CCCLXXXIV.—*The Temperature Effects of Mixing Non-aqueous Liquids.*

By WALTER MATTHEW MADGIN, JOHN BUTTERY PEEL, and HENRY VINCENT AIRD BRISCOE.

A GENERAL survey of the temperature changes occurring on mixing 628 pairs chosen from 37 non-aqueous liquids has shown that these changes are frequently of considerable magnitude (Madgin and Briscoe, *J. Soc. Chem. Ind.*, 1927, **46**, 107T). The present paper describes the further investigation of these changes in selected cases, undertaken in the expectation that some light might thereby be thrown upon the nature of liquids and liquid mixtures.

Relationship of Thermal Changes to the Polarity of the Constituent Liquids.—It has frequently been assumed (*e.g.*, Hildebrand, "Solubility," p. 85) that solubility is largely influenced by the relative polarity of the molecules concerned. The idea seems to be that a liquid composed of strongly polar molecules may easily dissolve another very polar liquid, but that the strong attraction between such polar molecules may hinder the interposition of non-polar molecules, and thus may even cause immiscibility with a non-polar liquid.

Detailed examination of the cases included in our original survey leads to the conclusion that there are many groups of liquids for which the relative values of the thermal effect of mixing differ widely from those to be expected from considerations of relative polarity. For example, hexane, benzene, and toluene are all very slightly polar by ordinary standards, and their polarities, as measured by the dielectric constant (*D.C.* = 1·85, 2·27, 2·34, respectively), increase slightly in the order named. In most cases the thermal effect of hexane with other liquids is more negative than that of benzene, which is again more negative than that of toluene. This is illustrated by the fact (Madgin and Briscoe, *loc. cit.*) that the number of positive heats of mixing given by hexane, benzene, and toluene, respectively, with the same set of other liquids is 0, 7, and 12. But in the case of the alcohols and carbon disulphide, benzene gives a greater decrease of temperature than either hexane or toluene; with alcohols, except methyl alcohol, toluene gives a greater negative effect than hexane; with methyl alcohol and carbon disulphide, hexane gives the greatest negative effect. These effects are not then in accordance with the order of dielectric constant.

Again, ethyl iodide generally gives a greater negative effect than ethyl bromide, which accords with the greater polarity of the former corresponding with the *D.C.* values : 9·4, 7·4; but exceptions to this order occur in the heat effects with certain alcohols and carbon disulphide. Comparing the results of mixing ethylene dibromide, ethylene dichloride, chloroform, and bromoform with other liquids, it is noticeable that the chloro-compound generally gives the more positive heat of mixing, but exceptions occur in admixtures with ethyl and methyl iodides, with tetrachloroethane, and with aniline and carbon disulphide.

The doubt whether polarity can be assigned as a major cause of the temperature effects is intensified when we consider the cases in Table I and also that of water and ethyl alcohol (both having a high *D.C.* and giving a rise of temperature on mixing), for it is apparent that either positive or negative heats of mixing may occur (*a*) with two liquids of small and similar *D.C.*, (*b*) with two liquids having respectively large and small *D.C.*'s, and (*c*) with two liquids both having large *D.C.*'s. Hence there seems to be no simple relationship between the heat of mixing and the polarity of the constituent molecules.

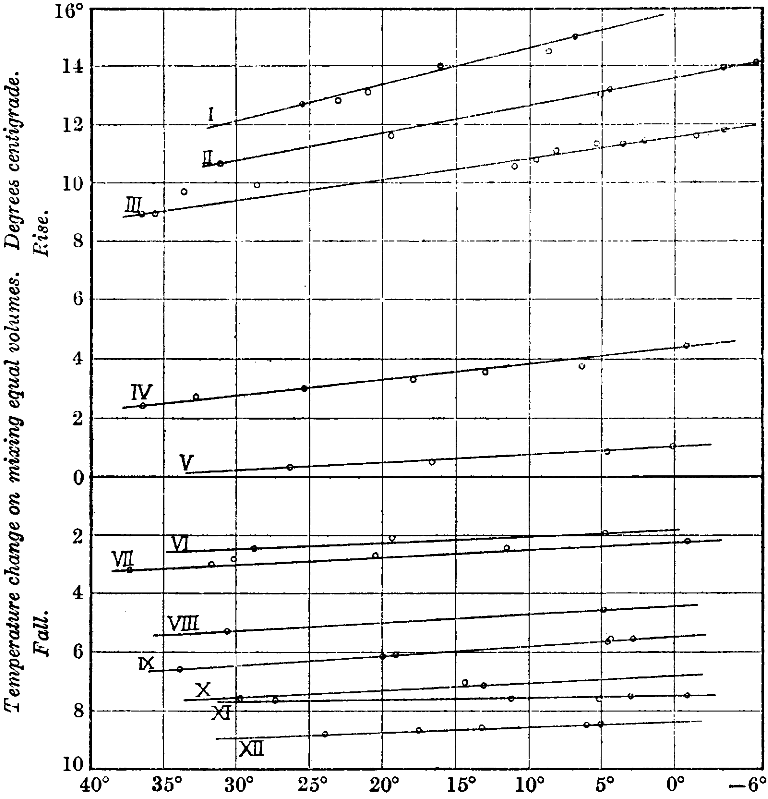
TABLE I.

	Dielectric constant.	Temperature change on mixing equal volumes.
Methyl acetate	7·1	− 5·1°
Ethyl iodide	7·4	
Ether	4·3	+ 14·2
Chloroform	5·1	
Acetone	21	+ 12·65
Chloroform	5·1	
Acetone	21	− 9·75
Carbon disulphide	2·6	
Acetone	21	− 6·95
Ethyl alcohol	25	

Effect of Variations of Initial Temperature on the Temperature Change on Mixing.—The literature contains very few references to investigations on the manner in which the temperature change on mixing varies with the initial temperature of the liquids mixed. Three isolated cases, two including water as one liquid, were investigated by Bussy and Buignet (*Ann. Chim. Phys.*, 1865, **4**, 5), and five cases, of which three included aniline as one liquid, have been investigated by Kremann and others (Kremann, *Monatsh.*, 1906, **27**, 91; Kremann and Pilch, *ibid.*, 1910, **31**, 203; Kremann, Meingast, and Guge, *ibid.*, 1914, **35**, 1235).

Therefore, as our general survey provided the necessary material for selection, it seemed well worth while to examine more widely the general trend of the thermal change with temperature for a series of mixtures ranging from those with large positive to those with large negative temperature changes on mixing. For this purpose, the apparatus used was a silvered Dewar tube (1″ diam. × 7″ deep nternally) with narrow observation windows of the full height on opposite sides, provided near the mouth with three internal projections, on which rested the flange of a test-tube of such length that its thinly-blown closed end was about $\frac{1}{2}''$ from the bottom of the

FIG. 1.



Pairs of liquids.

I o-*Chlorophenol* : *aniline*. II *Chloroform* : *ether*. III *Chloroform* : *acetone*. IV *Chloroform* : *toluene*. V *Ether* : *toluene*. VI *Acetone* : *ether*. VII *Chloroform* : *hexane*. VIII *Ethyl alcohol* : *methyl acetate*. IX *Acetone* : *hexane*. X *Carbon disulphide* : *aniline*. XI *Carbon disulphide* : *ethyl oxalate*. XII *Carbon disulphide* : *acetone*.

Dewar tube. One liquid (10 c.c.) was placed in the Dewar tube, the other (10 c.c.) was within the test-tube : both were previously brought approximately to the desired temperature. In the test-tube were also a thermometer (— 20° to + 50° by 0·1°) and a pointed glass rod; when the tubes and liquids had attained the same constant temperature, the end of the test-tube was pierced by the glass rod, the liquids were well mixed, and the temperature change was noted. To facilitate mixing, the denser of the two liquids was always put inside the test-tube. Twelve pairs of liquids were thus examined over a range of temperature; in most cases 6—8 observations were made, in some as many as 12. The whole of the observations are plotted in Fig. 1, and Table II gives for each pair of liquids (1) the temperature change from an initial temperature of 5°, (2) that from an initial temperature of 30°, and (3) the difference due to this change of 25° in the initial temperature.

TABLE II.

Pair of liquids.	1.	2.	3.	Pair of liquids.	1.	2.	3.
I	15·2	12·1	3·1	VII	−2·35	−3·0	0·65
II	13·1	10·8	2·3	VIII	−4·6	−5·3	0·7
III	11·15	9·4	1·75	IX	−5·65	−6·5	0·85
IV	4·1	2·8	1·3	X	−6·9	−7·6	0·7
V	0·9	0·2	0·7	XI	−7·6	−7·7	0·1
VI	−1·9	−2·4	0·5	XII	−8·5	−8·9	0·4

Inspection of the table shows at once that, whether the temperature change is positive or negative, its variation with initial temperature is always in the same direction; the temperature change is more positive (or less negative) the lower the initial temperature. On the other hand, the *magnitude* of the variation in temperature change obviously varies considerably throughout the series of mixtures, being generally greater the more positive (or less negative) the temperature change for a given initial temperature.

These observations receive a simple interpretation if, supposing each of the two liquids A and B to contain complex (A_x and B_y) and simple molecules, we assume that the latter, on admixture, may associate to form compound molecules, according to the scheme

$$\left.\begin{array}{l} A_x \rightleftharpoons xA \\ B_y \rightleftharpoons yB \end{array}\right\} \rightleftharpoons zA_nB_m$$

and that the dissociations to the simple molecules are endothermic. The data here recorded are consistent with the view that alteration of the initial temperature changes the thermal effect in the A_nB_m equilibrium more than that in the A_x and B_y equilibria. This may occur through a change in the heat of reaction or through a shift of equilibrium, or for both of these reasons.

On entirely different grounds, Bramley (J., 1916, **109**, 43) reached a similar conclusion, which, therefore, whilst clearly needing further investigation, has a certain measure of probability.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research enabling the participation in

this work of one of us (J. B. P.), who has made a large number of the determinations of temperature change on which the present paper is based.

ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE.

[*Received, April* 30*th,* 1927.]