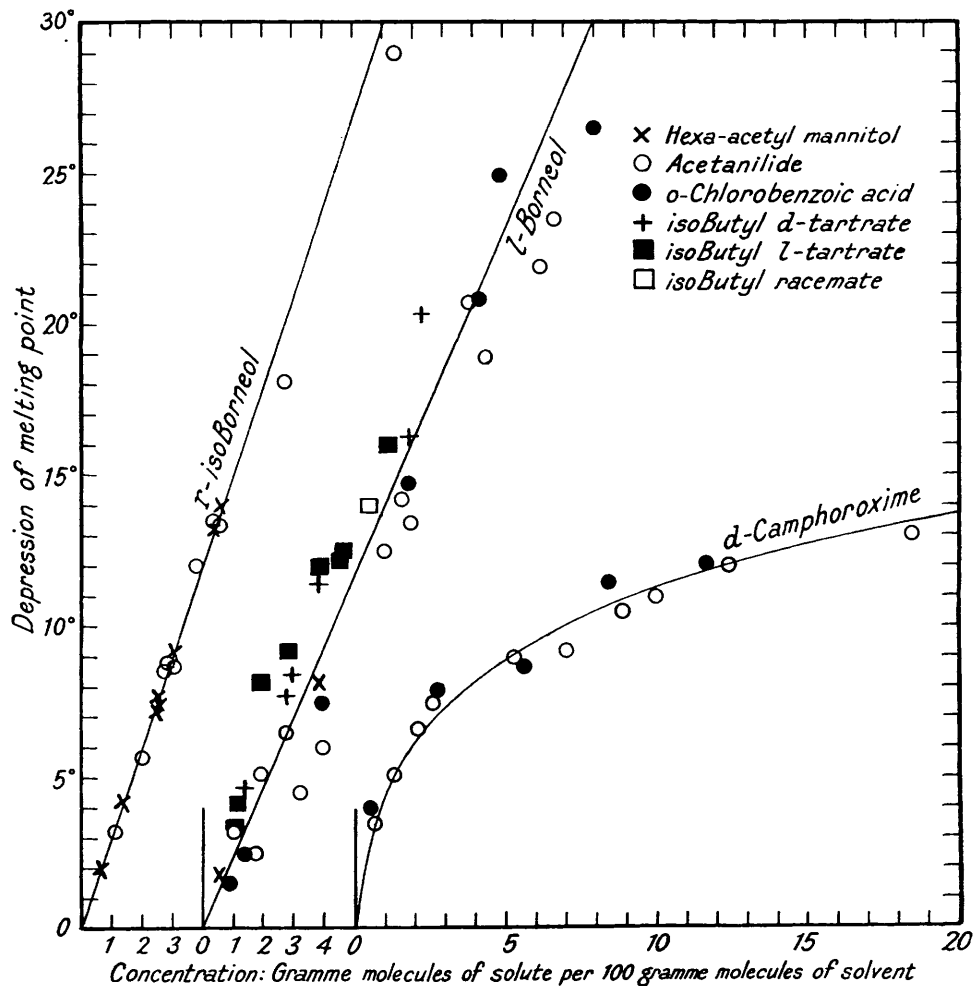
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THE possibility of using camphor as a solvent for cryoscopic molecular weight determination, first pointed out by Jouniaux (*Bull. Soc. chim.*, 1912, **11**, 546, 722), was demonstrated by Rast (*Ber.*, 1922, **55**, 1051; see Le Fèvre, *Nature*, 1930, **126**, 760). The method, however, presents some difficulties due to the high melting point and the easy volatility of camphor. We have therefore made experiments to ascertain (1) whether other substances—perhaps those related to camphor—would show a similar high depression, and (2) whether any of these might be more suitable for cryoscopic determinations than camphor itself. Some of the experiments recorded here were made several years ago by one of us, and the remainder were carried out more recently by another. The data of the two observers agreed well. Since we commenced our work Le Fèvre, with Webb and with Miss Tidemann (*J.*, 1931, 1211, 1729), has published papers on a similar subject, and communications by Firsch (*Ber.*, 1932, **65**, 862, 1839) include some of the solvents examined by us.

The technique employed was similar to that suggested by Rast. Definite proportions by weight of solute and solvent were placed in a small tube closed by a cork, into which was fixed a darning needle. The solid was melted and stirred thoroughly with the needle. After cooling, the solid mixture was ground up, pressed into rather wide melting-point

tubes, and the disappearance of a "skeleton," similar to that seen in camphor solutions, was taken as the true m. p. By diluting an approximately 10% stock solution, solutions of lower concentrations were obtained. The method, we consider, is, in general, not one of great accuracy, and is not suitable for isolated, but only for a series of, observations.

r-isoBorneol (m. p. 212°).—Our experiments with *r-isoborneol* as a solvent, and hexa-acetyl mannitol and acetanilide as solutes, are represented by one of the lines on the diagram, in which observed depression is plotted against concentration expressed as *g.-mols. of solute per 100 g.-mols. of solvent*, a method which permits of direct comparison, on the same diagram, of results of this kind, not merely for different solutes in the same



solvent, but also in different solvents. Hexa-acetyl mannitol and acetanilide evidently depress the m. p. of *isoborneol* in a similar manner, and the relationship between molar concentration and depression is linear, at least up to mol. concn. = 10 ($c = 13$). The average constant (K) for *isoborneol* from these experiments is 466, as a mean of all the data; and 462, from the slope of the graph. *isoBorneol*, however, is rather more easily volatile than *l-borneol* (see on), and its m. p. is a little higher than that of camphor.

l-Borneol (m. p. 207.8°).—The m. p. depressions of *l-borneol* brought about by acetanilide, *o-chlorobenzoic acid*, hexa-acetyl mannitol, and—since we thought it of some interest to examine a pair of optical antipodes—*isobutyl d-tartrate*, *isobutyl l-tartrate*, and *isobutyl racemate* are also shown in the diagram, but to avoid confusion of the

experimental points, we have displaced the graph for *l*-borneol a little towards the right. All the data obtained are recorded, and they therefore give a good notion of the error inherent in the method, in the hands of independent observers. The depression of the m. p. of *l*-borneol is also very considerable and of the same order as in camphor. Further, within the limits of our experiments—up to concentrations of about 12%—the relationship between concentration and depression is practically linear, although there is considerable variation of individual observations. The maximum depression observed was 25° in a 10.04% solution of *o*-chlorobenzoic acid; the average constant for *l*-borneol is 384, taking the mean value of all the data, and 355, from the slope of the graph. That there is a slight difference between *l*- and *iso*-borneol is indicated by the slightly different slope of the two graphs. The data for the tartrates fit in with the rest; there is no appreciable difference between the three substances, they all appear to affect the m. p. of *l*-borneol in the same way as the other compounds examined. It seems likely, however, that any difference which might exist in their behaviour would be too small to be detected by this method.

d-Camphoroxime.—The data for camphoroxime as solvent differ from those already mentioned, and are recorded below in detail.

Solvent : Camphoroxime, $M = 167$; m. p. 119.6°.

Solute : Acetanilide, M 135.				Solute : <i>o</i> -Chlorobenzoic acid, M 156.5.			
Mol. C.*	Depn. of m. p.	C.†	K .‡	Mol. C.*	Depn. of m. p.	C.†	K .‡
0.64	3.5°	0.52	909	0.48	4.0°	0.45	1391
1.31	5.1	1.06	649	2.71	7.9	2.54	487
2.07	6.6	1.68	533	5.62	8.7	5.27	258
2.60	7.5	2.1	482	8.42	11.5	8.07	223
5.26	9.0	4.25	286	11.63	12.1	10.9	174
7.04	9.2	5.69	218				
8.88	10.5	7.18	197				
10.02	11.0	8.1	183				
12.42	12.0	10.04	162				
18.43	13.0	14.55	121				

* G.-mols. solute per 100 g.-mols. solvent.

† G. solute per 100 g. solvent.

‡ Usual cryoscopic constant.

The graph for camphoroxime is again displaced a little to the right in the diagram.

Acetanilide and *o*-chlorobenzoic acid depress the m. p. of camphoroxime in the same manner, but the depressions are not proportional to the concentration; from being very high in dilute solutions, they become, rapidly, less and less. Up to a concentration of about $C = 0.5$, K has a value of at least 1000, but falls off to a value of about 170 in 10% solutions. For molecular weight determination in extremely dilute solutions, with, perhaps, only a very small quantity of substance available, camphoroxime, which has the further advantage of a comparatively low m. p., might be of distinct value in exceptional cases. This kind of behaviour is usually attributed, but without any satisfactory reason, to association of the solute molecules; we prefer to consider it merely an interesting and hitherto unexplained property of the substances concerned.

Finally we examined bornyl methylxanthate as a solvent for acetanilide and *o*-chlorobenzoic acid, to ascertain whether the properties of borneol itself would be exhibited in such a derivative, but we found that even in 7 and 10% solutions there was no appreciable depression of the m. p.