

## LETTERS TO THE EDITOR

### STUDY OF IONIC HYDRATION AND ITS VARIATION WITH TEMPERATURE

In aqueous electrolytic solutions, the solute-solvent interactions result from the splitting up of the solute into ions when it diffuses through the solution and each ion is surrounded by a definite number of water molecules. Since water is considered as the best solvent, the solvation features are explained mostly to aqueous solutions only. Bockris<sup>1</sup> suggested the term "primary hydration" that should be used as a reference to the number of solvent molecules near to an ion which have lost their translational degree of freedom and move as one entity with the ion during its Brownian motion. In the present investigation, determination of primary hydration is considered.

Determination of hydration numbers is based on the measurement of the adiabatic compressibility of solution at infinite dilution. This measurement with acoustic interferometer yields ionic hydration numbers which are very close to those evaluated by ionic mobility and entropy methods. Variable path acoustic interferometer, working at 700 Kcs, is used to evaluate the hydration numbers of metallic ions belonging to (1-1), (2-1) valent type electrolytes at different temperatures ranging from 35° C to 55° C. Wada *et al.*<sup>2</sup> developed the expressions for hydration number  $n^\circ$ .

$$\phi^\circ (K) = -\beta_0 v_h$$

where  $\phi^\circ (K)$  is apparent molar compressibility at infinite dilution, and the volume of water molecules attached to each ion  $v_h$  is the product of  $n^\circ$  and molar volume of water  $v_0$  at the temperature of investigation. After studying the apparent molar compressibility  $\phi^\circ (K)$  in the case of  $\text{NH}_4\text{I}$  Owen and Brinkley<sup>3</sup> found positive values of  $\phi^\circ (K)$  in the case of  $\text{NH}_4\text{I}$ . Padova<sup>3</sup> has explained the situation by assuming that ions like  $\text{NH}_4^+$  and  $\text{I}^-$  are not hydrated. Padova has come to a conclusion that ion like  $\text{I}^-$  is not hydrated. Employing additive rule, cationic hydration numbers for  $\text{Li}^+$ ,  $\text{Rb}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Zn}^{++}$  and  $\text{Th}^{++++}$  have been evaluated, taking Padova's values of  $n^\circ$  for  $\text{I}^-$  and  $\text{NO}_3^-$ . These are compared against the computed values of Padova in Table I. There is close agreement between these values.

In the course of our study, we have an interesting situation in the cases of  $\text{Zn}^{++}$  and  $\text{Cd}^{++}$ . In these two cases, cationic hydration numbers evaluated from the corresponding halides do not show an

agreement among themselves and also against values computed by Padova. The results are presented in Table II.

TABLE I

Cationic hydration numbers compared between experimental data at 35° C and computed data of Padova at 25° C

Cation	Hydration numbers from	
	Experimental data	Computed data
$\text{Li}^+$	..	3
$\text{Rb}^+$	..	2
$\text{Ba}^{++}$	..	8
$\text{Ca}^{++}$	..	7
$\text{Th}^{++++}$	..	14

TABLE II

Hydration numbers of  $\text{Zn}^{++}$  and  $\text{Cd}^{++}$  compared against computed values of Padova

Cations $\text{M}^{++}$	Hydration numbers from <sup>5, 6</sup>			Computed values
	$\text{MCl}_2$	$\text{MBr}_2$	$\text{MI}_2$	
$\text{Zn}^{++}$	..	0	2	11
$\text{Cd}^{++}$	..	2	5	10

The hydration numbers for metallic ions of  $\text{Li}^+$ ,  $\text{Rb}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$  and  $\text{Zn}^{++}$  have been studied as a function of temperature. In all these cases ' $n^\circ$ ' decreased with increase in temperature.

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### CALCULATION OF CHARGE DENSITIES AT VARIOUS ATOMIC SITES OF PHTHALIC ACID

THE intermolecular resonance integrals play an important role in the calculation of energy band structures and mobilities of excess charge carriers in organic molecular crystals<sup>1-3</sup>. Such integrals require for their evaluation, a suitable molecular potential

TABLE I  
Wheland coefficients corresponding to filled orbitals of phthalic acid

Energy levels in units of $\beta$	Symmetry	Wheland coefficients					
		$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$
-0.8290	$A_1$	0.4156	-0.0223	-0.4343	-0.4343	-0.0223	0.4156
-1.1004	$A_1$	0.5099	0.2697	-0.1093	-0.1093	0.2697	0.5099
-1.1000	$A_2$	0.1918	0.4850	0.5497	-0.5497	-0.4850	-0.1918
-1.3053	$A_1$	-0.3278	-0.3572	-0.3732	-0.3732	-0.3572	-0.3278
-1.7033	$A_2$	-0.1022	-0.0391	-0.0097	-0.0097	0.0391	0.1022
-1.7385	$A_1$	-0.2129	0.0847	0.0399	0.0399	0.0847	0.2129

Energy levels in units of $\beta$	Symmetry	Wheland coefficients					
		$C_7$	$C_8$	$C_9$	$C_{10}$	$C_{11}$	$C_{12}$
-0.8290	$A_1$	0.0436	0.0436	-0.1531	-0.1531	-0.1531	-0.1531
-1.1004	$A_1$	0	0	-0.2111	-0.2111	-0.2111	-0.2111
-1.1000	$A_2$	0	0	0.0794	-0.0794	0.0794	-0.0794
-1.3053	$A_1$	0.0436	0.0436	0.1710	0.1710	0.1710	0.1710
-1.7033	$A_2$	0.3710	-0.3710	0.4202	-0.4202	0.4202	-0.4202
-1.7385	$A_1$	0.3673	0.3673	0.3867	0.3867	0.3867	0.3867

TABLE II  
Charge densities at various atomic sites of phthalic acid molecule

Atomic site No.	1	2	3	4	5	6	7	8	9	10	11	12
Charge density	1.7846	1.2692	1.5030	1.5030	1.2692	1.7846	0.9818	0.9818	1.0430	1.0430	1.0430	1.0430

and appropriate molecular orbitals<sup>1-3</sup>. For aromatic hydrocarbons having uniform  $\pi$  charge distribution, the potential of a neutral molecule is usually taken as the sum of Goeppert-Mayer and Sklar potential<sup>4</sup> of neutral carbon atoms but for heteroatomic molecules having non uniform  $\pi$  charge distribution, such molecular potential is modified<sup>5</sup> by taking proper consideration of charge distribution in them in order to get exact values of intermolecular resonance integrals. We are interested in the band structure calculations of phthalic acid hence as suggested above we have calculated here the electronic charge densities at various atomic sites of this molecule by LCAO method under Wheland approximation<sup>6</sup> (inclusion of overlap) using Slater type of atomic orbitals.

The methods adopted here is based on the work of Chirgwin and Coulson<sup>7</sup>. The  $12 \times 12$  determinant for this molecule has been broken by diagonalization method into smaller ones belonging to  $A_2$  and  $A_1$  representations respectively using its  $C_{2v}$  symmetry. The reduced secular determinants have been solved by Horner's method and the calculated values of energy levels along with coefficients are given in Table I. The charge density

on  $j$ -th atomic site has been calculated using the relation<sup>8</sup>

$$q_j = \sum_k n_k [c_{jk}^2 + c_{jk} \sum_{l (\neq j)} c_{lk} S_{lj}] \quad (1)$$

where  $l$  and  $j$  are neighbour atoms of phthalic acid,  $c_{jk}$ 's are Wheland coefficients,  $n_k$  is the number of electrons in the molecular orbital which may be 0, 1 or 2.  $S_{lj}$  represents overlap integral between adjacent atoms  $j$  and  $l$  and summation is carried out over all occupied molecular orbitals taking twice of those occupied by two electrons. The overlap integrals have been taken from Mulliken's table<sup>9</sup>. The calculated values of charge densities are given in Table II.

Since orbital overlap<sup>10</sup> also depends on the value of charge density we can locate the points of maximum and minimum overlapping in this molecule. From Fig. 1 and Table II, the maximum and minimum values of charge densities are found at atomic sites 1, 6 and 7, 8 respectively. Therefore there will be greater overlapping of molecular orbitals at atomic sites 1, 6 and smaller overlapping at atomic sites 7, 8 of this molecule. These calculated values of charge densities will be used in correct evaluation of intermolecular resonance integrals in



the energy band structures calculation of phthalic acid.

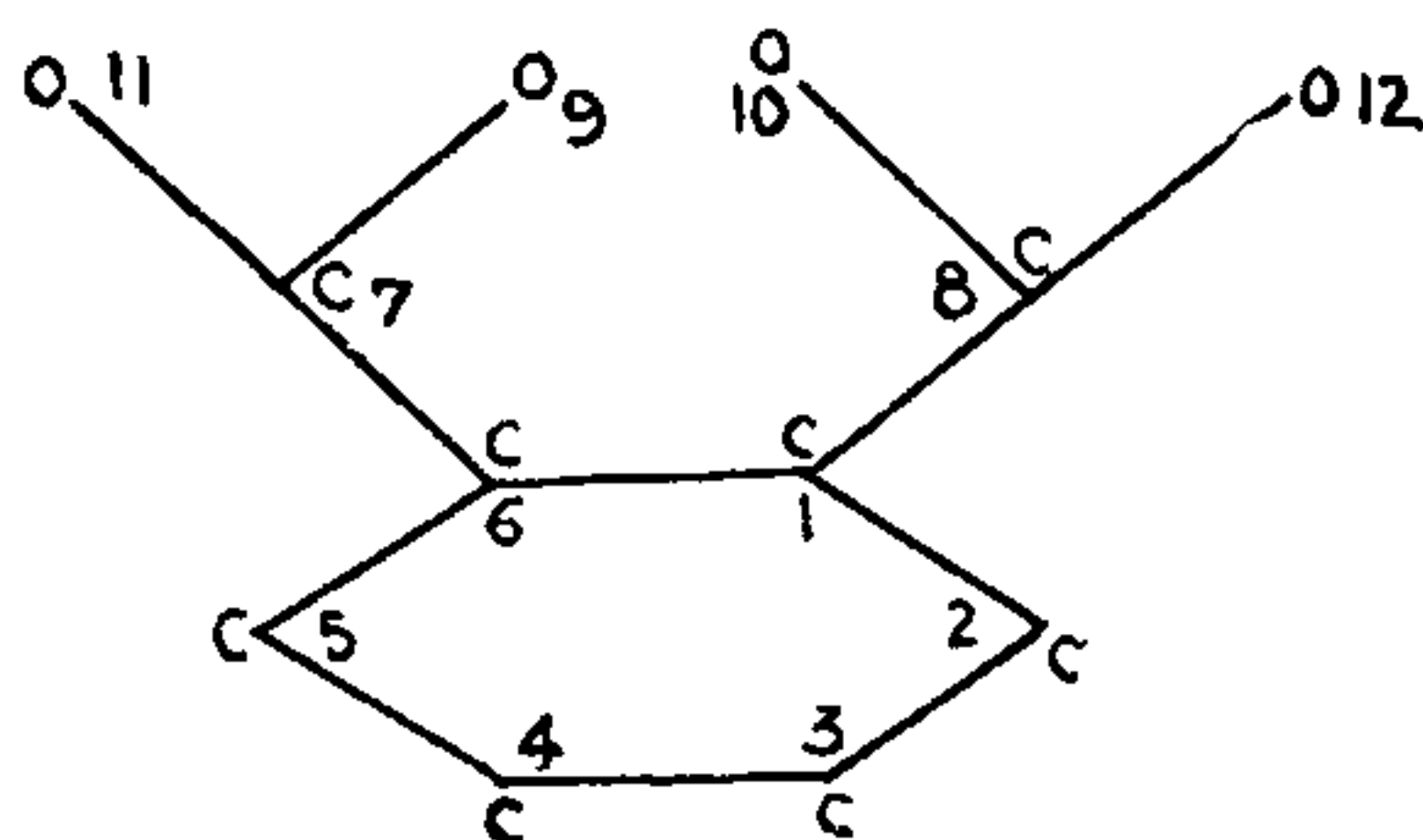


FIG. 1. Various atomic sites in the phthalic acid molecule.

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## NEW COMPOUNDS OF THE $A^+B^{5+}B^{6+}O_6^{2-}$ TYPE I STRUCTURE

FURTHER to our work on the titanates<sup>1,2</sup>, niobates<sup>3,4</sup>, tantalates<sup>5</sup> and molybdates<sup>6,7</sup> we have studied the present systems in order to investigate the solubility of  $MoO_3$  and  $WO_3$  in the  $A^+B^{5+}O_6^{2-}$  (where  $A^+ = Na^+$ ,  $K^+$  and  $B^{5+} = Ta^{5+}$ ,  $Nb^{5+}$ ). The samples were prepared by usual ceramic techniques, using as starting materials  $Na_2CO_3$ ,  $K_2CO_3$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ,  $MoO_3$  and  $WO_3$  of A.R. grade quality. The firing was done at 600°C to 900°C for 12 hrs and the samples were furnace cooled

to room temperature. X-ray powder photographs were taken on Debye-Scherrer powder camera of 14 cm diameter using  $CuK\alpha$  radiation filtered through Ni foil.

Table I summarises some of our results. The compounds  $NaTaMoO_6$  and  $NaTaWO_6$  both have columbite structure. The X-ray diagrams of  $NaNbWO_6$  and  $NaNbMoO_6$  were, however, complicated, showing a large departure from true columbite structure, part of the lines could, however, be indexed on the basis of a perovskite unit cell. It was also found that K compounds invariably gave rise to a perovskite (perhaps distorted) structure.

TABLE I

Summary of the results of  $A^+B^{5+}B^{6+}O_6^{2-}$  compositions

Composition	Structure type	Unit cell parameters Å
$NaTaMoO_6$	Columbite	Orthorhombic $a_0 = 5.20$ , $b_0 = 14.30$ , $c_0 = 5.90$
$NaTaWO_6$	do.	$a_0 = 5.21$ , $b_0 = 14.35$ , $c_0 = 5.96$
$NaNbMoO_6$	Perovskite	Orthorhombic $a_0 = 5.57$ , $b_0 = 3.88 \times 4$ , $c_0 = 5.50$
$NaNbWO_6$		

The following systems have been investigated in some details.

(a)  $NaNbO_3-WO_3$ .—This system shows a solid solution with  $NaNbO_3$  structure upto about 20 mole%  $WO_3$  and a columbite structure between 20–35%  $WO_3$ , whereafter lines due to  $WO_3$  begin to appear and the X-ray pattern becomes more complicated comprising of a mixed phase.

(b)  $NaTaO_3-WO_3$ .—This series showed a complete solid solution upto about 50 mole%  $WO_3$  whereafter a two phase region appears.

(c)  $NaNbO_3-MoO_3$  and  $NaTaO_3-MoO_3$ .—A one phase region with  $NaNbO_3$  structure upto about 0–10 and 0–20 mole%  $MoO_3$  respectively in the two systems is observed. Larger concentrations of  $MoO_3$  resulted in complicated X-ray patterns. The compounds  $KNb(Ta)O_3 + Mo(W)O_3$  invariably gave rise to the perovskite structure for low ( $\leq 50$  mole%)  $MoO_3$  and  $WO_3$  additions after which lines due to  $Mo(W)O_3$  begin to appear. Absence of a columbite structure in this series can be attributed to the large ionic size of  $K^+(1.33 \text{ Å})^8$  the columbite structure being restricted to ions of small size at the A site in the structure<sup>9</sup>. The  $a:b:c$  ratio in the  $NaTaMo(W)O_6$  is 0.88:2.42:1 as compared to 0.89:2.49:1 in the true columbite structure<sup>10</sup>, implying that the 'b' axis for these systems is comparatively smaller. This may be