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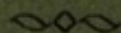
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ASSOCIATION IN MIXED SOLVENTS

BY

GEORGE BARGER, M.A., D.Sc.

(From the Transactions of the Chemical Society, 1905)



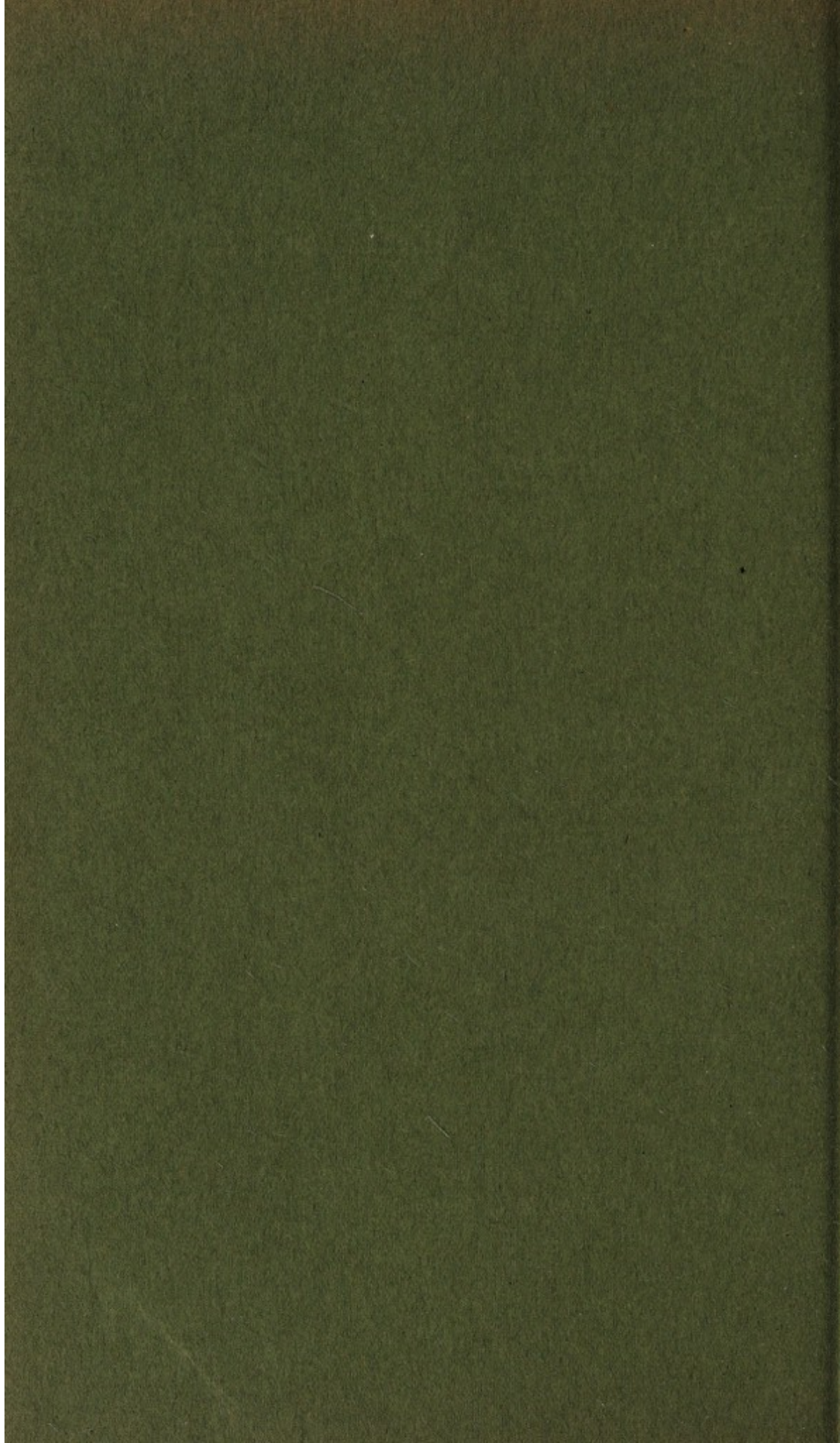
THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES

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CXI.—*Association in Mixed Solvents.*

By GEORGE BARGER.

A YEAR ago the author described a new method of determining molecular weights (Trans., 1904, 86, 286), based on the comparison of the vapour pressures of two solutions in a capillary tube, and it was pointed out that this method is especially useful for working with mixtures of solvents. It seemed, therefore, of interest to use it for the study of the degree of association of acids, phenols, &c., when dissolved in mixtures of an associative with a non-associative liquid. As was shown by Beckmann, Paternò, Biltz, Auwers, and others, substances containing a hydroxyl group generally have abnormally high molecular weights when dissolved in such solvents as benzene and chloroform which are themselves not associated. As these (hydroxylated) substances have normal molecular weights in such solvents as

phenol and acetic acid, the question arises: what is their molecular weight in mixtures of, say, alcohol and benzene? Two cases, those of benzoic acid in benzene and ethyl alcohol mixtures and of cinnamic acid in chloroform and methyl alcohol mixtures, were described in the previous paper (p. 325). Further examples have been studied in order that general conclusions might be deduced.

Of each pair of solvents, one was associative, the other non-associative; their boiling points, and probably, therefore, also their vapour pressures at the ordinary temperature, were not very different.

The solutes may be grouped as follows:

1. Acids. 2. Alcohols and phenols. 3. Oximes and other hydroxylated nitrogen compounds.

Organic acids are strongly associated in dilute solution, and with increase of concentration the association soon reaches a maximum. They were mostly examined in a concentration of 0.1—0.2 mole (compare footnote, *Trans.*, 1904, **36**, 295).

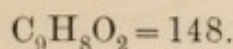
With phenols and alcohols, the association increases slowly but steadily with the concentration, and some members of this class were studied in more concentrated solutions.

Azobenzene was employed as the standard substance in nearly all cases. By the cryoscopic method, it had been shown to have a normal molecular weight over a large range of concentration in benzene solution (Auwers, *Zeit. physikal. Chem.*, 1893, **12**, 713). Moreover, its use as a standard was shown to be well justified in the previous communication on this method.

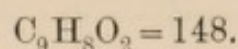
For a few mixtures containing a large percentage of alcohol, in which azobenzene was not sufficiently soluble, α -naphthol was used as a standard after it had been found that α -naphthol was normal in mixtures containing less alcohol.

In the following tables, the concentration is expressed in gram-molecules per litre of solution and the composition of the mixtures in percentages by weight of the non-associative solvent. For each determination, the two limiting concentrations of the standard are given in gram-molecules per litre. The molecular weights have been calculated for a solution midway between these limits; the association factor (A) or ratio of the observed molecular weight to the "normal" one has also been tabulated.

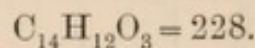
Curves were plotted with the association factor as ordinate and the percentage composition of the solvent as abscissa; these curves are distinguished by Roman numerals.

I. *Cinnamic Acid*, 0.10 mole in
Acetic Acid and Toluene.

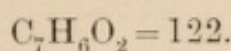
Percentage of acetic acid.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.10 — 0.105	144	0.97
82.6	0.10 — 0.105	144	0.97
61.2	0.095 — 0.10	152	1.03
40.0	0.085 — 0.09	167	1.13
20.0	0.08 — 0.085	179	1.21
0.0	0.075 — 0.08	194	1.31

II. *Cinnamic Acid*, 0.10 mole
in *Pyridine and Toluene*.

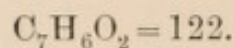
Percentage of pyridine.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.10 — 0.11	141	0.95
21.8	0.095 — 0.105	148	1.00
11.0	0.10 — 0.105	145	0.98
5.5	0.0975 — 0.10	149	1.01
2.8	0.095 — 0.099	152	1.03
1.1	0.085 — 0.09	170	1.15
0.0	0.075 — 0.08	194	1.31

III. *Cinnamic Acid*, 0.20 mole in
*Methyl Alcohol and Chloro-
form* (compare Trans., 1904,
86, 323).IV. *Benzilic Acid*, 0.10 mole in
Ethyl Alcohol and Chloroform.

Percentage of ethyl alcohol.	Benzil.	<i>M.</i>	<i>A.</i>
100.0	0.105 — 0.11	213	0.93
70.0	0.105 — 0.11	213	0.93
40.4	0.100 — 0.1025	225	0.99
29.5	0.095 — 0.0985	236	1.035
20.0	0.090 — 0.095	246	1.08
10.0	0.085 — 0.088	276	1.17
0.0	0.065 — 0.070	338	1.48

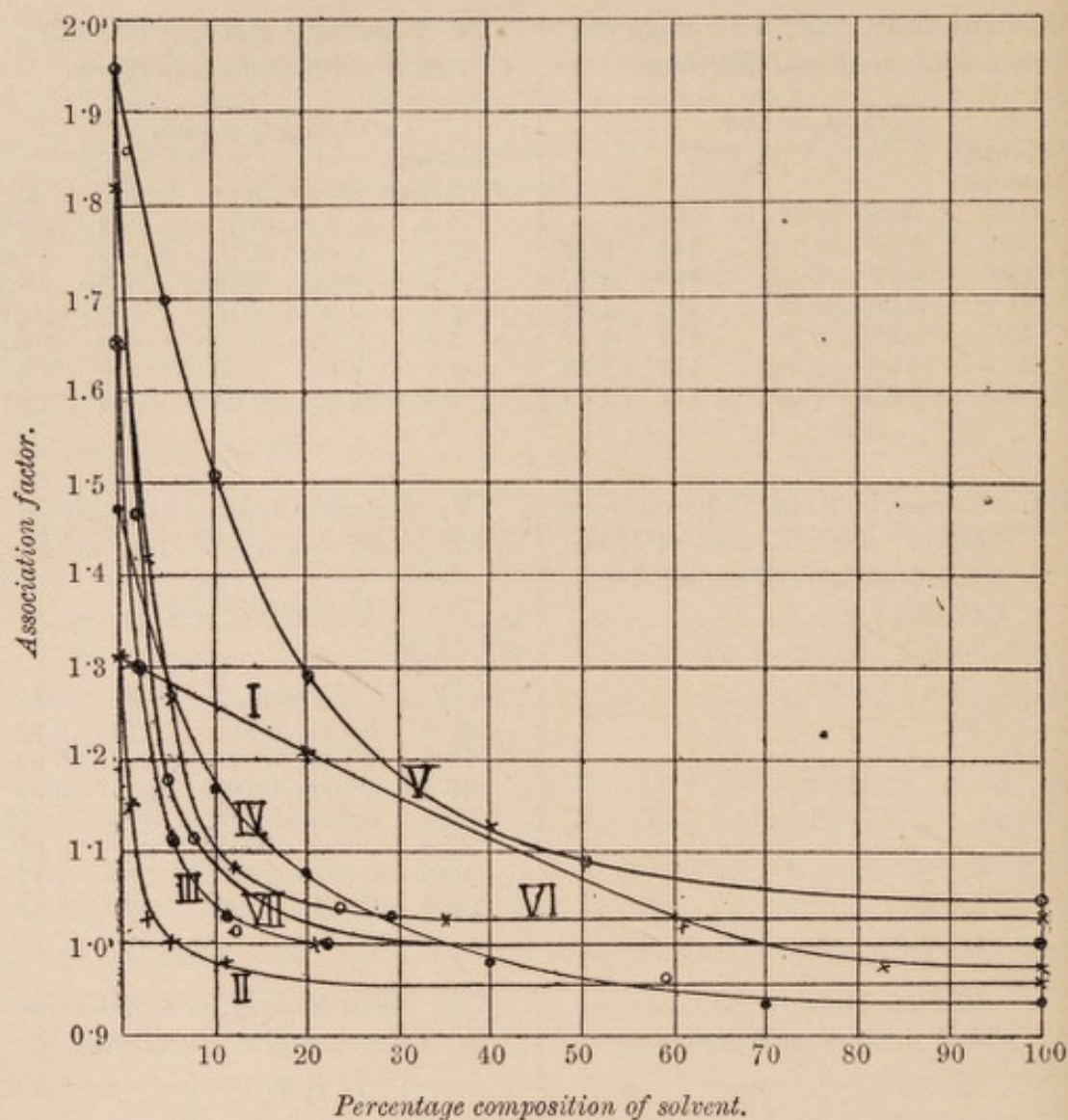
V. *Benzoic Acid*, 0.20 mole in
Ethyl Acetate and Benzene.

Percentage of ethyl acetate.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.185 — 0.195	128	1.05
50.5	0.180 — 0.185	133	1.09
20.2	0.150 — 0.160	157	1.29
10.1	0.130 — 0.135	184	1.51
5.0	0.115 — 0.12	208	1.70
3.0	0.11 — 0.115	217	1.78
1.0	0.105 — 0.11	227	1.86
0.0	0.10 — 0.105	238	1.95

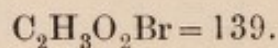
VI. *Benzoic Acid*, 0.20 mole in
Acetone and Chloroform.

Percentage of acetone.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.19 — 0.20	125	1.02
35.0	0.19 — 0.20	125	1.02
11.8	0.175 — 0.18	132	1.08
5.5	0.155 — 0.16	155	1.27
2.7	0.13 — 0.136	183	1.42
1.6	0.125 — 0.13	191	1.57
0.53	0.11 — 0.12	210	1.72
0.0	0.105 — 0.115	222	1.82

VII. *Benzoic Acid in Ethyl Alcohol and Benzene* (compare Trans., 1904,
86, 323).

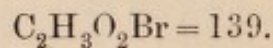
FIG. 1.—*Acids.*

VIII. *Bromoacetic Acid*, 0.20 mole in *Ethyl Formate* and *Chloroform*.

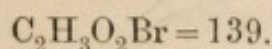


Percentage of ethyl formate.	Azobenzene.	<i>M.</i>	<i>A.</i>
100	0.18 — 0.19	150	1.08
75	0.175 — 0.185	154	1.11
50	0.17 — 0.175	161	1.16
25	0.155 — 0.165	174	1.25
10	0.14 — 0.15	192	1.38
5	0.13 — 0.14	206	1.48
0	0.12 — 0.13	222	1.60

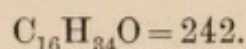
IX. *Bromoacetic Acid*, 0.20 mole in *Methyl Acetate* and *Chloroform*.



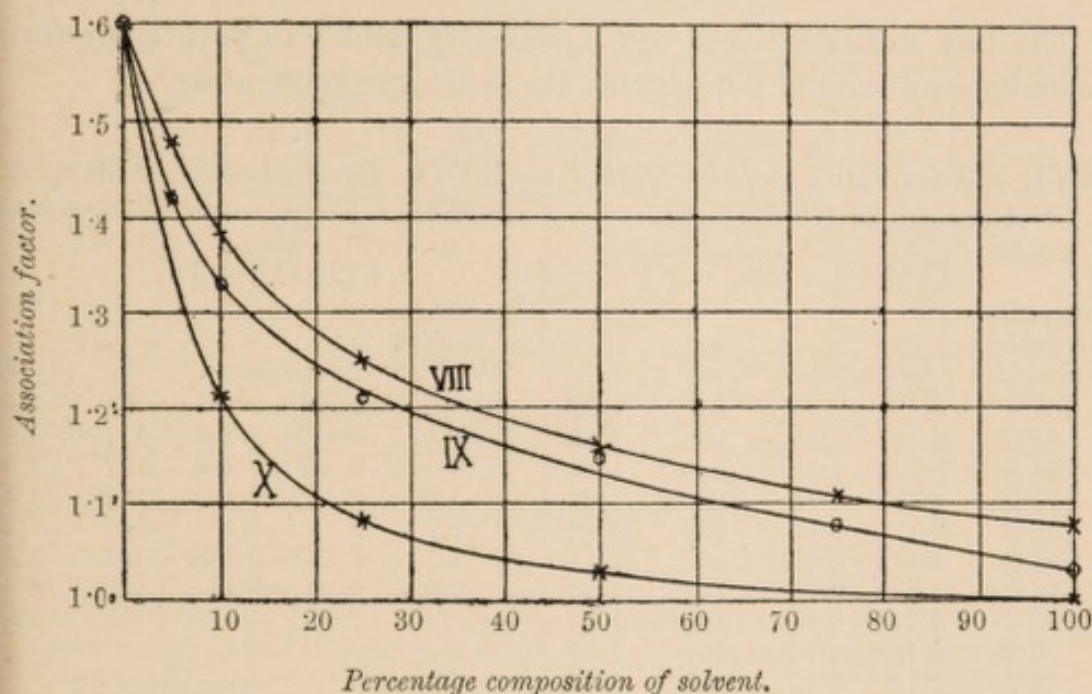
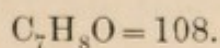
Percentage of methyl acetate.	Azobenzene.	<i>M.</i>	<i>A.</i>
100	0.19 — 0.20	143	1.03
75	0.18 — 0.19	150	1.08
50	0.17 — 0.18	159	1.15
25	0.16 — 0.17	168	1.21
10	0.145 — 0.155	185	1.33
5	0.135 — 0.145	198	1.42
0	0.12 — 0.13	222	1.60

X. *Bromoacetic Acid, 0.20 mole in Acetone and Chloroform.*

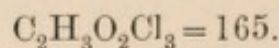
Percentage of acetone.	Azobenzene.	M.	A.
100	0.195—0.205	139	1.00
50	0.19 —0.20	143	1.03
25	0.18 —0.19	150	1.08
10	0.16 —0.17	168	1.21
5	0.135—0.145	198	1.42
0	0.12 —0.13	222	1.60

XI. *Cetyl Alcohol, 0.3 mole in Ethyl Alcohol and Benzene.*

Percentage of ethyl alcohol.	α -Naphthol; azobenzene.	M.	A.
100.0	0.29 —0.31	242	1.00
73.2	0.28 —0.29	255	1.05
47.6	0.26 —0.27	274	1.132
23.3	0.235—0.245	302	1.25
0.0	0.21 —0.23	331	1.37

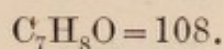
FIG. 2.—*Bromoacetic acid.*XII. *Benzyl Alcohol, 0.50 mole in Acetone and Chloroform.*

Percentage of acetone.	Azobenzene.	M.	A.
100.0	0.41—0.42	130	1.20
61.5	0.44—0.46	120	1.11
35.0	0.44—0.45	121	1.12
16.0	0.42—0.43	128	1.18
5.5	0.37—0.38	143	1.32
0.0	0.31—0.32	170	1.57

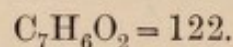
XIII. *Chloral Hydrate, 0.50 mole in Acetone and Chloroform.*

Percentage of acetone.	Azobenzene.	M.	A.
100.0	0.58 —0.60	140	0.85
61.5	0.55 —0.56	149	0.903
35.0	0.49 —0.50	166	1.006
16.0	0.44 —0.45	185	1.12
5.5	0.37 —0.38	220	1.33
2.7	0.32 —0.33	254	1.54
0.0	0.275—0.285	295	1.79

The abnormally low values of the molecular weight in the first two solutions is probably due to dissociation into chloral and water (compare Beckmann, *Zeit. physikal. Chem.*, 1888, 2, 724).

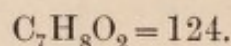
XIV. *p*-Cresol, 0.4 mole in
Acetone and Chloroform.

Percentage of acetone.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.375—0.385	114	1.055
35.0	0.375—0.385	114	1.055
16.0	0.37 —0.375	116	1.074
8.6	0.36 —0.37	118	1.092
5.5	0.345—0.35	124	1.15
2.7	0.31 —0.32	136	1.26
0.0	0.26 —0.27	163	1.51

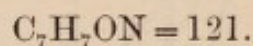
XV. *p*-Hydroxybenzaldehyde, 0.2
mole in Methyl Alcohol and
Chloroform.

Percentage of methyl alcohol.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.195—0.205	122	1.00
35.0	0.195—0.205	122	1.00
16.0	0.185—0.195	129	1.06
5.5	0.17 —0.175	141	1.16
2.7	0.155—0.165	153	1.25
1.6	0.14 —0.15	168	1.38
1.1	0.13 —0.14	181	1.48

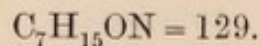
The last substance was not sufficiently soluble in pure chloroform to make a solution of 0.2 mole at the ordinary temperature.

XVI. Guaiacol, 0.2 mole in Methyl
Alcohol and Chloroform.

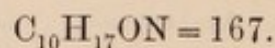
Percentage of methyl alcohol.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.18 —0.19	134	1.08
82.5	0.18 —0.19	134	1.08
61.5	0.17 —0.18	142	1.14
35.0	0.155—0.16	157	1.26
30.3	0.15 —0.16	160	1.29
22.3	0.145—0.15	167	1.35
16.0	0.145—0.15	165	1.33
5.5	0.145—0.15	165	1.33
3.8	0.155—0.16	157	1.26
2.7	0.16 —0.17	150	1.21
0.0	0.17 —0.18	142	1.14

XVII. Benzaldoxime, 0.20 mole
in Methyl Alcohol and Chloroform.

Percentage of methyl alcohol.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.195—0.205	121	1.00
35.0	0.195—0.205	121	1.00
16.0	0.185—0.195	127	1.05
5.5	0.17 —0.18	138	1.14
2.7	0.16 —0.17	146	1.20
1.1	0.145—0.155	161	1.33
0.0	0.13 —0.14	179	1.48

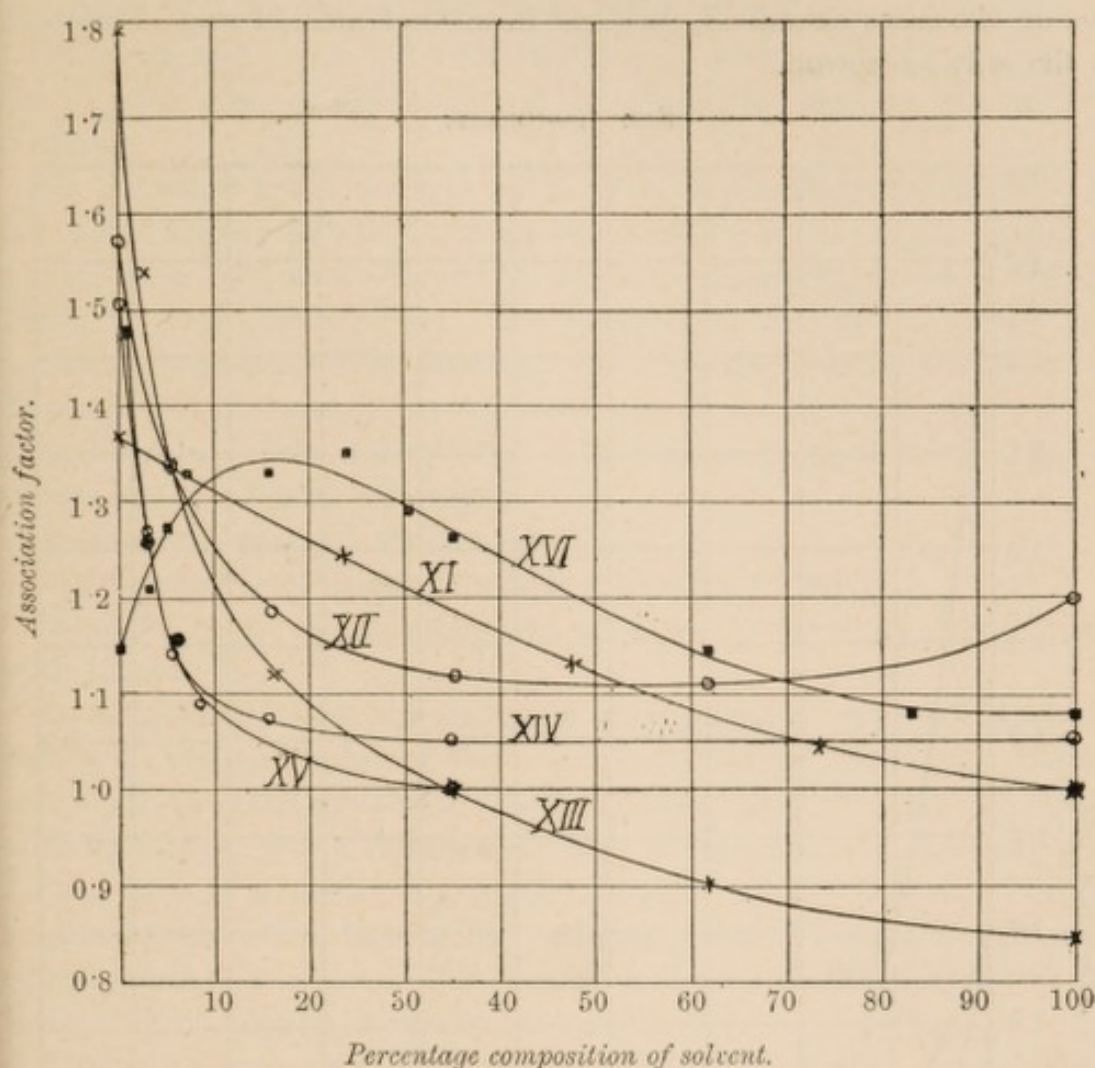
XVIII. *O*-Enanthaldoxime, 0.20
mole in Ethyl Acetate and
Benzene.

Percentage of ethyl acetate.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.185—0.195	136	1.05
75.4	0.18 —0.19	139	1.05
50.5	0.175—0.185	143	1.11
25.5	0.16 —0.17	156	1.21
10.2	0.14 —0.15	178	1.38
5.1	0.13 —0.14	191	1.48
0.0	0.12 —0.13	206	1.60

XIX. Camphoroxime, 0.20 mole
in Pyridine and Toluene.

Percentage of pyridine.	Azobenzene.	<i>M.</i>	<i>A.</i>
100.0	0.195—0.205	167	1.00
52.7	0.19 —0.20	171	1.02
27.1	0.18 —0.19	181	1.08
11.0	0.165—0.175	197	1.18
9.8	0.16 —0.17	202	1.21
5.5	0.14 —0.15	230	1.37
3.4	0.13 —0.14	247	1.48
1.1	0.125—0.135	260	1.56
0.0	0.12 —0.13	267	1.60

FIG. 3.—Alcohols and phenols.



XX. Acetophenoneoxime, 0.20 mole in Ethyl Alcohol and Carbon Tetrachloride.

$C_8H_9ON = 135$.			
Percentage of alcohol.	Azobenzene.	M.	A.
100	0.195—0.20	138	1.02
50	0.185—0.19	144	1.06
25	0.185—0.19	144	1.06
10	0.17 —0.18	154	1.14
5	0.16 —0.17	164	1.21
2	0.145—0.15	183	1.36
0	0.12 —0.13	216	1.60

XXI. Formanilide, 0.50 mole in Pyridine and Toluene.

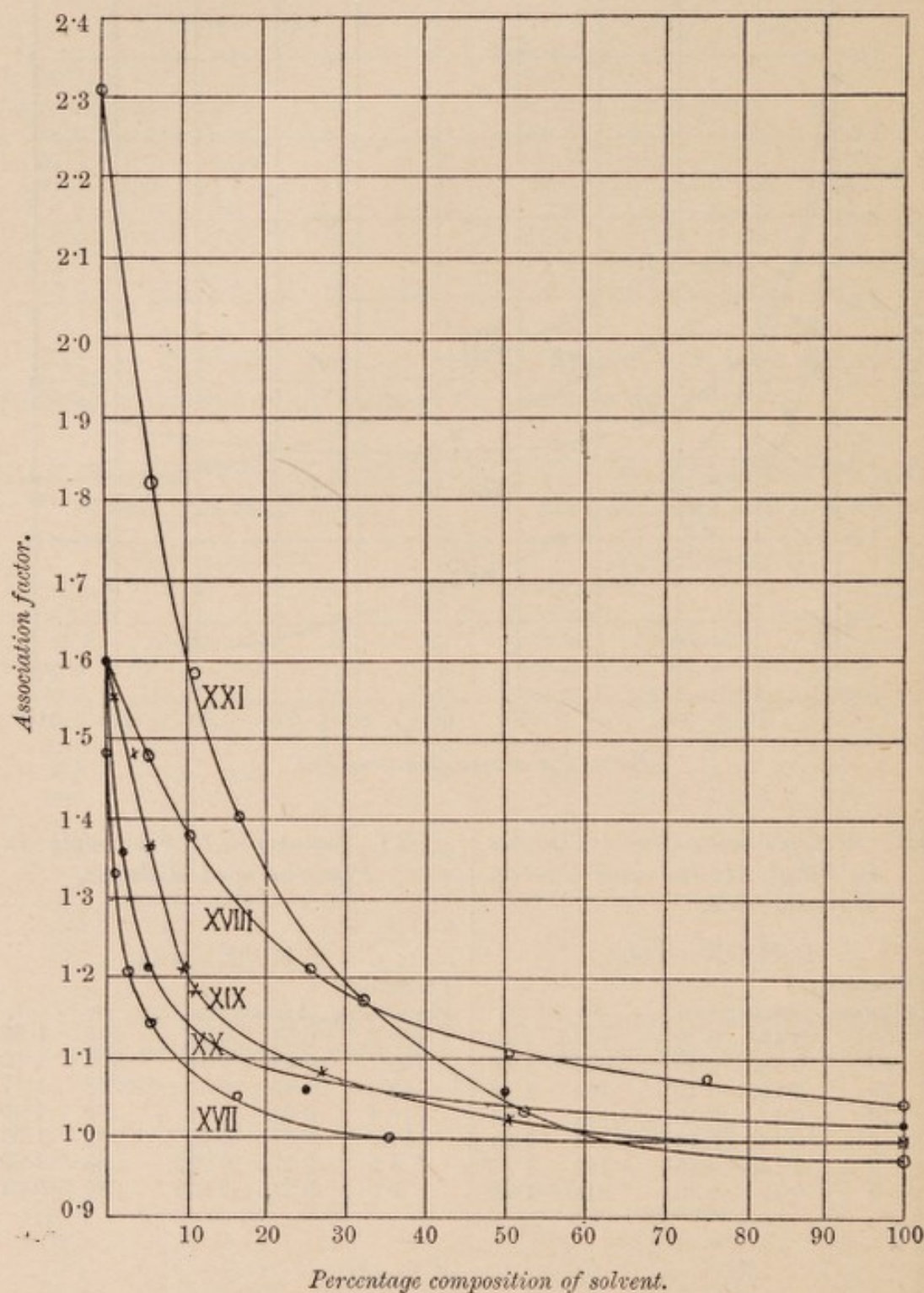
$C_7H_7ON = 121$.			
Percentage of pyridine.	Azobenzene.	M.	A.
100.0	0.51 —0.52	118	0.98
52.7	0.48 —0.49	125	1.03
32.3	0.42 —0.43	142	1.17
16.5	0.35 —0.36	170	1.40
11.0	0.31 —0.32	192	1.58
5.5	0.275—0.285	220	1.82
0.0	0.215—0.225	280	2.31

Discussion of Results.

The chief fact brought out by this work is that the molecular weight is normal in most mixtures; association only persists when the percentage of the dissociative solvent is small. The curves descend at first steeply and then more slowly until they become horizontal or

nearly so. This tendency is most marked with acids and oximes; among the cases examined, guaiacol in methyl alcohol and chloroform is the only exception.

FIG. 4.—*Oximes*.



The first explanation which suggested itself was that the surface layer of the mixture tends to be composed of the dissociative solvent only. This may be so to some slight extent, but the measurements of

the molecular surface-energy of mixtures, as carried out by Ramsay and Aston (*Trans. Royal Irish Acad.*, 1902, 32, 93), show that although a difference may exist between the surface layer and the interior of the liquid, such a difference is too small to explain the present results.

On the other hand, the general form of the curves is exactly what one would expect in the light of the modern views of the action of solvent on solute, as developed by Walden, Abegg (*Zeit. anorg. Chem.*, 1904, 39, 330), and others. The associative solvents allow the pre-existing complexes of the solute to continue their existence in solution. The solvents of the other group break up these complexes into single molecules, and then form loose molecular compounds with them by means of their latent valencies.

Hence two balanced actions take place:

- (1) Complexes of solute \rightleftharpoons single molecules of solute.
- (2) Solvent + single molecules of solute \rightleftharpoons compound of solvent with solute.

In a dilute solution, the influence of the solvent preponderates and nearly all the molecules of the solvent are singly combined with the solute so that the molecular weight appears normal. But the same will hold good for a mixture of, say, 90 per cent. of benzene with 10 per cent. of alcohol, for the concentration of the alcohol, although small compared with that of the benzene, is large compared with that of the solute (benzoic acid, for example), so that the association of the latter will be largely or wholly prevented.

This, or a very analogous behaviour, can be readily demonstrated with iodine solutions. According to Lachman (*J. Amer. Chem. Soc.*, 1903, 25, 50), the brown colour with which iodine dissolves in liquids with latent valencies is due to a combination of iodine with the solvent. Its solutions in liquids without latent valencies are violet. Now in a mixture of equal parts of chloroform and alcohol, one might expect that more than half the iodine is combined with the alcohol; accordingly, the colour should be brown, not violet. To show this, the following experiment was devised. Two similar cylinders were half-filled with a solution of iodine in chloroform containing 1 gram-molecule per litre. Equal quantities of an alcoholic iodine solution of the same strength were poured on the top of the chloroform solutions without mixing.

Looked at vertically from above, the tints in both cylinders of course appear equal, but when the solutions in one cylinder are mixed, the colour of the liquid in this cylinder becomes distinctly lighter than that of the other. Now since the original alcoholic solution is paler than the chloroform solution, one may assume that more iodine is in molecular combination with the alcohol than before.

The change is even more striking if a little pyridine is used instead of the alcohol.

Hitherto the dissociative solvents have been referred to as a homogeneous class, but they show some differences among themselves. Those curves relating to mixtures of which esters are one constituent will be seen to slope much more gradually than similar ones where acetone or alcohol is the dissociative solvent, for example, Curve V, Fig. 1, Curve XVIII, Fig. 4, and especially the three curves of bromoacetic acid in Fig. 2 (VIII with ethyl formate, IX with methyl acetate, and X with acetone).

This peculiar behaviour of esters agrees with other facts observed about them. Through the study of the boiling points of homologous series, Young assigns to them a position intermediate between associated and non-associated liquids (*Phil. Mag.*, 1905, [vi], 9, 1), and Baeyer and Villiger found that ethyl acetate had a much smaller tendency than acetone to combine with complex mineral acids such as hydroferricyanic acid (*Ber.*, 1901, 34, 2692).

Generally, non-associative solvents are themselves associated in the liquid state, but not necessarily. The esters are not associated according to Ramsay and Shields (*Trans.*, 1893, 62, 1089), nor is pyridine, yet pyridine is among the strongest dissociating substances examined. Compare, for instance, Curves I. and II, representing respectively cinnamic acid in acetic acid and toluene mixtures and in pyridine and toluene mixtures. The greater dissociative effect of the pyridine is here probably due to its basic nature.

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