


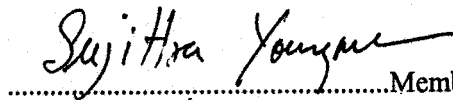
THESIS TITLE : INFRARED SPECTROSCOPIC STUDIES OFION-
WATER (H_2O, HOD, D_2O) INTERACTIONS IN
ALKALINE EARTH IODIDE CRYSTALLINE
HYDRATES BY ISOTOPIC DILUTION TECHNIQUE
COMPARED WITH RELATED HYDRATES

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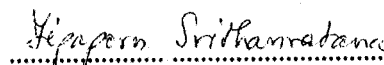
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ABSTRACT

Isotopically diluted or deuterated hydrates of $MgCl_2 \cdot H_2O$, $MgBr_2 \cdot 6H_2O$, $MgI_2 \cdot 8H_2O$, $CaCl_2 \cdot 2H_2O$, $CaBr_2 \cdot 2H_2O$, $CaI_2 \cdot 4H_2O$, $BaCl_2 \cdot 2H_2O$, $BaBr_2 \cdot 2H_2O$, $BaI_2 \cdot 2H_2O$, in the forms of $MgCl_2 \cdot 6H_2O-dx$, $MgBr_2 \cdot 6H_2O-dx$, $MgI_2 \cdot 8H_2O-dx$, $CaCl_2 \cdot 2H_2O-dx$, $CaBr_2 \cdot 2H_2O-dx$, $CaI_2 \cdot 4H_2O-dx$, $BaCl_2 \cdot 2H_2O-dx$, $BaBr_2 \cdot 2H_2O-dx$, and $BaI_2 \cdot 2H_2O$ were prepared in dry nitrogen atmosphere. Their infrared spectra were recorded on an infrared spectrophotometer Perkin Elmer 683 with the resolution of 1.2 cm^{-1} at 1000 cm^{-1} . Sample preparations used for recording infrared spectra are KBr press and nujol mull with parafin liquid and poly-(chlorotrifluoroethylene) oil as mulling agents and CsI as optical windows. Anion-water interactions of $MgCl_2 \cdot 6H_2O-dx$, $MgBr_2 \cdot 6H_2O-dx$, $MgI_2 \cdot 8H_2O-dx$

observed as uncoupled vibrations of OH, so called $V_{OH}(HOD)$ those average for all techniques are 3401, 3402, 3427 cm^{-1} respectively. Average $V_{OH}(HOD)$ of all techniques in the case of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O-dx}$, $\text{CaBr}_2 \cdot 2\text{H}_2\text{O-dx}$, $\text{CaI}_2 \cdot 4\text{H}_2\text{O-dx}$ are 3378, 3402, and 3443 respectively, whereas those for $\text{BaCl}_2 \cdot 2\text{H}_2\text{O-dx}$, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O-dx}$, and $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ are 3387, 3397 and 3427 cm^{-1} respectively. Thermodynamic data in terms of enthalpy of hydrogen bonding (ΔH_H) calculated from $\Delta V_{OH}(HOD)$ those indicate anion-water interactions of those mentioned hydrates average for all techniques are : 14.05, 14.05, 12.94 ; 15.03, 14.00, 12.26 ; and 14.61, 14.21, 12.99 kJ mol^{-1} OH respectively. The corresponding calculated equivalent $R_{O...O}/\text{\AA}$ for the mentioned hydrates are 2.796, 2.796, 2.812 ; 2.784, 2.797, 2.822 ; and 2.789, 2.793, 2.881. The anion-oxygen distances ($R_{O...Y}/\text{\AA}$) calculated from equivalent $R_{O...O}$ of same sequence are 3.196, 3.346, 3.562 ; 3.184, 3.347, 3.572 ; and 3.189, 3.343, 3.561 respectively. Clear doublets of $V_2(\text{H}_2\text{O})$ indicating about two crystallographic distinct water molecules in hydrates, were observed in almost cases. In $\text{MgX}_2 \cdot n\text{H}_2\text{O}$ and $\text{MgX}_2 \cdot n\text{H}_2\text{O-dx}$ cases, the medium to strong band at about 1016 cm^{-1} were observed and suggested to assign to a vibrating species of $V_1(A_1)$ of Mg-OH_2 or Mg-OD_2 of the type planar ZXY_2 vibrating molecule. In librational region, the average twisting (ρ_t), rocking (ρ_r), and wagging (ρ_w) were observed for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O-dx}$ at about 670, 580, and 523 cm^{-1} respectively. The cases of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O-dx}$ and $\text{MgI}_2 \cdot 8\text{H}_2\text{O-dx}$ two librational modes of ρ_r and ρ_w were found at about 601, 500 ; and 684, 480 cm^{-1} respectively. Cation-water interactions in terms of $V_{M...O}$ were found for Mg...O at 350 cm^{-1} . Librational mode of ρ_r and ρ_w and $V_{Ca...O}$ were observed at 600, 500 and 380 for $\text{CaCl}_2 \cdot 2\text{H}_2\text{O-dx}$. In $\text{CaBr}_2 \cdot 2\text{H}_2\text{O-dx}$ only ρ_w was observed at 450 cm^{-1} . The hydrate $\text{CaI}_2 \cdot 4\text{H}_2\text{O-dx}$ showed ρ_r and ρ_w at 625 and 459 cm^{-1} . The hydrate $\text{BaCl}_2 \cdot 2\text{H}_2\text{O-dx}$ exhibited ρ_t , ρ_r and ρ_w at 688, 593, and 465 respectively, whereas the $V_{Ba...O}$ was found at 350 cm^{-1} . Librational modes of ρ_r and ρ_w in $\text{BaBr}_2 \cdot 2\text{H}_2\text{O-dx}$ were observed at 569 and 435 cm^{-1} whereas the $V_{Ba...O}$ was seen at 361 cm^{-1} . All librational modes of ρ_t , ρ_r and ρ_w were observed in $\text{BaI}_2 \cdot 2\text{H}_2\text{O-dx}$ at 698, 593, and 462 cm^{-1} whereas the $V_{Ba...O}$ was found at 340 cm^{-1} .