CXXVIII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XV. Mixed Solvents.*

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THE variation of the rotation of an active substance under the simultaneous action of two indifferent solvents has already been the subject of several investigations by Oudemans (*Annalen*, 1873, 166, 71; 1876, 182, 47), Hesse (*Annalen*, 1875, 176, 219), and Rimbach (*Zeitsch. physikal. Chem.*, 1892, 9, 698). The results of these researches are summarised in Landolt's "*Das optische Drehungs-*

vermögen," 2^{te} Auflage, p. 211; therefore we need only say here, regarding the experiments of Oudemans and Hesse, that cases were observed in which certain alkaloids showed a higher rotation in a mixture of two solvents at a given concentration than in either solvent separately, a phenomenon which seems to deserve some further investigation.

Rimbach's accurate and very complete research dealt with the rotation of camphor in benzene, in ethyl acetate, and in mixtures of these solvents; of turpentine in acetic acid and alcohol, and of dextrose in aqueous solutions of magnesium chloride and in aqueous solutions of calcium chloride. For camphor in ethyl acetate and benzene, and for turpentine in alcohol and acetic acid, he shows that the rotation of the active substance in the mixed solvent may be calculated approximately by a simple mixture-formula :

$$[\alpha] = [\alpha]_1 P_1 + [\alpha]_2 P_2,$$

where P_1 and P_2 are the quantities of the components contained in unit weight of the mixed solvent, $[\alpha]$ is the specific rotation of the mixture, $[\alpha]_1$ and $[\alpha]_2$ the specific rotations of the active substances in the respective solvents separately. There was, however, a slight but distinct difference in each case, which could not be accounted for by making allowance, in calculating the specific rotation of the solution, for the slight change of density on mixing. Rimbach found, further, that magnesium chloride exerted, practically speaking, no effect on the rotation of dextrose, whereas calcium chloride had a very powerful influence.

In undertaking some further work on this subject, we were actuated by the desire to throw some light on the cause of rotation-change due to solution in a single solvent, especially perhaps in regard to the possibility of the occurrence of chemical combination between solute and solvent, and we also thought that, in at least two respects, an improvement could be effected on Rimbach's choice of material. It is clearly desirable that the solvents used should have effects on the rotation of the active substance as divergent as possible, and also that the densities of the solvents should lie considerably apart; in short, that all differences should be emphasised to the maximum extent. From Rimbach's data, a $c=20$ solution of camphor in benzene has $[\alpha]_D^{20} + 43.3^\circ$, whilst at the same concentration it has in ethyl acetate $[\alpha]_D^{20} + 51.9^\circ$. There is thus only a difference of 8.6° in the rotations, whilst the maximum difference which it is possible to consider is one of less than 12° ; also, the specific gravities of the solvents lie very close together. For turpentine in acetic acid and in alcohol there is only a difference of less than 2° in rotation, but a somewhat greater difference than in the former case, in regard to the density of the solvents.

We chose as active substance ethyl tartrate, and as solvents, nitrobenzene and ethylene bromide. In nitrobenzene at infinite dilution ethyl tartrate has $[\alpha]_D^{20} + 41^\circ$ (Trans., 1908, 93, 1837), and in ethylene bromide, $[\alpha]_D^{20} - 19^\circ$, so that the effect of these two solvents is very different indeed. We were then enabled to work with fairly concentrated solutions (about $c=24$), which, of course, renders the rotation data the more accurate. At $c=23.938$ in nitrobenzene, ethyl tartrate has $[\alpha]_D^{20} + 25.9^\circ$, and at $c=23.832$ in ethylene bromide, $[\alpha]_D^{20} - 10.72^\circ$, a difference of 36.62° , or about four times as great as in Rimbach's experiments. The density also of ethylene bromide ($d_4^{20} = 2.18141$) is nearly twice as great as that of nitrobenzene ($d_4^{20} = 1.20346$), so that solutions of equal concentration (c) are very different in weight.

It is somewhat easier, experimentally, to make up solutions with a mixed solvent to a certain definite concentration (c =grams per 100 c.c.) than to a definite percentage composition (p =grams per 100 grams solution), so in our first series of experiments we used always the same quantity (10 c.c.) of ethyl tartrate in 50 c.c. of solution, varying the relative proportions of nitrobenzene and ethylene bromide.

In preparing all the solutions care was taken to mix the liquids thoroughly before making up to the mark, to ensure that any change of volume due to mixing should be practically complete before the final adjustment was made. The concentrations quoted, however, do not depend on the graduation of the flask, but are calculated from the weight of the solution and its density. The results of our first series of experiments are given in table I.

TABLE I.

Ethyl Tartrate in Nitrobenzene, in Ethylene Bromide, and in Mixtures of these Solvents.

(Ethyl tartrate, α_D^{20} (100 mm.) + 9.372° , $d_4^{20} = 1.20539$; nitrobenzene, $d_4^{20} = 1.20346$; ethylene bromide, $d_4^{20} = 2.18141$.)

Number of solution.	Composition of solvent.		<i>c</i> .	<i>p</i> .	<i>d</i> ₄ ²⁰ .	α_D^{20} (200 mm.).	$[\alpha]_D^{20}$.
	Grams of nitrobenzene in 100 grams of mixed solvent.						
1	100.000	23.938	19.925	1.20144	+12.40°	+25.9°	
2	61.915	23.88	17.105	1.39611	7.62	15.95	
3	35.627	23.83	15.022	1.58642	3.34	7.01	
4	35.034	23.75	14.928	1.59099	3.225	6.80	
5	15.547	23.84	13.391	1.78028	-0.81	-1.70	
6	0.000	23.832	12.061	1.97599	-5.11	-10.72	

When from the two extreme values the rotations are calculated for the intermediate solutions on the assumption that the effect of the nitrobenzene or of the ethylene bromide should be proportional to its volume in the mixed solvent, the following data are obtained.

TABLE II.

Number of solution.	Composition of solvent. Parts by volume of nitrobenzene per 100 parts by volume of mixed solvent.	$[\alpha]_D^{20^\circ}$.			Expansion per 100 c.c. c.c.
		Observed.	Calculated.	Δ .	
1	100.00	+25.9°	—	—	0.200
2	74.65	15.95	16.61°	-0.66°	0.438
3	49.98	7.01	7.58	-0.57	0.572
4	49.42	6.80	7.38	-0.58	0.564
5	25.01	-1.70	-1.56	-0.14	0.588
6	0.00	-10.72	—	—	0.570

The agreement between the calculated and observed values is thus fair, but differences, which cannot be neglected, certainly occur—differences of just the same order of magnitude as those observed by Rimbach. The calculated is always higher than the actual value, and in the first three cases certainly, but probably in all, the difference is much above the experimental error. That the experimental error is not great may be judged by comparison of the data for solutions 3 and 4, which were made up purposely of an almost identical concentration. It will be seen that the differences between the calculated and observed values in these two cases are, as they should be, practically identical.

As in the case of the differences observed by Rimbach, these deviations from the calculated values cannot be explained by the slight density change on mixing. In the first place this change is in the wrong direction. The observed rotation is less than the calculated value, and to bring about this result, the density of the mixed liquid would require to be greater than that calculated from the separate values; the actual behaviour is just the opposite of this. Secondly, the change in density, even if it were in the proper sense, would require to be ten times greater than it is to annul numerically the departure of the rotation from the calculated value.

This departure from the calculated rotation values may perhaps be accounted for as follows. Each pair of the three liquids used mix with expansion. For ethyl tartrate in nitrobenzene, and ethyl tartrate in ethylene bromide, this can be shown by means of the data already given, whilst for mixtures of ethylene bromide and nitrobenzene we obtained the following numbers:

Composition of mixture in grams.		d_4^{20} (experimental).	d_4^{20} (calculated).	Expansion per 100 c.c. c.c.
Nitrobenzene.	Ethylene bromide.			
23.9307	28.7086	1.58799	1.5929	0.312
31.5120	19.3252	1.44710	1.4505	0.228

The calculated density is in both cases greater than that found. In the last column is shown the expansion on mixture of such quantities, taken in the proportions quoted, as, separately, occupy 100 c.c.

Now it has been shown by one of us that, at least for ethyl tartrate in a variety of solvents, there appears to be a relationship between the volumes of the dissolved ester and its rotation in a given solvent. Roughly speaking, it is to be expected that if ethyl tartrate be dissolved separately in two liquids, the rotation will be greater in the solution having the smaller volume. For instance, as is shown in table II, the expansion (0.2 c.c.) on mixing 19.86 c.c. of ethyl tartrate with 79.94 c.c. of nitrobenzene is only about one-third of the expansion (0.57 c.c.) which occurs on mixing 19.77 c.c. of ethyl tartrate with 79.66 c.c. of ethylene bromide. In harmony with this, the rotation in the nitrobenzene solution is much higher than in the ethylene bromide solution.* Now since the expansion is greater for the three component than for the two component mixtures (see the last column of table II), the internal forces in the former may be less than a simple mixture law would lead us to expect, for which reason the rotation has a lower than the calculated value.

As an alternative explanation it might be supposed that the ethylene bromide has a slightly superior "attraction" for the ethyl tartrate, so that its influence preponderates in the mixture. By "attraction" we mean that property of a liquid, or a property similar to that in consequence of which it is capable of holding another substance in solution, a mutual affinity which it does not seem necessary to regard as identical with chemical combination. This attraction would presumably be composed of two factors, one due to the solvent and one to the solute, and a relative measurement of it is probably obtained by distributing a given solute between two immiscible solvents.

The idea that the influence of a solvent on the rotation of an active compound may be a measure of this affinity is of interest, but only very little experimental work exists by which it can be tested. Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 586) has examined the distribution of ethyl tartrate between ethylene bromide and water

* It is true, however, that this assumption of a relationship between volume and rotation in the above instances is very distinctly open to criticism, the chief reason being that, since ethyl tartrate and nitrobenzene mix with expansion, the specific rotation of the solution ought to be less than that of the homogeneous ester instead of being, as is actually the case, much greater.

and finds it to be, in dilute solution, about 1:6. The attraction of water for ethyl tartrate is thus much greater than that of ethylene bromide, and the rotation in the former is, of course, much greater than in the latter solvent. Winther's experiments also show that the attraction of formamide for ethyl tartrate is very much greater than that of ethylene bromide—but this case seems to be peculiar—whilst the distribution ratio of ethyl tartrate in benzene:water is about 1:5, which is again in qualitative agreement with the rotation data. From these facts, however, it would hardly seem probable that ethylene bromide should have a stronger attraction for ethyl tartrate than has nitrobenzene, but the matter is worth some further investigation.

It appears then from our experiments that if two solutions of ethyl tartrate of equal volume-concentration (c),* one in nitrobenzene and one in ethylene bromide, be filled respectively into two tubes of equal length (l), the rotation, taken through these two tubes placed one behind the other, will be almost the same as the rotation observed in a tube of length $2l$, after mixing the two solutions.

As already mentioned, the two solvents we used were very different in density, and therefore in discussing the rotations of solutions in nitrobenzene and ethylene bromide it may make a great deal of difference whether comparison be instituted between solutions of equal percentage composition or of equal volume-concentration. We thought therefore that it would be of interest also to carry out a series of experiments in which the percentage composition of the solution, with reference to ethyl tartrate, was kept constant and the proportion of the two solvents varied. Our results are shown in table III. Solutions Nos. 7, 8, and 9 were made up specially for this purpose solution No. 1 is the same as appears in tables I and II.

TABLE III.

Number of solution.	Proportion of nitrobenzene in solvent.		p .	c .	d_4^{20} .	$\alpha_D^{20} (l=2)$.	$[\alpha]_D^{20}$.
	Weight.	Volume.					
1....	100.00	100.00	19.925	23.938	1.20144	+12.4°	+25.90°
7....	49.95	63.17	19.922	29.08	1.45966	6.69	11.50
8....	33.35	47.55	19.926	31.34	1.57267	3.8	6.06
9....	0.00	0.00	19.942	37.19	1.86496	-5.77	-7.56

TABLE IV.

Number of solution.	$[\alpha]_D^{20}$.						
	Observed.	Calculated. I.	Δ .	Calculated. II.	Δ .	Calculated. III.	Δ .
1...	+25.90°	—	—	—	—	—	—
7...	11.50	+9.1°	+2.40°	+12.3°	-0.8°	+11.36°	+0.14°
8...	6.06	3.6	+2.46	6.47	-0.4	5.97	+0.09
9...	-7.56	—	—	—	—	—	—

* Solutions presumably of equal osmotic pressure.

In table IV are shown the observed rotations along with values calculated on different assumptions. The first assumption one would naturally make is that the rotation should vary directly with the weight proportion of the constituents of the mixed solvent. This is the same thing as supposing solution No. 7, for instance, to be split up into two solutions, one of 9.951 grams of ethyl tartrate in 40 grams of nitrobenzene, and the other of 9.971 grams of ethyl tartrate in 40.078 grams of ethylene bromide. These two solutions are of the same percentage composition as the original solution, but whilst the volume of the former would be 41.58 c.c., that of the latter would only be 26.84. These two solutions may be supposed to be placed in a tube of 1 sq. cm. cross section and divided by a partition into two compartments just long enough to contain the two solutions, and it can easily be calculated from the data for solutions Nos. 1 and 9 that the superimposed observed rotations in the divided tube would amount to $+18.04^\circ$, whence taking into account the density of solution No. 7, the theoretical rotation for the mixed solution, if no change occurred on mixing, would be $+9.1^\circ$.

It is clear, however, from our data that if the partition in the tube were removed and the solutions allowed to mix, the observed rotation would alter from $+18.04^\circ$ to $+22.88^\circ$, an increase of about 27 per cent. of the original value.

This is a result we had not foreseen, but it is probably to be explained as follows, and this constitutes our second method of calculation in table IV. The osmotic pressure of the two solutions just discussed would, of course, have very different values, and if we imagine the partition in the tube to be a semipermeable membrane, allowing ethyl tartrate to pass freely, but confining the solvents to their respective divisions of the tube, then the active ester would diffuse out of the ethylene bromide into the nitrobenzene until the concentrations in the two solvents were equalised.* At the same time the volume of the nitrobenzene solution would increase, whilst that of the ethylene bromide diminished, to allow for which we may suppose the partition to change its position in the tube. Neglecting small volume changes due to the fact that the volume of the mixtures is not strictly additive, the tube will now contain 43.88 c.c. of a $p=24.29$ ($c=29.23$) solution of ethyl tartrate in nitrobenzene, and 24.26 c.c. of a $p=15.04$ ($c=29.23$)† solution of ethyl tartrate in

* This ignores the possibility of a different degree of association of the ethyl tartrate in the two solvents. The degree of association is in fact, however, much the same in both.

† These concentrations are greater than that of the original solution (No. 7), because the sum of the separate volumes (68.14 c.c.) is less than that of the mixed solution (68.51 c.c.).

ethylene bromide. The observed rotation of the former, from data given by one of us (*Trans.*, 1908, **98**, 1856), would be $+31.28^\circ$, and of the latter, from data by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 578) and some of our own observations, it would be -6.84° , the sum being therefore $+24.44^\circ$ instead of the 22.88° actually determined. The specific rotation calculated in this manner would thus have the value $+12.3^\circ$, which is in excess of the observed value, $+11.5^\circ$, by a quantity of the same order as the differences in table II.

The series of observations for constant concentration and the series for constant percentage composition are thus brought into harmony, and it seems fairly clear that the influence of either of these two solvents on the rotation of ethyl tartrate may be taken as almost directly proportional to its volume, but not to its weight.

We noticed, however, by chance, that the rotation values for this series can be calculated very closely when the specific rotation of a mixture is assumed to be proportional to the mean of the percentage composition of the solvent by weight and by volume. Thus, for solution No. 7 in table III, the rotation is proportional to 56.56, the mean of 49.95 and 63.17. This gives the value 11.36° instead of the experimental 11.5° , the difference being thus very slight, whilst the agreement is even better for solution No. 8. The specific rotation, $[\alpha]$, of the mixed solution is thus given by the expression :

$$[\alpha] = \frac{1}{2} \left\{ [\alpha]_1 \frac{w_1}{w_1 + w_2} + [\alpha]_2 \frac{w_2}{w_1 + w_2} + [\alpha]_1 \frac{\frac{w_1}{d_1}}{\frac{w_1}{d_1} + \frac{w_2}{d_2}} + [\alpha]_2 \frac{\frac{w_2}{d_2}}{\frac{w_1}{d_1} + \frac{w_2}{d_2}} \right\},$$

where $[\alpha]_1$ and $[\alpha]_2$ are the specific rotations of solutions of a given percentage composition in the two solvents, w_1 and w_2 the percentage weight of each solvent in the mixed solvent, d_1 and d_2 the densities of the solvents. The numbers in the seventh column of table IV were calculated in this way, but the physical meaning of this method of calculation is not quite clear.

It seemed also worth while to determine whether the calculated value for rotation agrees more closely with that found experimentally,

TABLE V.

Number of solution.	<i>p.</i>	Composition of 100 grams of solution in gram-mols.			Composition of solvent. Percentage number of molecules of nitrobenzene.	$[\alpha]_D^{20^\circ}$.		
		Ethyl tartrate.	Nitro-benzene.	Ethylene bromide.		Obs.	Calc.	Δ .
<i>V</i>	21.1	0.0729	0.5371	0.0000	100.00	+25.6°	—	—
3.....	15.02	0.0729	0.2461	0.2910	45.82	7.01	6.2°	+0.81°
<i>W</i> ...	12.95	0.0729	0.0000	0.5371	0.00	-10.3	—	—

when the influence of a solvent is regarded as proportional to the number of its molecules present in the solution. This method has recently been warmly advocated by Armstrong. Table V shows the kind of agreement that is obtained.

The rotation of solution *V* is derived from experiments by Patterson (Trans., 1908, **93**, 1856), and that of solution *W* from data recorded by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 578). It will be observed that the calculated value is in this case less than that observed. The deviation is thus in the opposite sense from, and is also somewhat greater than, that found in table II, where the composition of the solvent is taken by volume.

Heat of Mixture of Various Liquids.

It seems strange that the heat and volume changes accompanying the mixture of indifferent liquids should have attracted comparatively little attention. Work has been done on the subject by Bussy and Buignet (*Ann. Chim. Phys.*, 1865, (iv), **4**, 5), by Dupré (*Proc. Roy. Soc.*, 1872, **20**, 336), by Guthrie (*Phil. Mag.*, 1884, (v), **18**, 495), by Clarke (*Physikal. Zeitsch.*, 1905, **6**, 154), and particularly by Timoféeff, whose paper, however, is only accessible to us in abstract (*Chem. Zentr.*, 1905, ii, 429; Abstr., 1905, **86**, ii, 678). Since no generalisation has been arrived at which we could consider with reference to rotation in solution, we measured some temperature changes which occur on mixing ethyl tartrate and a number of the solvents that have been used at various times in this investigation. Ethyl tartrate (10 c.c.), contained in a test-tube provided with a stirrer, was placed in a thermostat at or near 20°. An equal quantity of solvent was placed in another test-tube in the same thermostat. The liquids,

TABLE VI.

Volume Change and Temperature Change Attending Mixture of Certain Liquids.

Mixture of	Δt .*	Δv * in c.c.	Volume of first liquid in c.c.	Volume of second liquid in c.c.	<i>p</i> .
Ethyl tartrate : water	+0.5°	-2.03	54.47	45.53	50.225†
„ „ : ethylene bromide	-2.75	+0.57	19.88	80.12	12.061
„ „ : nitrobenzene.....	-1.2	+0.20	19.9	80.10	19.925
„ „ : methyl alcohol....	+0.05	-1.52	39.63	60.37	50.00 ‡
„ „ : benzaldehyde ...	+0.35	-0.24	32.41	67.59	35.5
„ „ : quinoline	+9.5	-0.70	19.75	80.25	21.34
Ethylene bromide : quinoline ...	-0.5	+0.03	34.46	65.54	51.19
„ „ : nitrobenzene.	-2.2	+0.32	39.82	60.18	54.54

* It is particularly to be observed that whereas the temperature changes are for equal volumes of the liquids, the volume changes are those which result on mixture of the quantities quoted in columns 4 and 5 of the table.

† Trans., 1904, **85**, 1154. ‡ Trans., 1901, **79**, 201. || Trans., 1909, **95**, 325.

when they had attained to the same temperature, were mixed, and the change of temperature noted. The results, which of course do not indicate the quantity of heat evolved, are given in table VI, a rise being denoted by the + sign and a fall by the - sign. In the table are also given some data for the volume changes on mixing these different liquids.

Thus, 54.47 c.c. of ethyl tartrate and 45.53 c.c. of water give 97.97 c.c. of the mixture. The resulting contraction of 2.03 c.c. is entered in column 3, and the percentage composition of the solution, in terms of the first of the two liquids under consideration, is shown in the last column.

Although Bussy and Buignet, and also Timoféeff, have noticed in certain instances a different behaviour,* the volume and temperature changes recorded above are entirely in (qualitative) harmony, and the same was found by Guthrie and by Clarke for the mixtures which they examined. In each case a rise of temperature is accompanied by contraction, and a fall of temperature by expansion.

The temperature or volume changes are, however, not apparently connected with rotation in solution. Thus, water and nitrobenzene both cause a considerable rise in the rotation of ethyl tartrate, but they produce opposite temperature effects, and, on the other hand, whilst nitrobenzene causes a great increase of rotation and ethylene bromide a great depression, the temperature change is, in both cases, in the same sense. Further, whilst benzaldehyde and quinoline at about $p=50$ produce, in ethyl tartrate, nearly the same specific rotation, the temperature effects differ greatly.

Very various opinions seem to be held as to the reason for temperature and volume changes on mixture of such liquids. The phenomenon is probably complex; true solution, whatever that may turn out to be, has perhaps always one definite effect, or it may have none, as some appear to hold, and association, dissociation, chemical combination may produce other effects, superposition of which makes investigation of the question difficult. But since one of the most important accompaniments of a spontaneous chemical combination is development of heat, it seems justifiable, where a heat development seems exceptionally great, to adopt, as a preliminary working hypothesis, the idea of combination.

Of the substances in the above table, that which mixes with ethyl tartrate with the greatest elevation of temperature is quinoline, and quinoline had already attracted our attention as a solvent for ethyl

* The behaviour of twenty-four pairs of liquids is shown in a table on p. 257 of Sydney Young's *Stoichiometry*. In six cases, the heat and volume changes are not in harmony.

tartrate, it having shown itself to be peculiar in regard to its influence on the rotation of the ester (Trans., 1909, 95, 323), and this might possibly be due to combination of solvent with solute.

Cryoscopic Experiments with Two Solutes Present Together.

Thinking that cryoscopic molecular-weight determinations might be of interest in this connexion, we carried out the following experiments. Nitrobenzene in regard to its influence on the rotation of ethyl tartrate may be said to be normal,* whence we should be inclined to postulate the absence of chemical combination between the two substances, more especially since the heat of mixture is negative. The same remarks apply to a solution of ethyl tartrate in ethylene bromide. We therefore determined, firstly, the depression of the freezing point of ethylene bromide produced by addition of ethyl tartrate; secondly, the depression of the freezing point of ethylene bromide produced by addition of nitrobenzene, and, thirdly, the depression due to an equimolecular mixture of ethyl tartrate and nitrobenzene. If in the last case no combination occurs between the two solutes, the depression of freezing point might be expected to be practically the sum of the separate depressions. The results were as follows:

TABLE VII.

Ethyl Tartrate (M.W. = 206) in Ethylene Bromide (K=118).

Weight of solute.	Weight of solvent.	Grams solute per 100 grams solvent.	Centigram-molecules solute per 100 grams solvent.	Δ .	M.W.
0.3603	45.55	0.791	0.38	0.41°	228
0.6392	45.55	1.4033	0.68	0.69	240
1.2059	41.127	2.932	1.42	1.323	261
2.4018	41.127	5.839	2.83	2.252	306
3.8518	41.127	9.365	4.55	3.125	354

Nitrobenzene (M.W. = 123) in Ethylene Bromide.

1.0137	39.6705	2.555	2.08	2.297°	131
1.7640	39.6705	4.447	3.61	3.762	139
2.2441	39.6705	5.657	4.60	4.667	143
1.2448	34.4451	3.614	2.93	3.190	134
1.6119	34.4451	4.680	3.80	4.025	137
2.0291	34.4451	5.891	4.79	4.942	141

* These results agree closely with data given by Winther (*Zeitsch. physikal. Chem.*, 1907, 60, 584).

* Since the rotation of the dissolved ester appears to vary, on change of temperature, according to the same law as holds for many other solvents (Trans., 1909, 95, 323).

Mixture of Ethyl Tartrate (1 mol) and Nitrobenzene (1 mol.) in Ethylene Bromide.

Weight of solute.	Weight of solvent.	Centigram-molecules of each constituent per 100 grams solvent.	Δ .		
			Observed.	Calculated.	Difference.
0.5508	35.7865	0.4678	1.083°	1.02°	+0.06°
1.0966	35.7865	0.9314	2.020	1.97	+0.05
1.7639	35.7865	1.4982	2.948	3.15	-0.20
2.2950	35.7865	1.9492	3.665	3.85	-0.19
3.0266	35.7865	2.5706	4.563	4.89	-0.33
—	—	3.12 *	5.22 *	5.67	-0.45

* By extrapolation.

It will be observed from these results that the apparent association of ethyl tartrate in ethylene bromide is considerable. The molecular weight of the ester at the highest concentration ($p=8.56$) is almost twice the theoretical. On the other hand, nitrobenzene shows but little association in ethylene bromide.

When the two substances are dissolved together in ethylene bromide, they seem to interfere with one another only to a slight extent, since the observed depression is nearly that which was to be expected from the separate depressions.

We next carried out similar experiments, first with quinoline and then with a mixture of quinoline and ethyl tartrate in ethylene bromide, and obtained the results shown in table VIII.

TABLE VIII.

Quinoline (M.W. = 129) in Ethylene Bromide.

Weight of solute.	Weight of solvent.	Grams solute per 100 grams solvent.	Centigram-molecules solute per 100 grams solvent.	Δ .		M.W.
0.7746	45.79	1.692	1.3116	1.490°		134
1.4288	45.79	3.120	2.4185	2.697		136
1.8877	45.79	4.122	3.195	3.587		136
2.3143	45.79	5.054	3.918	4.327		138
2.6057	45.79	5.690	4.411	4.80		140

Mixture of Ethyl Tartrate (1 mol.) and Quinoline (1 mol.) in Ethylene Bromide

Weight of solute.	Weight of solvent.	Centigram-molecules of each constituent per 100 grams solvent.	Δ .		
			Observed.	Calculated.	Difference.
0.5274	39.081	0.40	0.853°	0.895°	0.04°
1.2220	39.081	0.93	1.780	1.97	0.19
1.9607	39.081	1.50	2.615	3.03	0.42
2.6812	39.081	2.05	3.330	4.01	0.68
4.08	39.081	3.12	4.563	5.81	1.25

Quinoline and nitrobenzene thus behave very similarly in ethylene bromide solution, quinoline showing, however, slightly less apparent association than nitrobenzene.

From the second set of figures it appears that ethyl tartrate and quinoline interfere much more with each other in ethylene bromide solution than do ethyl tartrate and nitrobenzene, since the observed depression is very distinctly less than the sum of the separate depressions. For the latter pair at a concentration of 3.12 ggm.-mols. per 100 grams of solvent, the sum of the separate depressions should be 5.67° , whilst the experiments give (on extrapolation) 5.22° , a difference of only 0.45° , whilst in the case of ethyl tartrate and quinoline the corresponding difference is 1.247° .

Although we are not prepared to admit that numbers obtained even in only moderately concentrated solution by the cryoscopic method really represent average molecular weights,* we think the above facts may be regarded at least as presumptive evidence in favour of combination between ethyl tartrate and quinoline, and we may also point out that if, in the last solution in the tables, the quinoline were to be replaced by ethyl tartrate molecules, making the concentration of the tartrate 6.24 ggm.-mols. per 100 grams of ethylene bromide, the observed depression would then be 3.65° instead of $2 \times 2.38 = 4.76^\circ$ (that is, twice the depression observed in a solution of 3.12 ggm.-mols. per 100 grams of ethylene bromide †). The difference, 1.11° , is thus less than that found for the quinoline-ethyl tartrate solution, so that the apparent tendency of the quinoline molecules to combine with ethyl tartrate molecules is greater than the tendency of ethyl tartrate molecules to combine amongst themselves.

The Rotation of Ethyl Tartrate in Mixtures of Quinoline and Ethylene Bromide.

Since the solvent influence on rotation, the temperature change on mixing, and these cryoscopic experiments all seemed to indicate a difference either of degree or kind in the behaviour of quinoline as compared with a number of other solvents, we thought it would also be of interest to examine the solvent effect of mixtures of quinoline and ethylene bromide on the rotation of ethyl tartrate in the same manner as already described for mixtures of nitrobenzene and ethylene bromide. The concentration of the ethyl tartrate was kept constant

* The formula being valid only for infinitely dilute solution. We have no theoretically sound way of modifying the formula to suit concentrated solutions.

† By interpolation from data given in the first part of table VII.

and at the same value as before. The quinoline had d_4^{20} 1.09392, and the ethylene bromide (a fresh sample), d_4^{20} 2.18157.

TABLE IX.

No. of solu- tion.	Composition of solvent. Quinoline.		c.	p.	d_4^{20} .	α_D^{20} (200 mm.).	$[\alpha]_D^{20}$			Ex- pansion per 100 c.c. in c.c.
	Per 100 grams mixed solvent.	Per 100 c.c. mixed solvent.					Obs.	Calc.	Δ .	
10	100.0	100.0	23.9604	21.3389	1.12396	+12.62°	+26.32°	—	—	-0.70
11	42.3	58.96	23.9604	16.177	—	+7.02	+14.65	+11.1°	+3.55°	—
12	32.95	49.5	23.9606	15.3182	1.56068	+5.25	+10.98	+7.9	+3.08	-0.26
6	0.0	0.0	23.832	12.061	1.97599	-5.11	-10.72	—	—	+0.57

It will be seen from these data that the value of the rotation in the mixed solvent (+14.65°) is much higher than that calculated (+11.1°) on the assumption that the effect of the solvent is proportional to its volume. There is thus a distinct contrast between the quinoline-ethylene bromide and the nitrobenzene-ethylene bromide mixtures. The numerical difference between the calculated and observed values is about five times as great in the former case as in the latter, and it is in the opposite sense. The fact that the observed value is greater than the calculated would seem to indicate that the quinoline in the mixture has the preponderating influence, which is what might be expected from the cryoscopic and other experiments referred to above. It may also be remarked that the volume change (-0.26 c.c.) in the three component system (solution 12) is a greater contraction than would be expected (-0.055 c.c.) from the volume changes in solutions 10 and 6. This is also in agreement with the high rotation and in harmony with the relationship between volume change and rotation change which was referred to in connexion with the nitrobenzene-ethylene bromide mixtures.

Starting from the assumption that the rotation ought to be calculated as proportional to the molecular percentages of the solvents present, we find for the quinoline-ethylene bromide solutions the figures of table X, in which the data for solutions X and Y are

TABLE X.

Number of solution.	p.	Composition of 100 grams of solution in gram-molecules.			Composition of solvent. Percentage number of mole- cules of quinoline.	$[\alpha]_D^{20}$.		
		Ethyl tartrate.	Quin- oline.	Ethylene bromide.		Obs.	Calc.	Δ .
X ...	18.6	0.07436	0.5182	0.0000	100.00	+26.00°	—	—
12 ...	15.3182	0.07436	0.2162	0.3020	41.74	10.98	+5.0°	+5.98°
Y ...	13.589	0.07436	0.0000	0.5182	0.00	-9.95	—	—

calculated from results recorded in *Trans.*, 1909, **95**, 326, and *Zeitsch. physikal. Chem.*, 1907, **60**, 578, respectively. By this method the difference between the calculated and observed rotations is thus much greater than when the influence of each solvent is taken as proportional to its volume, but that of course does not decide which process, if either, is correct.

In conclusion we may summarise our results as follows :

1. The influence of mixtures of nitrobenzene and ethylene bromide on the rotation of ethyl tartrate is approximately proportional to the volume composition, but not to the weight composition of the mixed solvent. From a consideration of Rimbach's data and our own, we are inclined to think that this will prove to be the normal behaviour.

2. The influence of mixtures of quinoline and ethylene bromide on the rotation of ethyl tartrate is neither proportional to the volume nor to the weight composition of the mixed solvent.

3. The depression of the freezing point of ethylene bromide produced by a mixture of ethyl tartrate and nitrobenzene is only slightly less than the sum of the depressions that would be produced by the two solutes separately. A mixture of ethyl tartrate and quinoline, on the other hand, gives a depression considerably less than that which might be expected. It would thus appear that ethyl tartrate and quinoline have at least a greater tendency to combine with each other than have ethyl tartrate and nitrobenzene.

4. Ethyl tartrate and nitrobenzene mix with absorption of heat ; quinoline and ethyl tartrate mix with a very decided rise of temperature. This behaviour is also suggestive of compound formation in the latter case.

5. The peculiar influence of quinoline as a solvent on the rotation of ethyl tartrate, in regard particularly to change of rotation on heating, may perhaps also be a manifestation of compound formation.

The polarimetric measurements here recorded were carried out by means of a large Schmidt and Haensch polarimeter kindly placed at our disposal by the Carnegie Trustees for the Universities of Scotland, to whom, therefore, we beg to offer our hearty thanks.

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