

not designed to be used, just as erroneous results may be obtained as when the original b. p. n.'s are used in an erroneous fashion. Since these calculations also show that it is not possible to obtain universal b. p. n.'s for the alkyl groups as Dr. Neyman-Pilat has attempted, it seems advisable to retain the original values which were obtained on the basis that the alkyl radicals were derivatives of the normal paraffin hydrocarbons and not of the 2-methylparaffins. It is essential that the longest chain in the molecule be considered as the base to which the smallest possible radicals are attached. Following this procedure always gives uniform results. The underlying reason is well known to organic chemists in the fact that the boiling point of a substance is not only dependent upon the kind and number of atoms in the molecule, but is also dependent upon the arrangement of those atoms and especially upon the length of the chain.

Dr. Neyman-Pilat has suggested that a higher b. p. n. for the ethyl group than that given in the original paper would give better results. However, it should be pointed out that this is true particularly for the paraffin hydrocarbons and that the value was adopted because it gave more uniform results with all types of organic compounds.

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Parachor of Aluminum Bromide in Benzene

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The work described here was carried out with the object of determining if the molecular formula of aluminum bromide when dissolved in benzene is the same as that determined for molten aluminum bromide.¹ The method used was to determine the mean parachor of solutions of aluminum bromide in benzene, and to see whether an extrapolation (assuming that the parachor obeys the straight line mixture law) to 100% solute using the formula of Hammick and Andrew² would lead to a value of the parachor of pure aluminum bromide that agrees with the value determined by Sugden.¹

In this method

$$P_m = M_m \gamma^{1/4} / d$$

$$M_m = M_2(X) + M_1(1 - X)$$

(1) Sugden, *J. Chem. Soc.*, 320 (1929).

(2) Hammick and Andrew, *ibid.*, 754 (1929).

Before many measurements had been made, however, it was noticed that the solutions of aluminum bromide in benzene gradually separated into two layers: one, a dense light red oil which turned dark brown-purple on standing, and a less dense colorless layer. All our measurements were made before the separation into the second phase occurred. B. Menshutkin³ found that the presence of moisture or the introduction of hydrogen bromide into solutions of aluminum bromide in benzene caused the separation into two layers. In our work no hydrogen bromide had been introduced, so it is probable that some water vapor had reacted with the aluminum bromide in the benzene, liberating hydrogen bromide, which in turn caused the formation of the heavy oil. Norris and Rubinstein⁴ investigating the formation of complexes of aluminum bromide with toluene in the presence of hydrogen bromide, found by analysis that the complex was $Al_2Br_6 \cdot 6C_6H_5CH_3$. The oil in the case of benzene is probably $Al_2Br_6 \cdot 6C_6H_6$.

Because of the formation of this oil we were unable to carry on work in more concentrated solutions.

Experimental.—The benzene was allowed to stand for one week over mercury, fractionated three times, and dried over phosphorus pentoxide.

Bromine was purified by the method of P. C. Terwogt.⁵

Aluminum bromide was prepared by the method of Kaveler and Monroe.⁶ Samples were distilled directly into weighing vials in an atmosphere of dry carbon dioxide.

Densities were determined with a pycnometer with ground glass caps.

Surface tensions were determined using a slightly modified form of Sugden's apparatus.⁷ Successive readings were consistent to within 0.4%.

All measurements were made at $34.90 \pm 0.03^\circ$.

Table I lists the results obtained when the formula Al_2Br_6 is assumed.

Density of solution, d	Mole fraction Al_2Br_6 , X	Mean mol. wt., M_m	Surface tension, γ dyne/cm.	Mean parachor P_m
0.9454	0.01737	84.21	26.55	206.6
1.0035	.03330	93.21	27.07	211.9
1.0250	.04195	97.15	27.45	217.0
1.1070	.06345	106.95	27.64	221.5
1.1173	.08325	115.96	27.74	238.3
Extrapolated value of mean parachor when $X = 1.00$				470.4

When plotted, the mean parachors deviate

(3) Menshutkin, *J. Russ. Phys.-Chem. Soc.*, 41, 1089 (1909).

(4) Norris and Rubinstein, *THIS JOURNAL*, 61, 1163 (1939).

(5) P. C. Terwogt, *Z. anorg. Chem.*, 47, 203 (1905).

(6) Kaveler and Monroe, *THIS JOURNAL*, 50, 2421 (1928).

(7) Sugden, *J. Chem. Soc.*, 125, 27 (1924).

from a straight line over the region investigated by 1% (the total change in the parachor in this range being 11%).

Sugden¹ had obtained 457.6 as the parachor of molten aluminum bromide, assuming the same formula Al_2Br_6 . The value obtained here deviates by 3% from Sugden's value. If Sugden had used the formulas $AlBr_3$ or Al_3Br_9 , he would have obtained parachors of 228.8 and 686.4, respectively; in this work the same formulas give values of 232.9 and 703.2 after extrapolation, which represent deviations of a little less than 3%.

Our extrapolation is over a large range, so that any errors made at low concentrations will magnify greatly the error in the final value of the parachor. For this reason, it is somewhat surprising that the extrapolated values for the solution fall so near the values for the molten salt.

Owing to the above uncertainty, we can say only that the results obtained here tend to indicate that the formula of aluminum bromide dissolved in benzene is the same as that for the molten compound.

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Preparation of Di-*o*-tolylchloromethane

BY EUGENE B. REID

Incidental to a program of measurement of physical properties, di-*o*-tolylchloromethane was prepared. It has not been described previously in the literature.

o,o'-Dimethylbenzohydrol was prepared by reducing *o,o'*-dimethylbenzophenone with 2% sodium amalgam; m. p. 120.5–121.5°. Boyd and Hatt¹ found 119–119.5°. A benzene solution of the carbinol was kept in contact with a concentrated aqueous hydrochloric acid solution for two days; the two layers were separated, and the benzene solvent evaporated. The di-*o*-tolylchloromethane crystallized from petroleum ether as long prisms; m. p. 70–71°; yield 90%.

Anal. Calcd. for $C_{15}H_{15}Cl$: Cl, 15.37. Found: Cl, 15.44.

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(1) Boyd and Hatt, *J. Chem. Soc.*, 898 (1927).

The Dipole Moment of the Amino Benzoic Acids in Dioxane

BY LLOYD VAN BLARICOM AND E. C. GILBERT

The dipole moments of *o*-, *m*- and *p*-aminobenzoic acid have been determined in water solution¹ in which solvent they occur partially in the zwitter-ion form. In non-polar solvents they should exist in ordinary molecular form but their low solubility has precluded measurements of their moment in such solvents. However, their solubility in dioxane proved upon examination to be sufficiently high to allow satisfactory measurements, which are reported in this paper. Dioxane has an additional advantage in that it does not cause association, in general, and it has therefore been used in the determination of the moments of many acids which associate in the ordinary non-polar solvents.²

Apparatus and Method.—The apparatus has been described previously.³ It is based upon the heterodyne beat method and has been demonstrated to give correct results on substances of known dielectric constant. Refractive index was measured with a Bausch and Lomb dipping refractometer. Densities were determined with a pycnometer designed to avoid evaporation losses.⁴ All weights were reduced to vacuum.

Materials.—Eastman Kodak Co. dioxane was refluxed with sodium hydroxide for ten hours and fractionated, discarding the first and last portions. It was then refluxed over sodium metal for another ten hours, and again distilled. That used for the measurements had the following constants: m. p. 11.7°; n_D^{25} 1.41990; e_D^{25} 2.2266; d_4^{25} 1.02681.

The amino acids were Eastman best grade, further recrystallized three times. They were boiled with charcoal when necessary to improve the color and fractionally crystallized. They had the melting points: ortho, 144.5–145°; meta, 173–174°; para, 187–188° (all corrected for emergent stem).

Results

The results are shown in Table I, and summarized in Table II. It is frequently assumed that the dipole moments of acids will be similar to those of their methyl esters. Estermann has determined the moments of the three methyl esters of these acids and they are included in the tables for comparison.⁵ In each case the moment of the free acid is greater than that of the ester by a considerable percentage.

Dielectric studies of these acids in aqueous solu-

(1) (a) Hedestrand, *Z. physik. Chem.*, **135A**, 36 (1928); (b) Devoto, *Gazz. chim. ital.*, **63**, 247 (1933).

(2) Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

(3) Frey and Gilbert, *THIS JOURNAL*, **59**, 1344 (1937).

(4) Gilbert and Stark, *ibid.*, **59**, 1818 (1937).

(5) Estermann, *Z. physik. Chem.*, **1B**, 134 (1928).