XCVI.—*Cryoscopic Evidence of Compound Formation in Mixtures of Organic Liquids.*

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PREVIOUS work on binary mixtures of non-aqueous liquids has led to the view that in many cases, and especially when the mixture is formed with considerable rise in temperature, the constituents are to some extent associated together in a manner indistinguishable from chemical union (Madgin and Briscoe, *J. Soc. Chem. Ind.*, 1927, **46**, 107T; Madgin, Peel, and Briscoe, J., 1927, 2873). The present paper records attempts to test this view by cryoscopic methods.

Evidently, if freezing-point depressions were strictly proportional to the concentration of the solute, and constant, with a given solvent, for equimolecular proportions of different solutes, the depressions for mixed solutes having no effect on each other should follow the mixture law. If the solutes associate together, the depression for the mixed solutes should be less than that to be expected from the mixture law. This argument has been applied to show that compounds are formed (*a*) between quinoline and ethyl tartrate in ethylene dibromide as solvent (Patterson and Montgomerie, J., 1909, **95**, 1138), and (*b*) between ethyl acetate and acetic or trichloroacetic acid in benzene solution (Kendall and Booge, J., 1925, **127**, 1776).

There is, however, in all such evidence, an intrinsic weakness, explicitly admitted by Patterson and Montgomerie, arising from our ignorance of the mechanism of the depression of the freezing point, and from the fact that, in the concentration usually employed, the observed depressions often deviate considerably from those calculated according to the mixture law.

Cryoscopic determinations of the molecular weights of organic compounds in apparently inert solvents have often given values considerably greater than those corresponding with the accepted formulæ of the solutes; *e.g.*, in the cases of hydroxy-compounds and phenols in benzene and naphthalene (Auwers, *Z. physikal. Chem.*, 1894, **15**, 33; 1895, **18**, 595); alcohols, acids, and phenol in bromoform (Ampola and Manuelli, *Gazzetta*, 1895, **25**, ii, 91); alcohols and phenols in *p*-bromotoluene (Paterno, *ibid.*, 1896, **26**, ii, 1); acetic acid in benzene (Kendall and Booge, *loc. cit.*); alcohols, phenols, and acids in nitrobenzene (Bury, *J. Physical Chem.*, 1926, **30**, 694).

It has frequently been held that an abnormally small depression of the freezing point is evidence that the solute is associated (see *e.g.*, Turner and Pollard, J., 1914, **105**, 1751; Brown and Bury, *loc. cit.*), but such effects have also been attributed to the formation of solid solutions of the solvent and solute (Garelli, *Gazzetta*, 1894, **24**, ii, 229) or, more vaguely, to their mutual influence (Auwers, *Z. physikal. Chem.*, 1899, **30**, 300).

In general, the abnormalities in freezing-point depressions increase with the concentration of the solute (see, *e.g.*, Ampola and Manuelli, and Brown and Bury, *locc. cit.*), but Paternò (*Gazzetta*, 1896, **26**, ii, 363) has found that, with phenol as the solvent, several solutes give depressions that become less abnormal as the concentration increases. Ethyl alcohol as a solute has often been found to behave very abnormally; thus, the molecular weight for this alcohol in benzene (Auwers, *loc. cit.*) was seven times, and in bromoform (Ampola and Manuelli, *loc. cit.*) nine times that corresponding with the simple formula. We have confirmed the general trend of these results with ethyl alcohol in both benzene and nitrobenzene as solvents, as is shown by the following data :

Solvent.	Benzene.	Nitrobenzene.
Range of composition of solutions (weight of ethyl alcohol)	5·0—0·5%	4·6—0·2%
Range of variation of molecular weight ($C_2H_5{\cdot}OH = 46$)	130—62	108—55

Without entering into a discussion of these curious results, it is obvious that any attempt to obtain evidence of compound formation between solutes must be subject to grave uncertainty if based merely on calculation. We have sought, therefore, to apply the cryoscopic test for compound formation in such a manner that the result is obtained directly and without any calculation whatever. Whereas previous workers have proceeded by adding one solute to a solution of the other, we, in investigating each pair of liquids, have dissolved them separately in a given solvent to give solutions having the *same depression* of the freezing point : these solutions have then been mixed, and the depression has been determined for the mixed solutions.

The selection of liquid pairs for investigation was based upon the previous survey of the temperature change produced on mixing in equal volumes 628 pairs among 37 liquids (Madgin and Briscoe, *loc. cit.*). In an extended study of compound formation in pairs of organic liquids, Bramley (J., 1916, **109**, 10, 434, 469, 496) found that a marked rise of temperature accompanied the mixing of liquids in those cases where it was probable, on other grounds, that compounds were formed, and his results show that *o*-chlorophenol forms compounds of considerable stability with both pyridine and aniline. The pairs of liquids investigated therefore comprise these two pairs (for comparison), several other pairs which give a rise of temperature on mixing, though there is no other reason to suspect compound formation, and also a few pairs where the thermal effect of mixing is negative.

The experimental procedure calls for little description. Freezing points were determined in a standard Beckmann apparatus, with all usual precautions and with a thermometer divided to 0·01°. Solutions of the two solutes in a solvent were made of approximately the desired strength by using calculated quantities, and then adjusted by trial until both gave substantially the same depression of freezing point. As soon as these depressions had been finally determined, the solutions were transferred to stoppered flasks and, with the least possible delay, equal volumes were mixed and the freezing point of the mixture was determined.

Three solvents were used: benzene, nitrobenzene, and bromoform: the concentration of the solutions was of the order of 0·05 molar fraction of solute, and the data recorded are in every case the mean of at least three closely concordant observations. The results are in Table I, the columns of which show (I) the serial number of the experiment, (II) the constituents A and B of the mixture, (III) the solvent, (IV and V) the depressions for A and B separately, (VI) the depression for the mixed solutions of A and B, (VII) the alteration of freezing point produced by mixing, and (VIII) the temperature change produced on mixing equal volumes of the pure liquids A and B (Madgin and Briscoe, *loc. cit.*). The data in column (VII) are, in effect, a measure of the deviation from the simple mixture law and are accordingly marked + and —.

On examining the table it is at once evident that in many cases the depressions for mixtures, Δ_{A+B}, are markedly less than those, Δ_A and Δ_B, for the constituent solutions. This is so in experiments 1—8 inclusive, and 11, 12, 13, and 15. As this effect is identical with that produced by diminishing the concentration of either solute singly in its solution, it appears to prove quite definitely and irrespective of any calculation that in the mixed solutions the effective molecular concentration of the solutes has been diminished, and hence that association of the two solutes with each other has occurred. Association of either solute with the solvent or dissociation of complex molecules of either solute (both of which might occur, for on mixing the solutions the concentration of solution with respect to either solute is halved) would, in effect, increase the concentration of the solute, and would tend to produce a greater depression of the freezing point (see, *e.g.*, Jones and Chambers, *Amer. Chem. J.*, 1900, **23**, 89). Hence the data prove that compounds are formed in solution by *o*-chlorophenol with pyridine, aniline, or ether; by chloroform with ether or acetone; and by bromoform with acetone.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
			Δ_A.	Δ_B.	Δ_{A+B}.		
1	A. *o*-Chlorophenol	Y	1·985	2·005	1·590	−0·405	
2	B. Pyridine	X	2·018	2·027	1·791	−0·232	
3	A. *o*-Chlorophenol	Y	1·990	1·985	1·945	−0·042	+13·85°
4	B. Aniline	X	1·990	2·030	1·940	−0·07	
5	A. *o*-Chlorophenol	Y	2·070	2·070	1·950	−0·12	+21·5
6	B. Ether	X	2·045	2·040	1·915	−0·127	
7	A. Ether	X	2·040	2·030	2·000	−0·03	+14·2
8	B. Chloroform	Y	2·015	2·018	1·975	−0·042	
9	A. Chloroform	X	2·030	2·020	2·030	+0·005	+12·65
10	B. Acetone	X	2·040	2·018	2·030	+0·006	
11		Y	2·018	2·030	1·985	−0·039	
12	A. Acetone	X	2·020	2·030	2·005	−0·02	+ 8·3
13	B. Bromoform	Y	2·020	2·030	2·015	−0·01	
14	A. Acetone	X	2·020	2·025	2·020	−0·0025	− 9·75
15	B. Carbon disulphide	Y	2·020	2·025	1·990	−0·033	
16	A. Carbon disulphide	X	2·025	2·025	2·030	+0·005	− 8·5
17	B. Aniline	Y	2·010	2·015	2·015	+0·003	
18	A. Chloroform	X	2·000	2·005	2·000	−0·0025	− 4·4
19	B. Carbon disulphide	Y	1·755	1·750	1·740	−0·013	
20	A. Chloroform	X	2·000	2·025	2·020	+0·008	− 1·0
21	B. Aniline	Y	2·018	2·025	2·020	−0·002	
22	A. Ether	X	2·020	2·025	2·025	+0·002	+ 3·1
23	B. Aniline	Y	1·980	1·990	1·990	+0·005	
24	A. Ethyl acetate B. Methyl acetate	X	2·015	2·025	2·020	0	− 0·05
25	A. Ethyl acetate B. Ether	X	2·015	2·010	2·010	−0·002	− 1·2
26	A. Methyl acetate B. Ether	X	2·025	2·010	2·020	+0·002	− 2·3
27	A. Methyl acetate B. Aniline	X	2·025	2·025	2·025	0	+ 3·15
28		X	1·990	2·005	2·230	+0·233	+ 3·95
29	A. Ethyl alcohol	X	2·018	2·020	2·268	+0·25	
30	B. Chloroform	Y	1·918	1·930	2·045	+0·121	
31		Z	1·960	1·970	2·100	+0·135	

Solvents. X = Benzene. Y = Nitrobenzene. Z = Bromoform.

If confirmation of this view were needed it is to be found in Bramley's evidence (*loc. cit.*) that *o*-chlorophenol forms definite compounds with pyridine and aniline : evidently these compounds persist to some extent in solution. Recently, also, a study of the turbulent streaming of liquids has afforded evidence that acetone–chloroform mixtures contain a compound (Kremann, Springer, and Roth, *Z. physikal. Chem.*, 1927, **130**, 415).

It is noticeable that in Expt. 2 Δ_{A+B} differs less from Δ_A or Δ_B than in Expt. 1. Thus, apparently, nitrobenzene as solvent is less effective than benzene in causing dissociation of the *o*-chlorophenol–pyridine compound. Other examples of such differences in the effect of different solvents are to be found, notably in Expts. 9, 10, and 11 for chloroform–acetone, and in Expts. 14 and 15 for acetone–carbon disulphide. With regard to the latter pair, indeed, it appears that the compound which evidently exists in nitrobenzene solution is practically completely dissociated in benzene solution. There are also cases, *e.g.*, Expts. 3 and 4, where apparently nitrobenzene is the solvent which is more effective in causing dissociation.

Expts. 28—31 inclusive are remarkable in that the depression for the mixture is greater than that for the constituents, but this curious effect may readily be explained by reference to the behaviour of ethyl alcohol referred to above. It appears probable that the effect of dissociation of complex alcohol molecules outweighs any effect due to compound formation between alcohol and chloroform. Expt. 15 may show that compound formation can occur in certain solvents between solutes whose admixture in the pure state is attended by a substantial fall in temperature, but, evidently, no generalisation can safely be based on a single instance of this kind.

The essential point which emerges clearly from the experiments here reported is that in the liquid pairs involved in Expts. 1—13 inclusive, admixture of the pure liquids is attended by a considerable rise of temperature. Thus our earlier view, that in general such a rise of temperature is evidence of compound formation, is confirmed.

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