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Electric Field Assisted Deaquation in Sodium Molybdate Dihydrate

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Abstract* – *The calculation of activation energy of water groups embedded in the skeleton of sodium tungstate dihydrate, after their being released from normal lattice sites, has been presented by assuming Maxwell Boltzmann distribution of energies among the different water groups, at their characteristic temperature of release. The characteristic temperature has been assumed to be the one at which current versus time/temperature peak starts just building up.

These is strong logic behind the assumption that H^+ and OH^- ions created due to the dissociation of a fraction of total water groups released within the lattice of a hydrated compound may remain in the skeleton through a loose hydrogen bonding. Such H^+ and OH^- ions would definitely take some finite time for diffusion within the skeleton and thus the crest of the current versus time plot may occur after some finite time of few minutes as observed in Fig. 4.2 for the case of sodium tungstate dihydrate.

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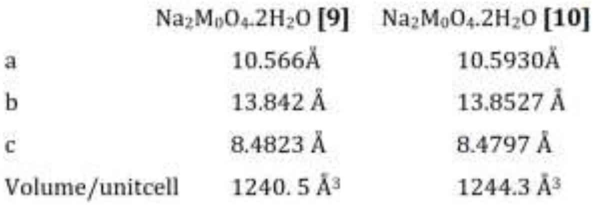
The rearrangement of H^+ and OH^- as above in a heated hydrated compound, finds weightage through the works of Kuroda et al [1,2] who have investigated spontaneous rearrangement of hydrogen bonding network initiated by the loss of volatile compound from the crystal system of 1 : 1 racemic bis-β-naphthol : benzoquinone. This problem was futher investigated by Kuroda and Imai [3]. Their works [3] suggest that the diffusion of molecules in a solid state can be considerable, and hydroxyl group could easily change hydrogen bonding partners in solid systems, where volatile or sublimable compounds are involved.

The energy of dissociation E_d of water groups in sodium tungstate dihydrate crystalline samples, as determined by the procedure developed in this work, is found to be 0.391 eV and is much less than 1.2 eV, the free space dissociation energy of water group. The above determined value of E_d for water groups in sodium tungstate dihydrate was found to be of the same order as found for other hydrated salts investigated by other workers [4-8] through a slightly different but less logical pressumption about the distribution of energy among water groups released in a hydrated lattice due to heating.

Crystal structure of $Na_2M_0O_4.2H_2O$:

$Na_2M_0O_4.2H_2O$ is isostructural to $Na_2M_0O_4.2H_2O$. Both belong to the space group P_{bca} and possess orthorhomic unit cells.

The unit cell dimensions a,b,c of $Na_2M_0O_4.2H_2O$ compare with that of $Na_2M_0O_4.2H_2O$ as under



	$Na_2M_0O_4.2H_2O$ **[9]**	$Na_2M_0O_4.2H_2O$ **[10]**
a	10.566Å	10.5930Å
b	13.842 Å	13.8527 Å
c	8.4823 Å	8.4797 Å
Volume/unitcell	1240. 5 Å³	1244.3 Å³

It is seen that the unit cell of $Na_2M_0O_4.2H_2O$ is slightly shorter than that of $Na_2M_0O_4.2H_2O$.

Similar catalytic nature of sodium molybdate & Sodium tungstate:

Both $Na_2M_0O_4$ and $Na_2M_0O_4$ in water have been found to act as catalysts by Payne & Williams [11], Ahmad & Beg[12] and Krishenbum and Sharpless [13] in the process of epoxy formation from crotonic acid citraconic acid. The above catalytic behaviour is further investigated by Hong-chang Shi et al [14].

Accordingly, it has been found interesting to determine the dissociation energy of water groups within the lattice of $Na_2M_0O_4.2H_2O$ salts as well. The details of experiments & results are given forthwith.

Experimental:

The starting material was the A.R. Grade s.d. fine-chem Ltd crystalline powder sodium molybdate dihydrate. It contained elemental impurities of arsenic, copper, iron & tungsten upto 0.01%. The material was recrystallized in distilled water. The resulting mass was dried and suitably grinded. The pellets of the compound were made with a suitable die arrangement and a hydrolic press at 400 MPa. A thin coating of silver paint was laid on both the sides of the pellet for good electrical contacts.

The sample holder used for electric field assisted deaquation was as shown in Fig. 4.1. An ECIL EA 815 electrometer amplifier was used for current measurements. This amplifier has standard input resistors which enabled us to use it in its different ranges for measurements of currents up to 10^{-5}A.

The temperature of the sample pellet was increased at approximate rates of 1°C/min and 2°C/min manually in various sets. The current values through the sample (I) were noted as a function of time. Table 5.1 shows corresponding data obtained for $Na_2M_0O_4.2H_2O$, when the sample was heated at a linear rate of 1°C/min. Fig. 5.1 shows plots of log I versus time plot for both the1°C/minute and the1°C/minute heating rates. A single broad peak is noticed in the log I versus time plot for both the heating rates. It is again seen that the height of the peak increases as the heating rate is increased, but the width of the peak becomes narrower with this change. The total areas under the peaks however remain almost equal.

Calculation of charge through pellet of $Na_2M_0O_4.2H_2O$:

To obtain the charge flown through the pellet, the area under the current I versus heating time (t) plot of Fig. 5.1, in the semi-Log scale was subdivided into the topmost triangular area and small trapezoidal strips. The area was then found by adding the area of the triangle and those of strips by the formula given already in Chapter-4.

Calculation of N_0, N and f:

The different quantities N_0, N and f needed for the estimation of apparent dissociation energy E_d of water groups for the case of sodium molybdate dihydrate were calculated as under:

Total number N_0 :

Mass of sodium molybdate dihydrate powder = 0.160 gm.

Molecular weight of compound = 242

Mass in number of moles

$$= \frac{0.160}{242}$$

As only one peak has been observed in the current versus time plot of the sodium molybdate dihydrate pellet, heated at a linear rate, both the water groups per molecule of the compound must be getting released together from the lattice sites. Taking care of the dihydrate nature of present salt N0, the total number of water groups released in the pellet are given by

$$= \frac{0.160}{242} \times 2 \times \text{Avogrado's number}$$

$$= \frac{0.160}{242} \times 2 \times 6.03 \times 10^{23} = 7.97 \times 10^{20}$$

Number N of water groups dissociated:

The number N is related to the charge flowing through the pellet q as

$$N = \frac{q}{2e}$$

Estimation of q:

The area under the curve I versus time (t) of Fig. 5.1 was sub divided into a number of sub-areas by lines parallel to the time axis and the charge q flowing through the pellet was calculated, as per the formula $q = (I_m - I_1)\Delta t_1 + \sum_{n=1}^{N} (I_n - I_{n+1})\Delta t_{n+1}$ given in Chapter-4.

However, as the current values in Fig. 5.1 decrease exponentially from the top to the bottom, we need consider only a limited number N (here 19) of sub-areas and q comes out to be

$$q = (9\times10^{-7} - 8\times10^{-7})\times3.5\times60$$

$$+(8\times10^{-7} - 6\times10^{-7})\times11\times60 + (6\times10^{-7} - 4\times10^{-7})\times15\times60$$

$$+(4\times10^{-7} - 3\times10^{-7})\times20\times60 + (3\times10^{-7} - 2\times10^{-7})\times23\times60$$

$$+(2\times10^{-7} - 1\times10^{-7})\times27\times60 + (1\times10^{-7} - 8\times10^{-8})\times29\times60$$

$$+(8\times10^{-8} - 6\times10^{-8})\times30\times60 + (6\times10^{-8} - 4\times10^{-8})\times32\times60$$

$$+(4\times10^{-8} - 3\times10^{-8})\times33\times60 + (3\times10^{-8} - 2\times10^{-8})\times34\times60$$

$$+(2\times10^{-8} - 1\times10^{-8})\times36\times60 + (1\times10^{-8} - 8\times10^{-8})\times39\times60$$

$$+(8\times10^{-9} - 6\times10^{-9})\times39\times60 + (6\times10^{-9} - 4\times10^{-9})\times40\times60$$

$$+(4\times10^{-9} - 3\times10^{-9})\times42\times60 + (3\times10^{-9} - 2\times10^{-9})\times42\times60$$

$$+(2\times10^{-9} - 1\times10^{-9})\times44\times60 + (1\times10^{-9} - 8\times10^{-10})\times47\times60$$

In the above expression, the first term is the contribution of the topmost triangular area and the rest are due to trapezoids. For trapezoids the quantities enclosed by brackets are the current differences for their tops and bottoms and the terms outside the brackets on the right do represent average time intervals in seconds.

The above expression for q on summation yields

$$q = 4.55\times10^{-3}\text{Coulomb}$$

Thus we get

$$N = \frac{q}{2e} = \frac{4.55\times10^{-3}}{2\times1.6\times10^{-19}}$$

$$= 1.42\times10^{16}$$

Calculation of ‘f’, the fraction of water groups dissociated :

Obviously

$$f = \frac{N}{N_0}$$

$$= \frac{1.42\times10^{16}}{7.97\times10^{20}}$$

$$= 1.78\times10^{-5}$$

RESULTS:

The fraction ‘f’ of dissociated water molecules is given as

$$f = \frac{\int_{E_d}^{\infty}\sqrt{E}\exp(-E/kT_k)dE}{\int_{0}^{\infty}\sqrt{E}\exp(-E/kT_k)dE}$$

where T_k is the characteristic temperature at which the current versus time graph starts to build up the peak. This differs from substance to substance and in the case of water groups of sodium molybdate is found to be

$$T_k = 75\,^{\circ}\mathrm{C} = 348\ \mathrm{K}$$

Thus

$$kT_k = 1.38\times10^{-23}\times 348\mathrm{J}$$

$$= \frac{1.38\times10^{-23}\times348}{1.6\times10^{-19}}\ \mathrm{eV} = 0.030\ \mathrm{e}\backslash$$

The denominator in the expression for ‘f’ in the present case was evaluated by measuring the area below the plot of $\sqrt{E}\exp(-E/kT)$ versus E shown in Fig. 5.2, in proper units. This value was evaluated to be of 1209 units, each unit representing a rectangle of sides 20×10^{-4} units along Y-axis and of 0.002eV along X-axis.

Thus the required denominator equals

$$= 1209\times20\times10^{-4}\times0.002$$

$$= 4.83\times10^{-3}\ \text{units}$$

Using the above value of denominator and already calculated ‘f’ value, the expected value of the numerator

$$\int_{E_d}^{\infty}\sqrt{E}\exp(-E/kT)dE$$

was found to be

$$= 1.78\times10^{-5}\times4.83\times10^{-3}$$

$$= 8.61\times10^{\ 8}\ \text{units}$$

The values of the definite integral

$$\int_{E}^{\infty}\sqrt{E}\exp(-E/kT)dE$$

for different initial values of E as 0.36, 0.38, 0.40, 0.42, 0.45 & 0.50 eV were then evaluated by the procedure described in Appendix ‘A’. The value of $kT{=}kT_k$ used in the present case was 0.03 eV.

Table 5.2 gives data for different $\int_{E}^{\infty}\sqrt{E}\exp(-E/kT)dE$ values as a function of E. A graph for such data is shown in Fig. 5.3.

From this graph and using the earlier estimated value for the integral of the numerator as 8.61×10^{-8} the E_d for water groups in sodium molybdate dihydrate was evaluated to be 0.369 eV.

DISCUSSION:

The discussion energy E_d of water groups in the hydrated system of sodium molybdate dihydrate, as obtained by electric field assisted deaquation has been found to be 0.369 eV.

As described in Chapter-4, the corresponding dissociation energy E_d of water groups in isomorphous system of sodium tungstate dihydrate was obtained as 0.391 Å. The E_d values of water groups for the two systems are therefore of the same order of magnitude.

The present results, therefore, support the isomorphous nature of sodium tungstate dihydrate and sodium molybdate dehydrate

We had presumed that released water groups are in M.B. distribution equilibrium at the temperature of start of the current versus time plot. Almost equal E_d values for the two salts therefore support our new presumption about M.B. distribution equilibrium temperature of water groups in a hydrated salt in contrast to those of other workers [4-8].

As only one peak each has been observed in the current versus time plots for the dihydrates of sodium tungstate and sodium molybdate, the electric field assisted deaquation studies indicate that both water groups are equivalently placed in each dihydrate salt under reference.

However, the I.R. spectra for the two dihydrates [15] indicate slightly different characteristics. The peak in the deaquation may thus be though as a composite one. The resulting implications are discussed in Chapter-6.

Table

Current as a function of Time, through a pelletized sample of $Na_2M_0O_4.2H_2O$, the temperature increasing at a linear rate of 1^oC/minute

S. No.	Time (min)	Current (amp)
1	20	2.1×10^{-8}
2	24	6.5×10^{-9}
3	28	3.0×10^{-9}
4	32	1.3×10^{-9}
5	36	9.0×10^{-10}
6	40	7.0×10^{-10}
7	44	7.0×10^{-10}
8	48	1.8×10^{-9}
9	52	4.0×10^{-8}
10	56	3.2×10^{-7}
11	60	1.2×10^{-6}
12	64	3.5×10^{-6}
13	68	6.0×10^{-6}
14	70	6.0×10^{-6}
15	72	4.2×10^{-6}
16	76	1.8×10^{-6}
17	80	5.0×10^{-7}
18	84	9.0×10^{-8}
19	88	2.2×10^{-8}
20	92	2.5×10^{-9}
21	96	4.2×10^{-10}
22	100	3.0×10^{-10}
23	104	3.2×10^{-10}
24	108	3.4×10^{-10}
25	112	4.0×10^{-10}

Table

Variation $\int_E^\infty \sqrt{E}\exp(-E/kT)dE$ with E

S. No.	E(eV)	$\int_E^\infty \sqrt{E}\exp(-E/kT)dE$
1	0.36	1.19×10^{-7}
2	0.38	6.25×10^{-8}
3	0.40	3.26×10^{-8}
4	0.42	1.73×10^{-8}
5	0.45	6.54×10^{-9}
6	0.50	1.29×10^{-9}

Here $kT = 0.030\,\text{eV}$

REFERENCES

1. F. Toda, M. Senzaki & R. Kuroda (2002). Chem. Commun., 1pp. 788.

2. R. Kuroda, Y. Imai and N. Tajima (2002). Chem. Commun., pp. 2848.

3. R. Kuroda and Y. Imai (2003). Mendeleev Commun. , Electronic Version, Issue 3.

4. V. G. Kher, P.N. Nandi and D. A. Deshpande (1978). Indian J.. Pure & Appl. Phys.6. pp. 742.

5. P.N. Nandi, D.A. Deshpande & V.G. Kher (1979). Proc. Indian Acad. Sci. 88A. pp. 113.

6. K.M.K. Srivasta and S.D. Pandey (1984). Proc. Indian Acad . Sci. (Chem. Sci.) 93, pp. 1323.

7. K.M.K Srivasta and S.D. Pandey (1985). Indian J. Phys.59A, pp. 28.

8. K.M.K. Srivasta and S.D. Pandey (1985). Indian J. Phys. 59A, pp. 547.

9. J. Parks & G. McCarthy (1993). North Dakota State Univ. , Fargo, N.D., USA, ICDD Grant-in-Aid.

10. R.H. Blessing (1993). Acta Crystallogr. 51, pp. 33.

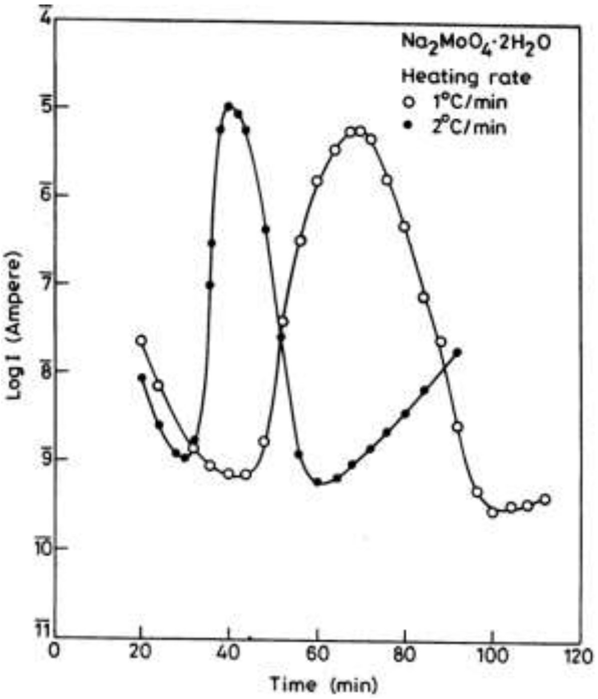
11. G.B. Payne & P.H. Williams (1959). J. Org. chem., 24, 54.

12. I. Ahmad & M.A. Beg (1978). Indian J. Chem. 16A, pp. 475.

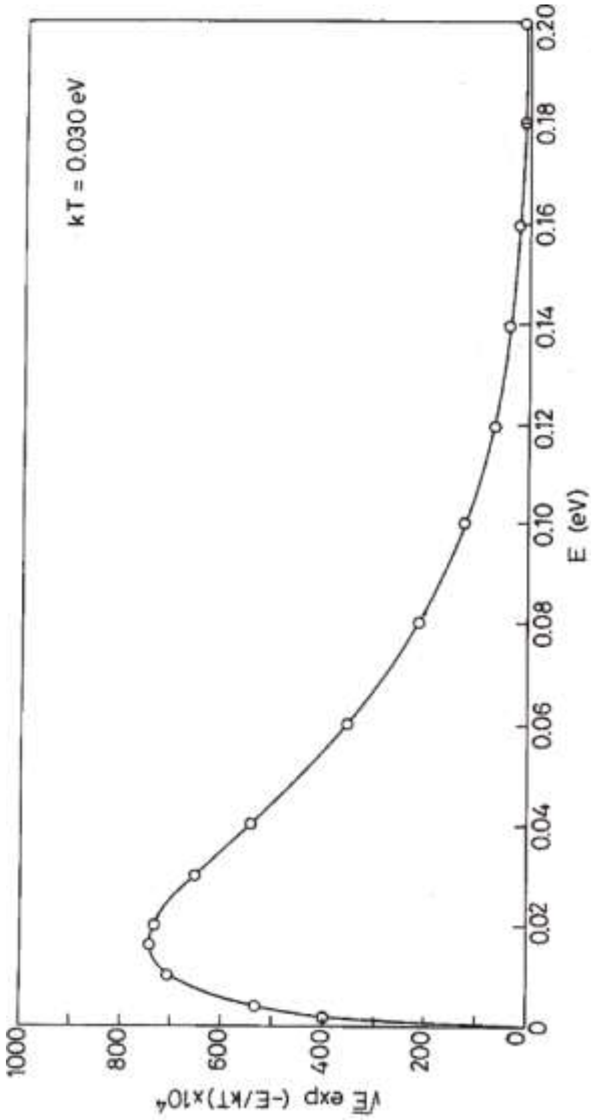
13. K.S. Krishenbum & K.B. Sharpless (1985). J. Org Chem.. 50, pp. 1979.

14. Hong-chang Shi, Gang Chen, Xin- yan Wang & Zhi-gus Zhang (2004). J. Molecular Catalysis A 216, pp. 29.

15. R.H. Busey and O.L. Keller (1964). Jr., J. Chem. Phys. 41, pp. 215.

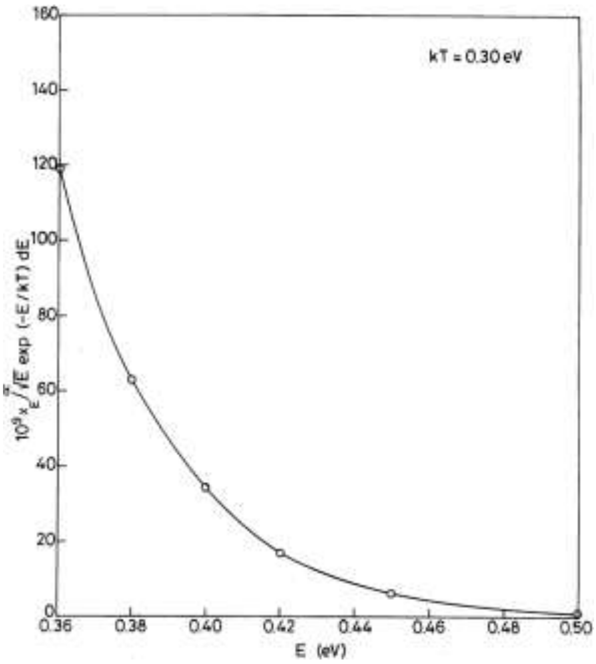


TEMPERATURE/TIME VARIATION OF CURRENT THROUGH PELLETS OF $Na_2M_0O_4.2H_2O$ FOR TWO DIFFERENT HEATING RATES.



THEORTICAL VARIATION OF

$\sqrt{E}\exp(-E/kT)\times10^4$ versus E(eV) (kT=0.030eV)



PLOT OF $10^9 \times \int_E^\infty \sqrt{E}\exp(-E/kT)dE$

FOR kT = 0.030 eV.

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