CCCI.—*Dibenzyl Ether as a Cryoscopic Solvent.*

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THE observation that dibenzyl ether may be induced to crystallise below 0°, in spite of a marked tendency to supercooling, afforded us the opportunity to add this substance to the list of available cryoscopic solvents. The pure substance melts at +3·60°. The following values of the cryoscopic constant K were found with various solutes : Phenetole 62·6, ethylene dibromide 61·8, dimethylaniline 62·8, naphthalene 63·6. From the mean of these values, *62·7*, the latent heat of fusion of dibenzyl ether is calculated to be 24·4 cals. per g.

A few cryoscopic observations were also made with benzoic and acetic acids and benzyl alcohol as solutes. A tendency for ethers to unite with hydroxylic substances to yield complexes of the type $R_2O \longrightarrow HOR'$ (Sidgwick, "The Electronic Theory of Valency,"

p. 137) should show itself by causing the apparent molecular weight of a substance R'OH to be less in solution in the ether R_2O than in a solvent chemically indifferent to it such as benzene, in which association of the hydroxylic substance is likely to be more pronounced. The only ether previously proposed as a cryoscopic solvent is diphenyl ether (Durand and Rougé, *Bull. Soc. chim.*, 1925, **37**, 697), but it is less suitable than dibenzyl ether for testing the point under discussion on account of the lower donating power which is to be expected in an oxygen atom attached directly to the benzene nucleus.

In Table I our values for the apparent molecular weights (M) of the hydroxylic substances examined in dibenzyl ether are compared with the values at corresponding concentrations and closely similar temperatures in benzene solution as recorded in the literature (Beckmann, *Z. physikal. Chem.*, 1888, **2**, 729; Auwers, *ibid.*, 1893, **12**, 689). The values for benzoic and acetic acids are definitely lower in dibenzyl ether than in benzene, but those for benzyl alcohol are not appreciably different in the two solvents. The ebullioscopic measurements of Beckmann (*ibid.*, 1890, **6**, 437) show a similar difference in the direction expected.

TABLE I.

Solute.	Solvent.	Concentration (%).	M.
Benzoic acid.	Benzene.	1·44—4·73	228—236
	Dibenzyl ether.	1·1 —5·3	147—177
Acetic acid.	Benzene.	1·19—4·47	115—122
	Dibenzyl ether.	1·6 —5·0	91·6—109
Benzyl alcohol.	Benzene.	1·57—5·12	116—165
	Dibenzyl ether.	2·0 —4·5	135—140

EXPERIMENTAL.

Preparation and Purification of Dibenzyl Ether.—The ether was conveniently prepared by boiling a mixture of benzyl alcohol (30 g.) and benzyl chloride (25 g.) with potassium hydroxide (25 g.) for 5 hours, and fractionating the product. Repeated distillation under diminished pressure did not eliminate the odour of benzaldehyde. It appears that the ether suffers a slight decomposition in distillation even at temperatures below 200°. After repeated fractional freezing, the substance had b. p. 184°/28 mm., 170°/16 mm., m. p. 3·60°, $d_4^{10\cdot5°}$ (vac.) 1·0504, $d_4^{20°}$ (vac.) 1·0428, and its faint odour was quite distinct from that of benzaldehyde. The liquid often remained for hours in the supercooled state without crystallising spontaneously. Crystallisation could always be induced, however, by vigorous stirring at a temperature below −15°.

Cryoscopic Measurements.—The observations were made with the

Beckmann apparatus, the usual precautions being adopted. Nucleation was always necessary in order to bring about crystallisation of the solvent without undue supercooling. The data obtained with standard substances are recorded in Table II, Δt being the observed depression of the freezing point of dibenzyl ether when w g. of solute were dissolved in 26·10 g. of solvent.

The values with benzil as solute are anomalous. These and the first value for naphthalene have been ignored in taking the mean value of K.

TABLE II.

Solute.	w.	Δt.	K.	Solute.	w.	Δt.	K.
Phenetole	0·5119	1·012°	63·0	Naphthalene	0·3645	0·745°	(68·2)
	0·7493	1·464	62·2		0·9946	1·907	64·1
Ethylene	0·5028	0·621	60·4		1·411	2·662	63·1
dibromide	1·065	1·391	63·9	Benzil	0·6610	0·887	(73·5)
	1·610	2·000	61·0		1·125	1·437	(70·1)
Dimethyl-	0·4153	0·832	63·4		1·646	2·005	(66·7)
aniline	0·8484	1·668	62·1				

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