CLI.—*Some Physical Properties of Acetic Anhydride and Related Substances and their Constitutional Significance.*

By DAVID CHARLES JONES.

Determination of the Molecular Weight of Acetic Anhydride in Benzene and in cyclo*Hexane.*—Apart from Pickering's cryoscopic determination (J., 1893, **63**, 1000) of the molecular weight of acetic anhydride in acetic acid, no results on the molecular weight of acetic anhydride are recorded in the literature. In this research the lowering of the freezing points of *cyclo*hexane and benzene by acetic anhydride was determined, and the results are shown in Tables I and III, respectively. In all cases, in dilute solution the anhydride gives values corresponding to the normal molecular weight (102).

TABLE I.

Solvent: *cyclo*hexane, m. p. 6·4°.

Conc.	F. p.	Lowering of f. p.	M (found).	$\frac{M \text{ (found)}}{M \text{ (calc.)}}$.
0·335	5·8°	0·603°	111·2	1·09
0·684	5·25	1·147	119·3	1·17
1·087	4·6	1·784	121·8	1·20
2·203	3·25	3·153	139·7	1·37
2·947	2·66	3·742	157·4	1·54
(5·33)	(2·269)	(4·131)	(272·5)	(2·67)

The concentration in Table I is expressed in g. per 100 g. of solvent. The molecular lowering of the freezing point of *cyclo*hexane is assumed to be 200 (Mascarelli and Benati, *Gazzetta*, 1909, **39**, ii, 642). The last values in Table I correspond to the invariant point, where solid *cyclo*hexane is in equilibrium with the two liquid phases; this was determined in the ordinary freezing-point apparatus by adding a sufficient quantity of acetic anhydride to give a two-liquid layer system, and precautions were taken, by a very slow temperature adjustment, to ensure the two liquid layers being in equilibrium. The corresponding concentration of the *cyclo*hexane-rich phase was read from the solubility curve (preceding paper). The supercooling in any determination did not exceed 0·05°, spontaneous freezing occurring in nearly all cases at this point. A slow stream of dried air was passed through the annular space round the stirrer to prevent absorption of moisture during the determination. Only the results for the very low concentrations are regarded as giving values for the molecular weight of acetic anhydride in this solvent; the rapid increase in the values with increasing concentration probably illustrates merely the positive deviation of the system from Raoult's law, since the two liquids form a two-liquid layer system. (The same value for the freezing point would be obtained whatever the concentrations of the solutions between 5·33% and 90·87% of acetic anhydride.)

It is interesting to compare these results with those obtained for aniline and acetic acid in *cyclo*hexane (see Table II). The theoretical value for the molecular weight of acetic acid is taken as that of the double molecule. The values for the so-called " association factor " in the case of aniline and acetic anhydride are very similar in solutions of about the same concentrations, probably because they both exhibit a positive deviation from Raoult's law to the extent of forming a two-layer system with similar C.S.T.'s, *e.g.*, aniline–*cyclo*hexane, 41°, 49·72% aniline (Chavanne and Simon, *Compt. rend.*, 1919, **168**, 1111); acetic anhydride–*cyclo*hexane, 52·45°, 47·33% anhydride (Jones and Betts, preceding paper). For acetic acid the association is much smaller in solutions of corresponding concentrations. In this case the liquids are completely miscible at the temperature reached by the freezing-point curve, but the metastable liquid–liquid solubility curve lies just below the freezing-point curve (Jones, J., 1923, **123**, 1374).

TABLE II.

	Conc.	*M* (calc.).	*M* (found).	*M* (found)/*M* (calc.).
Acetic acid *	0·86	120	127·7	1·064
	3·49	120	140·0	1·166
Aniline *	0·40	93·1	106	1·139
	3·05	93·1	136	1·461
Acetic anhydride	0·335	102	111·2	1·09
	2·947	102	157·4	1·54

* Turner, " Molecular Association," pp. 128, 143.

When acetic anhydride is dissolved in benzene the molecular weight is normal up to a concentration of 3·8%, with a slight tendency to increase at higher concentrations. In this case, although the solvent is similar in type to *cyclo*hexane, the two differ in that benzene is completely miscible with the anhydride.

TABLE III.

Solvent: benzene.

Conc.	Lowering of f. p.	*M* (found).	*M* (found)/*M* (calc.).
1·539	0·783°	98·30	0·97
2·205	1·090	101·20	0·99
3·761	1·770	106·1	1·04

The temperature coefficients of " molecular cohesion " and of " molecular surface energy," as determined by Walden and Swinne (*Z. physikal. Chem.*, 1913, **82**, 296) for the group of liquids concerned

TABLE IV.

	Temp. coeff. of molecular cohesion,		Temp. coeff. of molecular surface energy,	
	obs.	calc.	obs.	calc.
Acetic anhydride	0·0177	0·0177	2·13	2·25
Acetic acid	0·0077	0·0155	0·95	2·11
Carbon disulphide ...	0·0155	0·0151	2·08	2·09
Aniline	0·0177	0·0188	2·05	2·20
Hexane	0·0201	0·0201	2·21	2·30

in this paper, are given in Table IV. They support the conclusion reached from the freezing-point determination—acetic anhydride and aniline behave as " normal " liquids, whereas acetic acid gives about half the calculated values. Hexane and carbon disulphide are typical " normal " liquids. It has been suggested by Sidgwick (" Electronic Theory of Valency," p. 137) that it is the absence of co-ordinating hydrogen which accounts for the fact that ethyl ether, as judged by its properties in the pure state, is unassociated, as contrasted with, for instance, ethyl alcohol. Acetic anhydride probably affords another instance of this : there is no acceptor atom present.

The Parachor and the Constitutions of Acetic Acid, Acetic Anhydride, and Ethyl Alcohol.—Sugden (J., 1924, **125**, 1177) has compared molecular volumes at the same value of surface tension, and shown that these volumes can be calculated from values given to the various atoms present in the molecule if account is also taken of certain constitutive effects. From Orton and Jones's value for the density ($d_4^{20°}$ 1·0840) and Ramsay and Shields's corrected value for the surface tension ($\gamma_{20°} = 32·69$) the parachor for acetic anhydride is found to be 225·5. The calculated value is obtained thus : 4C = 19·2; 6H = 102·6; 1 double bond + 1O = 43·2; 2O + 1 double bond (as in the esters) = 60·0; total = 225·0. Acetic anhydride therefore gives a molecular volume value as if it were a ketonic ester. The parachor for acetic acid is fairly constant if it is calculated from Bennett's values for the surface tension at 20° and 130° (J., 1915, **107**, 315), and from Ramsay and Shields's values, as corrected by Sugden (J., 1924, **125**, 38), for other temperatures.* The following table is based on the foregoing data, together with a molecular weight of 60, and with Young's values for the orthobaric densities :

Temp.	γ.	P (obs.).	Temp.	γ.	P (obs.).
20°	27·90	131·5	190°	11·45	133·9
130	17·01	132·6	220	8·71	134·9
160	14·21	133·5	280	2·83	136·9

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* Ramsay and Shields's value for γ at 20° seems to be much too low; their corrected value at 130° is 17·05 (compare Bennett's 17·01).

Clearly the dissociation of the dimeric molecule occurs to a very slight extent up to temperatures well above the boiling point.

The constancy in the values of K (total molecular surface energy) obtained from Ramsay and Shields's values for the four higher aliphatic acids seems to indicate that in these acids also we have stable dimeric molecules at the ordinary temperature, *e.g.*, butyric acid gives $K = 1100$, 1072, and 1088 for temperature ranges of 16—46°, 46—78°, and 78—132°, respectively (Bennett and Mitchell, *Z. physikal. Chem.*, 1913, **84**, 475).

Using Ramsay and Shields's values for the aliphatic acids, and correcting them by the addition of 1 dyne, we obtain the following results for the observed parachors at 20° :

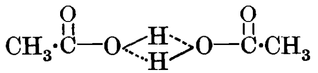
	P (obs.).	P_1 (calc.).	P_2 (calc.).	Δ_1.	Δ_2.
Acetic acid	131·5	141·2	138	−6·5	−13·0
Propionic acid	170·5	180·2	177	−6·5	−13·0
n-Butyric acid	208·6	219·2	216	−7·4	−14·8
n-Valeric acid	248·7	258·2	255	−6·3	−12·6

P_1 is calculated by summing the atomic constants + one double bond, as for the ordinary formula $CH_3{\cdot}CO{\cdot}OH$; P_2 is the parachor calculated on the assumption that the two oxygen atoms have the same value as in the esters. Δ_1 is the difference (a contraction) between P (obs.) and P_2 (calc.), and Δ_2 is the corresponding difference for the dimeric molecule.

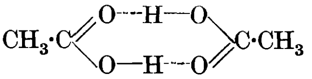
Although the data for the higher members may not be very accurate, yet there is distinct evidence that the structure of the associated dimeric molecule—an association which undoubtedly concerns the two carboxyl groups—involves a constant large contraction in the observed molecular volume. On the basis of this evidence alone, it cannot be decided whether this contraction is partly or wholly due to the association, for the parachor is determined on the associated acid, and gives no information regarding the volume of the single carboxyl group.

It is possible to account for these very large contractions on the assumption that the association involves single-electron linkings (Sugden, J., 1927, 1173). In this connexion two formulæ that have been proposed for the associated acetic acid are of interest : (I) (Hantzsch, *Ber.*, 1927, **60**, 1933), and (II) (Pfeiffer, " Organische Molekülverbindungen," 2nd Edition, p. 128). The calculated parachor for formula (I), if the dotted lines represent single-electron

(I.)



$CH_3{\cdot}\overset{\overset{O}{\|}}{C}{-}O{<}^{H}_{H}{>}O{-}\overset{\overset{O}{\|}}{C}{\cdot}CH_3$



(II.)

co-ordination bonds, is 276 (see P_2, above), plus 11·6 for a 4-membered ring, minus 24·8 for the two co-ordination bonds, *i.e.*, 262·8 units, whereas the observed parachor is 263·0 ($M = 120$). This assumes that the two pairs of oxygen atoms have the same value as in the esters. Similarly for (II) we have for the calculated value 282·4 (see P_1, p. 1196), plus 5·8 for an 8-membered ring, minus 24·8 for the two co-ordination bonds, *i.e.*, 263·4 units. This does not assume the contraction for the two pairs of oxygen atoms as in the esters.

In spite of the good numerical agreement, it seems doubtful whether formulæ (I) and (II), involving 4-ring and 8-ring structures with two singlet-electron bonds, would account for the great stability of the dimeric molecules of the fatty acids, although both formulæ appear to be in agreement with other properties of acetic acid. Formula (I) has the character of an ester, and as such would account for the low dielectric constant, the non-reactivity of the carbonyl groups, and the large solubility values in petroleum. In both formulæ there would be no tendency to associate further than the dimeric molecule.

It is of interest to compare the corresponding values for ethyl alcohol. Taking Richards and Carver's results (*J. Amer. Chem. Soc.*, 1921, **43**, 827) for the surface tension at 20°, and Ramsay and Shields's corrected results for the higher temperatures, we have the following values :

Temp.	20°	80°	110°	140°	170°	200°	230°
P (obs.)	126·7	128·7	128·1	129·4	130·1	130·9	132·9

The theoretical value for ethyl alcohol is 132·2. It is evident that the values increase more rapidly with rise in temperature than do the corresponding values for acetic acid, but apparently dissociation in the liquid is not complete even at 200°. A contraction also occurs here, and at 20° it is equal to $-$ 5·5 units for the single molecule, or $-$ 11 units for the double. This result is not inconsistent with the view that association of an alcohol takes place by co-ordination through hydrogen, if this is accomplished by a singlet co-ordination bond, *i.e.*, $C_2H_5{-}O{-}H{\cdots}OH{\cdot}C_2H_5$. One such bond requires a contraction of .12·4 units; this would mean, apparently, that the ethyl alcohol at 20° was, on the average, in the dimeric form.

The Solubility of some C_4 *Compounds in Saturated Hydrocarbons.*—The greater solubility of ethyl ether than ethyl alcohol, and of acetic acid than its anhydride, in saturated hydrocarbons is what would be expected from the dielectric constants : Ethyl alcohol (associated) $\varepsilon_{20^\circ} = 25{\cdot}8$, ether $\varepsilon_{20^\circ} = 4{\cdot}4$, acetic acid (associated) $\varepsilon_{19^\circ} = 6{\cdot}29$, acetic anhydride $\varepsilon_{20^\circ} = 20{\cdot}5$. The associated hydroxyl groups in alcohols are more polar than the ethereal oxygen group. The association of the acid takes place differently, the residual affinity of the active groups being conjugated in such a way that the resulting compound is less polar than its anhydride.

The Effect of Oxygen-containing Groups on the Solubility in Water of C_4 *Aliphatic Compounds.*—It should be possible to obtain important information concerning the structure of groups containing oxygen from a study of the solubility in water of the compounds containing them. Table V gives a list of some C_4 and C_5 compounds and their solubility in water at 20° (Landolt–Börnstein, " Tabellen " ; Seidell, " Solubilities of Inorganic and Organic Compounds "). (It would perhaps have been better to consider critical solution temperatures rather than solubility at a fixed arbitrary temperature, but very few data exist.)

TABLE V.

	%		%		%
Ethyl ether	7·0	*iso*Butyric acid ...	55·4	Diethyl ketone ...	4·6
Ethyl acetate ...	8·5	Methyl propionate	5·0	Acetylacetone ...	14·0
Acetic anhydride	12·0	Ethyl acetate	8·5	*n*-Valeric acid ...	3·4
*iso*Butyl alcohol	9·0	Propyl formate ...	2·1	*iso*Butyl formate	1·0
sec.- ,, ,,	22·5	*n*-Butaldehyde ...	3·6	Ethyl propionate	1·7
Trimethylcarbinol	misc.	*iso*Butaldehyde ...	10·0	Propionyl acetate	1·7
n-Butyric acid ...	misc.	Methyl ethyl ketone	24·0		

The carboxyl group is by far the most effective in promoting solubility in water; of the two butyric acids, one is completely miscible and the other has very great solubility (the C.S.T. of *iso*butyric acid is 24°). The carbonyl group is next in order of efficacy whether in ketones or in aldehydes, and the hydroxyl group appears to have almost the same effect (possibly a little less) if compounds containing a similar structure in the remainder of the molecule are compared, *e.g.*, *iso*butaldehyde with *iso*butyl alcohol, or methyl ethyl ketone with *sec.*-butyl alcohol. Ethereal oxygen has less effect than the hydroxyl group. It is unfortunate that we have no data for methyl propyl ether, for the position of the active group exercises a great influence on the solubility. Thus, we can arrange these groups in the order of their effect on the solubility in water as $CO_2H > CO > CH_2{\cdot}OH, CH{\cdot}OH > -O-$, there being little difference between CO and OH.

When two or more of these groups are present in the same molecule certain interesting results are obtained. The introduction of the very active carbonyl group into ethyl ether, with formation of ethyl acetate, produces the very small increase of solubility from 7% to 8·5%, and at the same time the dielectric constant is increased only from 4·37 to 5·85. It should be noted that, of the three isomeric esters, ethyl acetate has by far the largest solubility. This seems to afford very distinct evidence of that interaction between the two oxygen atoms which results in the chemical inactivity of the carbonyl group in esters and produces a contraction in the molecular volume (see above). This effect cannot be explained on the simple electronic theory if the octet rule is inviolable.

On the introduction of a further carbonyl group, with formation of acetic anhydride, a marked increase in solubility is produced (8·5 to 12%), and the dielectric constant is increased from 5·85 to 20·5. In discussing this in relation to the parachor value for acetic anhydride (p. 1195), it was concluded that the results were consistent with the view that one carbonyl group was present and also an ester group. This view seems to be supported by the above data; but it must be pointed out that the solubility is still markedly less than that of a compound, such as methyl ethyl ketone, which contains only one carbonyl group, and also that acetylacetone, in which the two carbonyl groups are separated by a CH_2 group, in spite of its containing one more carbon atom in the molecule, has a greater solubility (14%) than the anhydride and also a higher dielectric constant (23·0). This is remarkable when one considers the very large diminution in solubility produced by one additional carbon atom in the molecule (compare, *e.g.*, diethyl ketone and methyl ethyl ketone, *n*-valeric acid and *n*-butyric acid, Table V).

One must conclude that there is marked conjugation between the three oxygen atoms in the molecule of acetic anhydride, a result which is in agreement with the fact that this substance does not behave chemically as if there were a free carbonyl group present. The insensitiveness of a physical property such as the parachor to structural changes which would have large effects on properties such as solubility or chemical reactivity is well known, *e.g.*, the marked difference in solubility of the isomeric butyl alcohols or C_4 esters which possess the same parachor, or the identity in value for the double bond whether it is conjugated or not, as in ethylene and benzene.

On the introduction of a carbonyl group contiguous to a hydroxyl group, *e.g.*, *iso*butyl alcohol⟶*iso*butyric acid, *n*-butyl alcohol⟶*n*-butyric acid, an extremely large increase of solubility occurs. The resulting carboxyl group produces a much greater increase in solubility than does a single carbonyl group alone. (The corresponding decrease in dielectric constant is undoubtedly due to the fact that association into dimeric molecules occurs in the absence of water.) On the other hand, that some mutual interaction does occur between these groups is supported by the marked difference in solubility between valeric acid (3·4%) and acetylacetone (14%), both C_5 compounds. This large solubility of the acids in water would seem to be opposed to the view that the single carboxyl group is a four-membered chelate ring. On the other hand, it does not give much support to the view that the non-reactivity of the carbonyl group in acids and esters is due to the same cause.

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