

copper interaction. Our results on PMA, especially those from the vibrational spectrum, favor the latter explanation.

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## Acid-Base Reactions in Concentrated Aqueous Quaternary Ammonium

### Salt Solutions. III. Dicarboxylic Acids

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A number of dicarboxylic acids were titrated with KOH in aqueous 7.75 *m* tetra-*n*-butylammonium bromide solutions at 25°. The ratio of the two dissociation constants was greater than in water for the following acids: maleic, *o*-phthalic, malonic, dimethyl- and di-*n*-propylmalonic, and succinic. The maleic acid ratio was greater than in water by more than  $4 \times 10^3$ . That for succinic acid was five times greater. The ratios for oxalic acid, for *m*- and *p*-phthalic acids, for fumaric acid, and for the longer-chain aliphatic dicarboxylic acids from glutaric to suberic were almost unchanged. Infrared spectra of some of these acids, their acid salts, and their fully neutralized salts were made in D<sub>2</sub>O and in 7.75 *m* tetra-*n*-butylammonium bromide solutions in D<sub>2</sub>O. With the exception of oxalic acid, those compounds which showed small changes in their dissociation constant ratios on transfer from water to the quaternary ammonium salt solution had monoacid salt spectra which were simple composites of those of the free acid and the fully neutralized salt. Acids which showed large changes in their ratios had monoacid anion spectra in which the carbonyl frequency of the acid moved to a lower frequency and the asymmetric carboxylate stretching frequency of the fully neutralized salt moved to a higher frequency, an effect which became larger in the quaternary ammonium salt solution. It was concluded that an internally hydrogen-bonded monoacid anion was formed by the latter acids and that water was a part of this structure. Since such a structure was not possible for the acid oxalate anion and since a dimer of this ion does not appear to exist in aqueous solution, it was concluded that the effects observed in the oxalic acid system are probably due to electrostatic forces.

### Introduction

On statistical grounds, the ratio of the first to the second dissociation constant of a diprotic acid should be 4. In water, the first three members of the homologous aliphatic series—oxalic, malonic, and succinic acids—possess ratios which are much greater than 4, and the theoretical statistical value is not reached even for long-chain dicarboxylic acids. Bjerrum attributed these high ratios to the electrical work which is required to remove the second proton from the negatively charged monoanion, an approach which was further developed by other workers.<sup>2,3</sup> An alternative explanation for the first three members of the homologous series was put forth by Jones and Soper, who suggested that an internal hydrogen bond would stabilize the acid salt.<sup>4</sup> This would result in an increase in the value of the first dissociation constant and a decrease in the second constant, producing the high ratios which are observed. Eberson found that  $\alpha, \alpha'$ -disubstituted racemic succinic acids had dissociation constant ratios which were very much larger than those

of the corresponding meso compounds and he concluded that the difference between them was due to a hydrogen-bonded intermediate for the acid salt in the preferred conformation of the racemic compound.<sup>5</sup> Miles and his coworkers further supported the hypothesis of an internally hydrogen-bonded intermediate by a potentiometric and kinetic study of the dissociation of disubstituted malonic acids in water.<sup>6</sup> On the other hand, Chapman, Lloyd, and Prince concluded from an examination of the infrared spectra of D<sub>2</sub>O solutions of a number of dicarboxylic acids and their salts that the hydrogen malonate ion, the hydrogen maleate ion, and

(1) Taken from a thesis submitted by R. De Iasi to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 508 (1938).

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the hydrogen *o*-phthalate ion were not internally hydrogen bonded.<sup>7</sup>

This paper describes the results of the potentiometric titration of a number of dibasic acids with KOH in aqueous 7.75 *m* tetra-*n*-butylammonium bromide solution (*n*-Bu<sub>4</sub>NBr) at 25.0°. In addition, measurements of the principal frequencies between 1800 and 1300 cm<sup>-1</sup>, which are observed in the infrared absorption spectra of a number of these acids and their salts, were made in D<sub>2</sub>O and in 7.75 *m* *n*-Bu<sub>4</sub>NBr solution (in D<sub>2</sub>O). Marked changes in the ratio of the two dissociation constants of a number of dicarboxylic acids in *n*-Bu<sub>4</sub>NBr solution compared to water were correlated with shifts in the infrared spectra and the correlation led us to the conclusion that some type of internally hydrogen-bonded monoacid anion was formed.

### Experimental Section

**A. Chemicals.** The acids were reagent grade products of Brothers, Matheson Coleman and Bell, Eastman Kodak, or K & K. Oxalic acid was purified according to Kolthoff and Sandell.<sup>8</sup> Adipic acid was recrystallized once from 1 *M* nitric acid and twice from distilled water. The other acids were recrystallized two or more times from either water or ethanol. Deuterated acids were prepared by recrystallization of purified acids from D<sub>2</sub>O. The monoacid salts were prepared by potentiometric neutralization of an aqueous solution of the acid with NaOH at the second equivalence point, addition of an equivalent quantity of acid, evaporation *in vacuo*, and recrystallization from D<sub>2</sub>O. A few experiments were performed with acid salts recrystallized from H<sub>2</sub>O, since there was not enough dilution of the D<sub>2</sub>O by the protons of the salt to interfere with the infrared measurements. The disodium salts were prepared by neutralization, were recrystallized from water, and were dried *in vacuo*. Potassium hydrogen phthalate was of reagent grade (Fisher Scientific) and was recrystallized from D<sub>2</sub>O. Other chemicals were described in the preceding articles of this series.<sup>9,10</sup>

**B. Potentiometric Titrations.** The acids (approximately 0.02 *M*) were titrated with 1 *M* KOH at 25.00 ± 0.05° in 7.75 *m* *n*-Bu<sub>4</sub>NBr. A Beckman Model G pH meter and ordinary glass and calomel electrodes were used. The negative logarithms of the dissociation constants recorded are not thermodynamic values, but are mixed acidity constants.<sup>9</sup> They were calculated according to Noyes' method,<sup>11</sup> using a computer program drawn up in FORTRAN IV language.

**C. Spectrophotometric Measurements.** Infrared spectra were measured on a Perkin-Elmer Model 521 spectrophotometer. The scanning rate was 10 cm<sup>-1</sup> sec<sup>-1</sup>, and the wave-number scale was expanded by a factor of 2; water-vapor peaks were used for calibration in the region of interest. Each run was checked

against the wave-number scale. The frequencies which are reported are probably accurate to within 1–2 wave numbers. The sample solutions were held in a 0.1-mm pathlength demountable liquid cell (Barnes Engineering Co.). The reference solution was held in a Limit Corp. variable-thickness cell. Both cells were equipped with calcium fluoride windows. Path lengths were matched by adjusting the path length of the reference cell until all solvent bands were eliminated between 1800 and 1300 cm<sup>-1</sup>.

### Results and Discussion

Table I shows the values at 25° of the thermodynamic dissociation constants (called  $pK_{A,1}$  and  $pK_{A,2}$ ) in water of the dibasic acids under study, together with their mixed acidity constants called  $pK'_1$  and  $pK'_2$  in 7.75 *m* *n*-Bu<sub>4</sub>NBr. The table shows the values of the ratios  $K_{A,1}/K_{A,2}$  and  $K'_1/K'_2$ , as well as the ratio of the ratios  $(K'_1/K'_2)/(K_{A,1}/K_{A,2})$ . The constants for propionic acid and benzoic acid have been added<sup>9</sup> in order to show the behavior of typical carboxylic acids in this medium.

The results shown in Table I must be viewed in the light of the effect of quaternary ammonium salts on the structure of liquid water. Unlike most inorganic electrolytes, these compounds cause an increase in the hydrogen bonding of the water surrounding them.<sup>12</sup> This is evident from such properties as the high positive viscosity *B* coefficients of their aqueous solutions,<sup>13</sup> the high positive heat capacities of these solutions,<sup>12</sup> and their increased molar dielectric relaxation times.<sup>14</sup> Previous investigations of some chemical reactions in 7.75 *m* *n*-Bu<sub>4</sub>NBr at 25° showed that the mixed acidity constants of aliphatic carboxylic acids were approximately 2.2 units greater than their thermodynamic  $pK_A$  values in water.<sup>9</sup> Benzoic acid behaved similarly. *Meta*- and *para*-substituted benzoic acids showed somewhat smaller increases.<sup>10</sup> In this medium the *ortho* effect in monosubstituted benzoic acids was not observed, and the *ortho* isomers showed larger increases in  $pK'$  (about 2.7 units).

Table I shows that in 7.75 *m* *n*-Bu<sub>4</sub>NBr the mixed acidity constants of the longer-chain aliphatic dicarboxylic acids (from glutaric to suberic) are numerically

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**Table I:**  $pK_A$  and  $pK'$  Values of Dibasic Acids in Water and in 7.75 *m* *n*-Bu<sub>4</sub>NBr Solution at  $25 \pm 0.05^\circ$ , and Values of  $K_{A,1}/K_{A,2}$ ,  $K'_1/K'_2$ , and  $(K'_1/K'_2)/(K_{A,1}/K_{A,2})$ 

Acid	$pK_{A,1}^{a,b,c}$ (H <sub>2</sub> O)	$pK_{A,2}^{a,b,c}$ (H <sub>2</sub> O)	$pK'_1$ ( <i>n</i> -Bu <sub>4</sub> NBr)	$pK'_2$ ( <i>n</i> -Bu <sub>4</sub> NBr)	$K_{A,1}/K_{A,2}$ (H <sub>2</sub> O)	$K'_1/K'_2$ ( <i>n</i> -Bu <sub>4</sub> NBr)	$(K'_1/K'_2)/$ $(K_{A,1}/K_{A,2})$
Oxalic	1.27	4.27	$2.91 \pm 0.02$	$6.09 \pm 0.03$	1,000	1,510	1.51
Malonic	2.86	5.70	$3.43 \pm 0.03$	$8.39 \pm 0.03$	690	92,500	134
Succinic	4.21	5.64	$5.59 \pm 0.07$	$7.71 \pm 0.02$	26.9	132	4.9
Glutaric	4.34	5.27	$6.47 \pm 0.02$	$7.22 \pm 0.09$	8.50	5.61	0.67
Adipic	4.41	5.28	$6.70 \pm 0.05$	$7.48 \pm 0.04$	7.42	6.02	0.81
Pimelic	4.51	5.31	$6.59 \pm 0.02$	$7.25 \pm 0.01$	6.31	4.52	0.72
Suberic	4.52	5.33	$6.83 \pm 0.10$	$7.44 \pm 0.05$	6.30	4.09	0.65
Dimethylmalonic	3.15	6.20	$4.52 \pm 0.03$	$9.52 \pm 0.05$	1,120	102,000	91
Di- <i>n</i> -propylmalonic	2.15	7.34	$3.34 \pm 0.03$	$11.19 \pm 0.01$	316,000	72,000,000	228
Maleic	1.92	6.23	$1.93 \pm 0.03$	$9.86 \pm 0.06$	20,000	85,600,000	4280
Fumaric	3.02	4.38	$4.95 \pm 0.03$	$6.50 \pm 0.03$	23.0	36.2	1.57
Phthalic ( <i>ortho</i> )	2.95	5.41	$2.87 \pm 0.09$	$8.25 \pm 0.04$	290	240,000	827
Isophthalic ( <i>meta</i> )	3.62	4.60	$5.17 \pm 0.02$	$5.95 \pm 0.03$	9.56	6.2	0.65
Terephthalic ( <i>para</i> )	3.54	4.46	$5.27 \pm 0.03$	$6.58 \pm 0.03$	8.3	20.4	2.46
Propionic	4.87		$7.04 \pm 0.03$				
Benzoic	4.20		$6.30 \pm 0.01$				

<sup>a</sup> Reference 11, p 134. <sup>b</sup> H. C. Brown, D. H. McDaniel, and O. Haflinger in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955. <sup>c</sup> G. Kortum, W. Vogel, and K. Andrussov, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co. Ltd., London, 1961.

greater than the thermodynamic  $pK_A$  values in water by 2.0–2.3 units for both dissociations. They are behaving like normal aliphatic acids. The same change is evident in fumaric acid. Isophthalic and terephthalic acids show changes which are only several tenths of a  $pK'$  unit from other benzoic acids. Oxalic acid, which shows a change of about 1.6  $pK'$  units for both dissociations, represents a special case which is discussed below.

On the other hand, malonic acid, the substituted malonic acids, maleic acid, and *o*-phthalic acid show abnormal differences between the  $pK_A$  values in water and the  $pK'$  values in the quaternary ammonium salt solution. In each case the first mixed acidity constant ( $pK'$ ) is much smaller than that found for a normal aliphatic acid in this solvent, and the second constant ( $pK'_2$ ) is much larger. Thus the value of  $pK'_1$  for maleic acid is 2.2 units less than the expected value for the first dissociation process, and the value of  $pK'_2$  is 1.5 units greater than expected. Phthalic acid shows similar behavior if one takes into account the disappearance of the *ortho* effect for other monosubstituted benzoic acids. Succinic acid is tentatively included in this group; here the effect is small and is limited to the first dissociation. These results suggest that in this strongly organized solvent the monoprotic anion is being stabilized in some fashion, perhaps by incorporation into an organized cluster of water molecules. However, this explanation is insufficient to account for the difference between malonic and glutaric acids. It is necessary to attribute some specific structural effect to the monoacid malonate anion as well. This could be the internally hydrogen-bonded

anion described earlier,<sup>4–6</sup> which is evidently much more stable in the quaternary ammonium salt solution than in water.

In order to examine this hypothesis by another method, infrared studies of solutions of a number of the acids of Table I, their acid salts, and their fully neutralized salts were made at room temperature in D<sub>2</sub>O and in 7.75 *m* *n*-Bu<sub>4</sub>NBr in D<sub>2</sub>O. The solute concentrations were 1 *M* or less (depending on solubility). The results are shown in Table II, together with those of acetic acid and benzoic acid. The state of the acid refers to the solute: D<sub>2</sub>A stands for the dicarboxylic acid, DA<sup>−</sup> for the monoacid anion, and A<sup>2−</sup> for the fully neutralized salt. The symbols  $\nu_{CO(D_2A)}$  and  $\nu_{CO(DA^-)}$  represent the carbonyl stretching wave numbers of the D<sub>2</sub>A and DA<sup>−</sup> forms, respectively;  $\nu_{COO-(asym)(DA^-)}$  and  $\nu_{COO-(sym)(A^{2-})}$  stand for the asymmetric carboxylate stretches of the DA<sup>−</sup> and A<sup>2−</sup> forms, and  $\nu_{COO-(sym)(DA^-)}$  and  $\nu_{COO-(sym)(A^{2-})}$  stand for the symmetric carboxylate stretches of the same two forms.

The infrared spectra of some of these acids in D<sub>2</sub>O solution were previously measured by Chapman, Lloyd, and Prince.<sup>7</sup> There are some numerical differences between their values and those reported here. In general we believe that the present values are more accurate because of the difference in resolution between the Perkin-Elmer Model 21 (which they used) and the Model 521 used by us. With a sodium chloride prism the resolution of the Model 21 is approximately  $\pm 5$  cm<sup>−1</sup> in the region of interest. That of the Model 521 is  $\pm 1$  cm<sup>−1</sup>. In addition, our spectra were recorded with a slow scan on an expanded wave-number scale.

**Table II:** Wave Numbers of Dicarboxylic Acids and Salts in D<sub>2</sub>O and in 7.75 *m* *n*-Bu<sub>4</sub>NBr in D<sub>2</sub>O at Room Temperature

Acid	State	$\nu_{\text{C=O}}, \text{ cm}^{-1}$		$\nu_{\text{COO}^-}(\text{asym}), \text{ cm}^{-1}$		$\nu_{\text{COO}^-}(\text{sym}), \text{ cm}^{-1}$	
		D <sub>2</sub> O	<i>n</i> -Bu <sub>4</sub> NBr	D <sub>2</sub> O	<i>n</i> -Bu <sub>4</sub> NBr	D <sub>2</sub> O	<i>n</i> -Bu <sub>4</sub> NBr
Oxalic	D <sub>2</sub> O	1733	1741				
	DA <sup>-</sup>	1718, 1700	1736 (1766), 1711	1634	1643	1418	1400
	A <sup>2-</sup>			1573	1573	1308	1305
Malonic	D <sub>2</sub> A	1705	1722				
	DA <sup>-</sup>	1696	1706	1583	1600	1410	1398
	A <sup>2-</sup>			1571	1573	1433	1433
Di- <i>n</i> -propyl-malonic	D <sub>2</sub> A	1688	1705				
	DA <sup>-</sup>	1676	1693	1582	1611	1409	1401
	A <sup>2-</sup>			1549	1562	1410	1404
Succinic	D <sub>2</sub> A	1706	1717				
	DA <sup>-</sup>	1700	1701	1560	1565	1397	1398
	A <sup>2-</sup>			1559	1563	1394	1388
Glutaric	D <sub>2</sub> A	1699	1713				
	DA <sup>-</sup>	1695	1711	1554	1564	1405	1394
	A <sup>2-</sup>			1559	1561	1400	1396
Adipic	D <sub>2</sub> A	1695	1714				
	DA <sup>-</sup>	1694	1710	1550	1563	1406	1400
	A <sup>2-</sup>			1547	1563	1405	1397
Fumaric	D <sub>2</sub> A	1695	1700				
	DA <sup>-</sup>	1693	1698	1570	1582	1353	1333
	A <sup>2-</sup>			1565	1569	1375	1367
Maleic	D <sub>2</sub> A	1698	1708				
	DA <sup>-</sup>	1683	1683	1574	1599	1420	1401
	A <sup>2-</sup>			1559	1564	1431	1427
<i>o</i> -Phthalic	D <sub>2</sub> A	1693	1705				
	DA <sup>-</sup>	1693	1640	1583	1590	1402	1391
	A <sup>2-</sup>			1559	1565	1403	1399
Acetic	DA	1710	1721				
	A <sup>-</sup>			1560	1568	1415	1407
Benzoic	DA	1680	1695				
	A <sup>-</sup>			1545	1557	1388	1373

Table II shows that the spectra of the DA<sup>-</sup> forms of glutaric and adipic acids are almost exact superpositions of the spectra of the D<sub>2</sub>A and A<sup>2-</sup> species, both in D<sub>2</sub>O and in the quaternary ammonium salt solution. It can be concluded that these monoprotic anions possess a carboxylic acid group and a carboxylate group which do not interact with each other. This is further confirmed by the observation that the differences between the carboxylate asymmetric frequencies in the DA<sup>-</sup> states and the carbonyl stretches in the D<sub>2</sub>A states of these acids are almost the same as the difference between the acetate carboxylate frequency and the acetic acid carbonyl stretch (145–150 cm<sup>-1</sup>).

At the other extreme, the spectra of the acid oxalate anion in both media are very different from those of oxalic acid and oxalate ion. The differences in the asymmetric carboxylate modes between the DA<sup>-</sup> and A<sup>2-</sup> are particularly striking. The other acids in Table II fall between glutaric acid on the one hand and oxalic acid on the other. Table III represents an appropriate reorganization of the data of Table II. The symbol  $\Delta\nu_{\text{COO}^-}(\text{DA}^- - \text{A}^{2-})$  stands for the difference in the asymmetric carboxylate stretching frequencies of the two ions.

**Table III:** Differences in Carbonyl and Carboxylate Stretching Frequencies of Dicarboxylic Acids in D<sub>2</sub>O and in 7.75 *m* *n*-Bu<sub>4</sub>NBr in D<sub>2</sub>O at Room Temperature

Acid	$\Delta\nu_{\text{CO}}(\text{D}_2\text{A} - \text{DA}^-), \text{ cm}^{-1}$		$\Delta\nu_{\text{COO}^-}(\text{asym})(\text{DA}^- - \text{A}^{2-}), \text{ cm}^{-1}$	
	D <sub>2</sub> O	<i>n</i> -Bu <sub>4</sub> NBr	D <sub>2</sub> O	<i>n</i> -Bu <sub>4</sub> NBr
Glutaric	4	2	3	3
Adipic	1	4	3	0
Succinic	6	16	1	2
Malonic	9	16	12	27
Di- <i>n</i> -propyl-malonic	12	12	33	49
Maleic	15	25	15	35
Fumaric	2	2	5	13
Phthalic	0	65	24	25
Oxalic	15, 33	5, 31	61	70

Our interpretation of these results is based on the analysis of Chapman, *et al.*,<sup>7</sup> who pointed out that a hydrogen-bonded carboxyl group shows a lower carbonyl frequency than a nonhydrogen-bonded group, and that the asymmetric carboxylate frequency is raised by hydrogen bonding. They quote Ebersson, who found that substituted succinic acids in D<sub>2</sub>O

showed  $35\text{ cm}^{-1}$  increases in the carboxylate asymmetric stretch and  $30\text{ cm}^{-1}$  decreases in the carbonyl frequencies of COOH groups on hydrogen bonding.<sup>15</sup> Malonic acid, di-*n*-propylmalonic acid, *o*-phthalic acid, and maleic acid show differences in both sets of frequencies which become larger in the quaternary ammonium salt solution. Since the ratios of the dissociation constants of these acids are very much larger in  $7.75\text{ }m\text{ }n\text{-Bu}_4\text{NBr}$  than in water, the solvent is clearly involved in the stabilization of the acid anions. Both observations are consistent with an internally hydrogen-bonded monoacid anion in which one or more water molecules are hydrogen bonded to the carboxylate and carboxylic acid groups (a proposal originally advanced by Ives<sup>16</sup>). Such a hydrogen bond would be weaker than a simple hydrogen bond, because it would be subjected to collision and exchange with solvent molecules, but unlike a normal internal hydrogen bond it would be strengthened by the increased organization of the solvent in the  $n\text{-Bu}_4\text{NBr}$  solution.

Succinic acid shows these spectral shifts only in its carbonyl frequencies, and the ratio of its dissociation constants shows a small change on transfer to the quaternary ammonium salt solution. It is tentatively included in the preceding group of acids, but it probably forms a very weakly hydrogen-bonded acid anion.

Glutaric acid and the longer-chain dicarboxylic acids form acid anions in which there is no longer any interaction between the carboxylic acid group and the carboxylate anion. This is borne out by both the potentiometric and the spectroscopic results.

The spectroscopic behavior of fumaric acid is difficult to explain. It is impossible for it to form a simple internally hydrogen-bonded  $\text{DA}^-$  anion for geometrical reasons.<sup>7</sup> At the same time, the ratio of its dissociation constants shows very little change on transfer to  $n\text{-Bu}_4\text{NBr}$  solution, pointing to little or no solvent incorporation into the acid anion. In any event, the changes in its absorption band frequencies are much smaller than those of maleic acid. It is concluded that whereas maleic acid forms an internally hydrogen-bonded acid anion with solvent participation, fumaric acid does not do so.

The monoacid oxalate anion presents a special case. The ratio of the dissociation constants of the acid is practically the same in water and in  $7.75\text{ }m\text{ }n\text{-Bu}_4\text{NBr}$ . The differences in the carbonyl frequency between the  $\text{D}_2\text{A}$  and  $\text{DA}^-$  forms and in the asymmetric carboxylate frequency between the  $\text{DA}^-$  and  $\text{A}^{2-}$  forms are the largest shown in Table III. These results could be explained by the formation in the acid anion of a strong intramolecular hydrogen bond which is unaffected by the extent of organization of the solvent around it. However, there is reason to believe that such a hydrogen bond cannot be formed in the ion. The crystal structure of  $\text{KHC}_2\text{O}_4$  was partly elucidated by Hendricks.<sup>17</sup> From his data it was possible to calculate the various

distances and angles in the anion, which is planar. The two oxygen atoms between which an intramolecular hydrogen bond must be formed are about  $2.9\text{ \AA}$  apart, which is a little beyond the upper limit of known O-H-O linear distances.<sup>18</sup> However, the bond cannot be formed in a straight line between them. If it is assumed that there is a normal O-H bond distance on one carbon atom at a C-O-H angle of  $120^\circ$ , the distance between the hydrogen atom and the oxygen atom of the second carbon atom is  $2.5\text{ \AA}$  (the expected van der Waals distance) and, furthermore, the angle between them does not permit any interaction with the appropriate oxygen orbital. The situation is not improved by placing the hydrogen midway between the two oxygen atoms in a bent hydrogen bond. The O-H-O angle is then  $120^\circ$ , and in addition the contour length of the hydrogen bond is at least  $3.5\text{ \AA}$ . A final decision cannot be made until a more precisely measured anion structure is made, but certainly an intramolecular hydrogen bond is not possible in the light of presently available knowledge. The difficulty could be resolved by the formation of a stable dimeric acid anion in solution with two internal hydrogen bonds. However, an analysis of the electrical conductivity of sodium hydrogen oxalate in water shows, after appropriate corrections, that it behaves like a 1:1 electrolyte, and not like a 2:1 electrolyte.<sup>19</sup> Further, the molal freezing-point depression of aqueous potassium acid oxalate solutions is quite close to that of potassium bicarbonate at almost equivalent concentrations, and it is markedly different from those of  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{CO}_3$  (which in turn are almost the same).<sup>20</sup> It can be concluded that the acid oxalate ion is predominantly or entirely monomeric in water. It is possible that the carbonyl frequency differences between oxalic acid and the acid oxalate ion and the asymmetric carboxylate frequency difference between the acid oxalate and the oxalate ions are due to electrostatic forces. If so, these forces would also explain the value of the ratio of the dissociation constants in water.

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## Volume Changes on Mixing Solutions of Alkali Halides and Symmetrical

### Tetraalkylammonium Halides. II. Effects of Deuterium

#### Oxide and Temperature

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Volume changes on mixing aqueous solutions of potassium bromide and some tetraalkylammonium bromides have been measured at constant total ionic strength in  $D_2O$  at  $25^\circ$  and in  $H_2O$  at  $15$  and  $25^\circ$ . In addition, the volume changes on mixing solutions of  $Pr_4NBr$  and  $CsBr$ , as well as  $Pr_4NBr$  and  $Me_4NBr$ , have been determined at  $25^\circ$ . The results are explicable in terms of the solvent structural changes induced by the ion-ion and ion-solvent interaction.

#### Introduction

In a previous paper we have reported a study on volume changes on mixing aqueous solutions of potassium bromide and symmetrical tetraalkylammonium bromides at  $25^\circ$ .<sup>1</sup> The results obtained were analyzed in terms of the ionic solution theory of Friedman,<sup>2</sup> and evidence for the cation-cation interaction has been presented. To gain further understanding of the ion-ion and ion-solvent interaction, we have carried out the measurements of  $D_2O$  solutions at  $25^\circ$  and  $H_2O$  solutions at  $15$  and  $25^\circ$ . In addition, the volume changes on mixing solutions of  $Pr_4NBr$  and  $CsBr$ , as well as  $Pr_4NBr$  and  $Me_4NBr$ , have been determined at  $25^\circ$ .

#### Experimental Section

Fisher Certified potassium bromide was recrystallized twice from water and dried carefully before use. The bromide was analyzed gravimetrically and found to be 99.9% or better in agreement with the calculated value. Three tetraalkylammonium salts ( $Me_4NBr$ ,  $Et_4NBr$ , and  $Pr_4NBr$ ) were obtained from the Distillation Products Industries and each recrystallized twice or more from the suitable solvents<sup>3</sup> and dried at proper temperatures<sup>4</sup> before use. The gravimetric analyses of the cations<sup>5</sup> and the anions indicated their purities to be at least 99.9%. Deuterium oxide (99.8%) obtained from the Stohler Isotope Chemicals and cesium bromide (99.9%) obtained from the Chemi-

cals Procurement Laboratories were used without further purification.

Volume changes on mixing solutions of equal molal ionic strength were measured by use of a dilatometer similar to that reported by Wirth, Lindstrom, and Johnson.<sup>6</sup> The details of the apparatus and procedure for measurements have been described in paper I. The precision for values of  $\Delta_m V^{ex}$  obtained in our experiments at  $y = 0.5$  is  $\pm 0.008$  ml at  $I = 0.5$ ,  $\pm 0.004$  ml at  $I = 1.0$ , and  $\pm 0.002$  ml at  $I = 2.0$ .

#### Results and Discussion

We define the excess function on mixing as follows

$$\Delta_m V^{ex}(y, I) = V^{ex}(y, I) - yV^{ex}(1, I) - (1 - y)V^{ex}(0, I) \quad (1)$$

where  $I$  is the total ionic strength,  $y$  is the fraction of the molal ionic strength due to AX in a mixture of AX and BX, and  $V^{ex}(y, I)$  is the excess volume of the

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