10 cc. per mole, of which we may tentatively assign 6 cc. to the carboxyl and 4 cc. to the methylated amino group.[37] Groups producing this amount of electrostriction in water should from the tables of the above-named authors in ethanol produce 23 and 18 cc. of electrostriction respectively, or a total of 41 cc. The observed value in ethanol (Fig. 4) is 40 cc. The agreement is far better than we should have any right to expect, considering the approximations involved in the theory itself and in its application to such substances as the betaines.

The results in mixed solvents are more difficult to interpret. It should be noted, however, that the electrostriction produced by ortho benz betaine is markedly greater in alcohol–ether mixtures than in alcohol-benzene mixtures of the same dielectric constant. It seems probable that this difference is correlated with the fact that ether is much more compressible than benzene.

It will be noted from Fig. 4 that the electrostriction of dimethylanthranilic acid is almost zero in water, and in all solvents is much lower than that of any of the betaines. Qualitatively these low values appear to parallel the relatively low δ values of this substance, and suggest that its electrical constitution must differ in some significant respect from that of the betaines.

Summary

1. Dielectric constant increments and apparent molal volumes have been determined for various betaines, and for N-dimethylanthranilic acid and its methyl ester in a variety of solvents ranging from water to benzene.

2. For the relatively rigid benz betaines, approximate dipole moments have been calculated on the basis of known interatomic distances. These have been compared with the values calculated from the observed dielectric increments with the aid of theoretical considerations.

3. In solvents of low dielectric constant, the dielectric increments (and probably the moments) of all the betaines studied fall far below their values in water. This effect appears to be due to actual deformation of the molecules rather than to association.

4. N-Dimethylanthranilic acid appears to exist largely as a zwitterion, not only in water and alcohol, but also in pure benzene, in which its dipole moment is more than three times as great as that of its methyl ester.

5. The electrostriction of the solvent produced by betaines in water is less than that produced by similar amino acids, presumably due to the greater bulk of the positively charged group in the betaines.

6. The electrostriction due to the betaines is much greater in solvents of low dielectric constant than in water, and the magnitude of the effects observed is in good accord with theoretical predictions.

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[37] The results of the ensuing calculation would not be significantly altered if we assigned 5 cc. to each group, or 7 cc. to one group and 3 to the other.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The "Salting-in" of Hydrogen Peroxide by Electrolytes

BY M. H. GORIN

Non-electrolytes are in general salted out of solution by the addition of electrolytes. The magnitude of this effect varies widely with the nature of the electrolyte and non-electrolyte, and in a few cases even changes in sign. However a search of the literature revealed that sodium chloride and sodium sulfate give relatively large salting-out effects with all non-electrolytes so far investigated, excepting hydrogen peroxide; Livingston[1] found the activity coefficient, $\gamma_{H_2O_2}$, of hydrogen peroxide to be less than unity in aqueous solutions of these salts. This is a "salting-in" effect of sodium chloride and sodium sulfate on hydrogen peroxide. On account of the exceptional nature of this result it was considered worth while to check Livingston's work with sodium chloride, and to study the behavior of hydrogen peroxide with several other electrolytes. The data are presented in Table I and plotted together with Livingston's in Fig. 1.

The experimental method used was the same as Livingston's; the distribution ratio of hydrogen peroxide between the salt solutions and iso-

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[1] Livingston, THIS JOURNAL, 50, 3207 (1928).

Table I

Experimental Results at 25°

Salt	Ionic strength[c] μ	R	$\gamma_{H_2O_2} = R_0/R$	Log $\gamma_{H_2O_2}$	Log $\gamma_{H_2O_2}/\mu$
$NaCl$[a]	1.02	7.62	0.929	−0.032	−0.032
NH_4Cl[a]	0.51	7.79	.910	− .041	− .080
NH_4Cl[a]	1.04	8.07	.878	− .057	− .055
NH_4Cl[a]	1.60	8.35	.848	− .072	− .045
NH_4Cl[a]	2.17	8.89	.797	− .098	− .045
NH_4Cl[a]	3.41	10.02	.707	− .152	− .045
NH_4Cl[b]	0.51	20.02	.918	− .037	− .073
NH_4Cl[b]	1.60	21.70	.847	− .072	− .045
NH_4Cl[b]	2.17	23.22	.791	− .102	− .047
KCl[a]	1.03	9.04	.784	− .106	− .103
KCl[a]	2.13	11.00	.644	− .192	− .090
$NaNO_3$[a]	1.03	7.66	.925	− .034	− .033
$NaNO_3$[a]	2.13	8.15	.869	− .061	− .029
NH_4NO_3[a]	1.05	7.77	.912	− .040	− .038
NH_4NO_3[a]	2.22	8.39	.845	− .073	− .033
KNO_3[a]	1.04	8.30	.853	− .069	− .066
KNO_3[a]	2.18	10.06	.705	− .152	− .070
NH_4ClO_4[a]	1.07	7.63	.929	− .032	− .030
NH_4ClO_4[a]	1.55	7.70	.922	− .035	− .021
H_2SO_4[a]	1.54	6.79	1.043	+ .018	+ .012
H_2SO_4[a]	3.14	6.39	1.108	+ .044	+ .014

[a] Solvent is isoamyl alcohol. [b] Solvent is 3 parts acetophenone + 1 part carbon tetrachloride. [c] μ is given in moles per 1000 g. of water.

amyl alcohol was determined; $\gamma_{H_2O_2}$ is given by the expression $\gamma_{H_2O_2} = R_0/R$ where R_0 is the distribution ratio of hydrogen peroxide between pure water (*i. e.*, hydrogen peroxide in water/hydrogen peroxide in isoamyl alcohol), and isoamyl alcohol, and R the distribution ratio of hydrogen peroxide between the salt solutions and isoamyl alcohol. The value, 7.08 ± 0.01, was found for R_0, while Livingston[1] used 6.95, an average between his value, 6.87, and that of Calvert,[2] 7.03 ± 0.05. In the case of ammonium chloride a solvent made up by adding one part of carbon tetrachloride to three parts of acetophenone was also used for the partition experiments, in order to confirm the results. R_0 was found to be 18.37 ± 0.07 for this mixture. The partition coefficient for pure acetophenone was found to be 11.55 ± 0.08. This value is far greater than the one previously given in the literature,[3] and is probably very much more nearly correct since the permanganate method used by these investigators[3] was found to give high results in the presence of acetophenone.

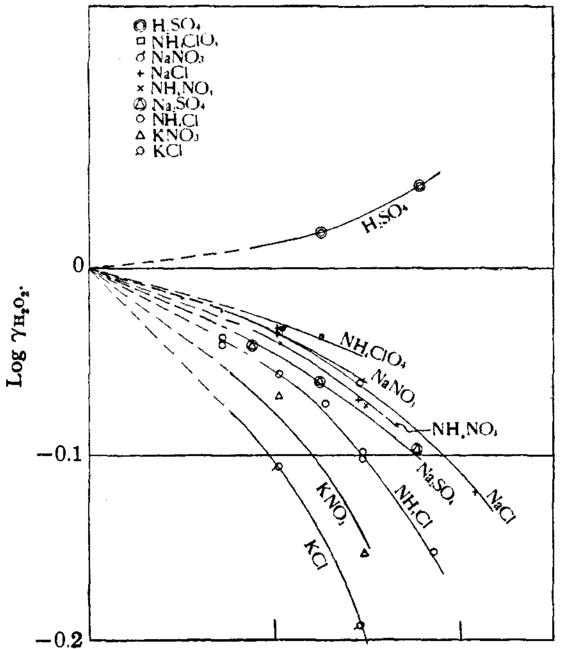

Fig. 1.

It is seen from Table I and Fig. 1 that $\gamma_{H_2O_2}$ is not only less than unity in sodium chloride and sodium sulfate solutions but also in solutions of all the salts studied; and that only in the case of sulfuric acid is $\gamma_{H_2O_2}$ greater than unity. Furthermore, the order of the "salting-in" of hydrogen peroxide by the ions under consideration as determined from Fig. 1, is as follows: $K^+ > NH_4^+ > Na^+ > H^+$ and for the negative ions, $SO_4^= > Cl^- > NO_3^- > ClO_4^-$. Randall and Failey[4] in an extensive survey of the subject, tentatively arranged these ions along with some others in the following order of decreasing "salting-out" power on non-electrolytes in general: $Na^+ > K^+ > NH_4^+ > H^+$ and $SO_4^= > Cl^- > NO_3^- > ClO_4^-$. A comparison of this classification with that found for hydrogen peroxide reveals that the order for the "salting-in" of hydrogen peroxide by negative ions is exactly the same as the order for the "salting-out" of non-electrolytes in general. The same could be said about the positive ions if sodium ion were excluded.

It should be noted that log $\gamma_{H_2O_2}$ has been plotted against $\mu^{1/2}$ instead of against μ, as would be required by the Debye–McAuley relation, log $\gamma = K\mu$. This was done because when plots of log $\gamma_{H_2O_2}$ against μ were tried, s-shaped curves resulted in the case of ammonium chloride; for this salt the measurements cover a wide range of ionic strength and the individual points were most closely determined. The other curves in Fig. 1

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(2) H. T. Calvert, *Z. physik. Chem.*, **38**, 513 (1901).

(3) See Walton and Lewis, This Journal, **38**, 634 (1916).

(4) Randall and Failey, *Chem. Rev.*, **4**, 290 (1927).

were drawn using the one for ammonium chloride as a model. It appears, therefore, that the Debye–McAuley law is not suitable for the case of hydrogen peroxide.

The evidence here presented proves that the behavior of hydrogen peroxide in solutions of electrolytes is different from that of other non-electrolytes; and requires that the hydrogen peroxide molecules tend to displace the water molecules surrounding all ions. However, in the case of the very small hydrogen ion there is a small "salting-out" effect instead of the relatively large "salting-in" effects shown by other ions. This is probably due to the preferential formation of hydronium ion, since it is reasonable to assume that the equilibrium

$$H_3O_2^+ + H_2O = H_3O^+ + H_2O_2$$

lies far to the right; and to the fact that hydronium ion carries relatively little hydrogen peroxide or water.

The displacement of water by hydrogen peroxide can be explained by the higher dipole moment of the peroxide molecule than that of the water molecule in the neighborhood of an ion. The following structure for hydrogen peroxide would yield a dipole moment of 3.01×10^{-18} as compared with 1.84×10^{-18} for water.

This structure differs from the one assigned to hydrogen peroxide in the gas phase by Penney and Sutherland[5] and can only exist in the strong potential fields surrounding an ion.

The dipole moment of gaseous hydrogen peroxide[6] is practically the same as that of water. Penney and Sutherland[5] have found that the most plausible structure of hydrogen peroxide is a highly skewed one, with an oxygen–oxygen single bond and a hydrogen atom on each oxygen, without free rotation around the O—O bond, the most stable configuration being the one in which the O—H bonds make an angle of 90° with each other. The $\mathrm{O{-}O}\diagup^{\mathrm{H}}$ bond angle is the same as in water, 110°, and the dipole moment for this model agrees very well with the observed one.[6] But the difference in potential between the model given in Fig. 2 and the stable configuration of the gaseous state was found by Penney and Sutherland[5] to be only of the order of magnitude of 25,000 calories. Therefore, it is probable that the hydrogen peroxide molecule assumes the structure shown in Fig. 2 as it approaches an ion, since the potential at the surface of even a large ion tending to rotate the O—H dipole is far greater in magnitude than 25,000 calories.

The order of the "salting-in" of hydrogen peroxide by the various positive and negative ions remains to be explained. The structure given in Fig. 2 for the hydrogen peroxide molecule is very similar to that of the water molecule as it orients itself around a negative ion; that is, the H—H distances are nearly the same in the two molecules and therefore it would be expected that hydrogen peroxide would tend to displace water around all negative ions since it has a higher dipole moment. Therefore, the order for the "salting-in" of hydrogen peroxide would be identical with the order for the "salting-out" of other non-electrolytes by negative ions, because the ions which hold the most water would be expected to hold the most hydrogen peroxide. This expectation agrees very well with the experimental findings for the four negative ions investigated. When oriented toward a positive ion, however, the water molecules can pack more closely around it than the peroxide molecules, since in this case the oxygen atoms rather than the hydrogen atoms are pointing toward the ion. Therefore, even though hydrogen peroxide has a higher dipole moment than water, it might be expected that in the case of the very smallest positive ions the equilibrium would favor water practically completely and as the ions increased in size hydrogen peroxide would begin to displace water. Only in the case of the larger positive ions, should hydrogen peroxide be "salted-in" in the same order as other non-electrolytes are "salted-out." The above discussion

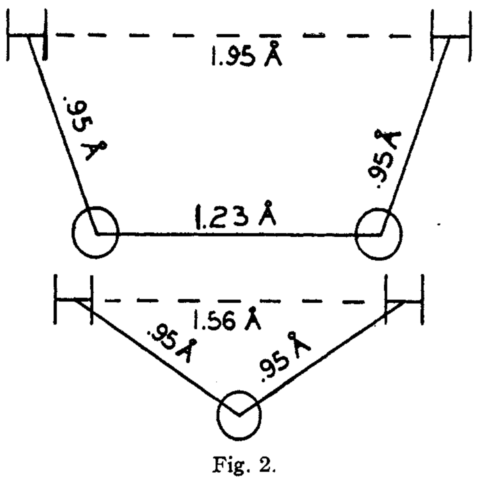

Fig. 2.

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[5] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

[6] See Linton and Maass, *Canadian J. Research*, **7**, 81 (1932).

explains the experimental result that hydrogen peroxide is "salted-in" more by potassium ion than by sodium ion, while other non-electrolytes are "salted-out" more by sodium ion than by potassium ion.

In conclusion I wish to express my gratitude to Professor W. C. Bray for suggesting the problem, and for his very helpful suggestions and criticism during the progress of the work.

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[CONTRIBUTION NO. 159 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXII. α-Dialkylaminomethyl-β-vinylacetylenes

BY DONALD D. COFFMAN

The reaction of primary acetylenic compounds with formaldehyde and secondary aliphatic amines in dioxane has recently been shown to give good yields of aminomethyl derivatives having the formula $RC{\equiv}CCH_2NR_2$.[1] This reaction has been applied to vinylacetylene, and it proceeds smoothly with low molecular weight secondary aliphatic amines according to the equation

$$CH_2{=}CHC{\equiv}CH + CH_2O + HNR_2 \longrightarrow$$
$$\text{(I) } CH_2{=}CHC{\equiv}CCH_2NR_2 + H_2O$$

Members of this new class of amines (I) have been prepared by allowing a dioxane solution of vinylacetylene and paraformaldehyde to react with dimethylamine, diethylamine, piperidine and dicyclohexylamine in an autoclave at 100°. The reaction furnishes the lower members of the series in good yields. The properties of the amines obtained in this way are indicated in Table I. The compounds are stable, colorless liquids with characteristic odors.

TABLE I

PHYSICAL PROPERTIES OF α-DIALKYLAMINOMETHYL-β-VINYLACETYLENES

Nature of amine		B. p., °C.	d^{20}_4	n^{20}_D	MR Calcd.	MR Found	Exaltation
(II)	$(CH_3)_2N$-	133–135 at 752 mm.	0.8208	1.4700	35.99	37.05	1.06
(III)	$(C_2H_5)_2N$-	166–167 at 766 mm.	.8272	1.4710	45.23	46.34	1.11
(IV)	$(CH_2)_5N$-	207–209 at 766 mm.	.9069	1.5064	47.65	48.89	1.24
(V)	$(C_6H_{11})_2N$-	138–140 at 0.5 mm.	.9492	1.5191	77.78	78.35	0.57

TABLE II

PROPERTIES OF α-DIALKYLAMINOMETHYL CHLOROPRENES

Nature of amine		B. p., °C.	d^{20}_4	n^{20}_D	MR Calcd.	MR Found	Exaltation
(VI)	$(CH_3)_2N$-	56–58 at 11 mm.	0.9615	1.4895	42.40	43.73	1.33
(VII)	$(C_2H_5)_2N$-	71–73 at 5 mm.	.9500	1.4895	51.63	52.78	1.15
(VIII)	$(CH_2)_5N$-	90–92 at 3.5 mm.	1.0137	1.5193	54.05	55.59	1.54

The reactions of several typical members of this new class of amines have been studied. Compounds (III) and (IV) are readily hydrogenated to the corresponding saturated tertiary amines whose properties and derivatives agree with those already recorded in the literature.

Compounds (II), (III) and (IV) add hydrogen chloride in the presence of cuprous chloride, but they react more slowly with aqueous hydrochloric acid than does the parent hydrocarbon[2] so that elevated temperatures are required. The products (VI), (VII) and (VIII) of the reaction correspond in composition to structure (IX). By analogy with the formation of chloroprene from vinylacetylene, structure (IX) seems most likely.

(IX) $CH_2{=}CHCCl{=}CHCH_2N(R)_2$
(X) $p\text{-}CH_3C_6H_4SCH_2CH_2C{\equiv}CCH_2N(CH_3)_2$

The physical properties of these substituted chloroprenes are indicated in Table II. They are colorless liquids which darken on standing. Like chloroprene, they react with α-naphthoquinone and with maleic anhydride but the products are black tars. Unlike chloroprene, they polymerize very slowly even at 100° or when exposed to light, and no rubber-like polymer has yet been obtained from them. It has already been shown that α-substitution in 1,3-dienes decreases con-

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[1] Mannick and Chang, *Ber.*, **66**, 418 (1933).

[2] Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).