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CORRELATION BETWEEN STANDARD ENTHALPY OF FORMATION AND REFRACTIVE INDEX IN ALKALI HALIDES

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ABSTRACT

The values of standard enthalpy of formation and refractive index of different alkali halides have been analysed and discussed in the light of ionic character of alkali metal-halogen bond. The correlation between these two parameters has been studied. An empirical second order polynomial equation of the following form

$$\Delta H^{\circ}_{exp} = a + b\,\eta + c\,\eta^2$$

has been proposed which, may be used to calculate standard enthalpy of formation of any alkali halide from the value of refractive index only.

Key words: Standard enthalpy, Refractive index, Alkali halide.

INTRODUCTION

The alkali halides are considered to be model ionic compounds for theoretical and experimental studies. In recent years, they have shown increased interest due to their applications in various electronic and optoelectronic devices. The refractive index is closely related with energy band gap and their mutual correlation in alkali halides has been extensively studied by many workers[1-6]. Reddy and Nazeer[7] have related the refractive indices with optical electronegativities of component elements for alkali halides along with II-VI and III-V compound semiconductors. Salem[6] has also studied the correlation of refractive indices with Pauling's electronegativities of component elements in alkali halides.

Since enthalpy of formation throws light on the ionic nature of bond and intrinsic

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stability of compound in condensed phase against changing environment, it has been considered worth to study the correlation between refractive index and enthalpy of formation in alkali halides. In this context, it is relevant to consider the fact that ionic character of bond is also related with the optical and electronic properties of materials. For example, more ionic compound shows larger energy gap between the valance and conduction band.

In the present work, the two parameters, viz., standard enthalpy of formation and refractive index have been interrelated and discussed in the light of ionic character of bond in alkali halides. An empirical relationship for the calculation of standard enthalpy of formation, from the value of refractive index only, for the different series of alkali halides has been developed.

Standard enthalpy of formation and ionicity

The enthalpy of formation of a compound is closely related to the nature of its bonding. A large negative value of enthalpy of formation of a compound indicates that its bonding is different from the bonding in the component elements. The numerical value generally increases with increasing ionic character of bond. Pauling[8] has proposed the following equation for the calculation of standard enthalpy of formation of an ionic compound:

$$- \Delta H^{\circ}_{AB,\,i} = 96508\,(x_A - x_B)^2 - 55.4\,n_N - 26\,n_O \qquad \ldots(1)$$

where, $\Delta H^{\circ}_{AB,\,i}$ is standard enthalpy of formation of an ionic compound AB in kJ/mol, x_A and x_B are the electronegatvities of the respective elements in eV, n_N and n_O are the number of nitrogen and oxygen atoms in the said ionic compound AB. The values of standard enthalpy of formation of different alkali halides as calculated by substituting the electronegativity values from the scale due to Pauling[8] are listed in Table 1. For a comparison, experimental values[9] are also incorporated in this table. Table 1 indicates that values of standard enthalpy of formation, as obtained from the ionic model of Pauling[8], are generally not in good agreement with those obtained experimentally. This clearly points out that bonding in alkali halides is not 100 % ionic. The values of percentage ionic character of bond in different alkali halides as calculated from the following Pauling's equation:

$$\% \text{ Ionicity} = 1 - \exp\left[-\tfrac{1}{4}(x_A - x_B)^2\right] \qquad \ldots(2)$$

are also listed in Table 1. This table shows that the ionic character of metal-halogen bond in alkali halides decreases with increasing size of anionic element. Gonclaves et al[10], have also observed the similar trend of decreasing ionic character of metal-halogen bond as anion

varies from F to I. This trend of variation is further associated with decrease in numerical value of standard enthalpy of formation compounds, in a homologous series of alkali halides, when cationic element is kept constant.

Table 1: Standard enthalpy of formation and ionicity of alkali halides

Compound	$-\Delta H^{\circ}_{exp}$ (kJ/mol)	$-\Delta H^{\circ}_{AB,\,i}$ (kJ/mol)	% Ionicity
LiF	612.1	868.6	89
LiCl	408.8	386.0	63
LiBr	350.3	312.7	55
LiI	271.1	217.1	43
NaF	569.0	927.4	91
NaCl	411.0	425.6	67
NaBr	359.9	348.4	59
NaI	288.0	247.1	47
KF	562.6	988.2	92
KCl	435.9	467.1	70
KBr	392.2	386.0	63
KI	327.6	278.9	51
RbF	549.3	988.2	92
RbCl	430.5	467.1	70
RbBr	389.2	386.0	63
RbI	328.4	278.9	51
CsF	530.9	1051.0	93
CsCl	433.0	510.5	73
CsBr	394.6	425.6	67
CsI	336.8	312.7	55

Standard enthalpy of formation and refractive index

Table 2 lists the values of standard enthalpy of formation and refractive index of alkali halides. This table clearly indicates that the values of refractive index, in a

homologous series of alkali halides, when cationic element is kept constant, increase with decrease of exothermic enthalpy of formation. The interrelation between values of standard enthalpy of formation (ΔH°) and refractive index (η) has been analysed in term of the following second order polynomial equation:

$$\Delta H^{\circ} = a + b\,\eta + c\,\eta^2 \qquad \ldots(3)$$

where, a, b and c are numerical constants and are presented in Table 3. The values of standard enthalpy of formation as calculated from above equation are also incorporated in Table 2. This table shows that the values, as obtained from the empirical polynomial equation, are in excellent agreement with the experimental values. This indicates that there is a very close interrelation between enthalpy of formation and refractive index in alkali halides. However, further work is needed in this direction.

Table 2: Values of experimental and calculated standard enthalpy of formation and refractive index of alkali halides

Compound	$-\Delta H^{\circ}_{exp}$ (kJ/mol)	η	$-\Delta H^{\circ}_{cal}$ (kJ/mol)
LiF	612.1	1.3915	611.4
LiCl	408.8	1.6620	413.2
LiBr	350.3	1.7840	345.2
LiI	271.1	1.9550	272.5
NaF	569.0	1.3258	568.3
NaCl	411.0	1.5443	413.8
NaBr	359.9	1.6412	356.5
NaI	288.0	1.7745	289.0
KF	562.6	1.3520	562.0
KCl	435.9	1.4904	438.6
KBr	392.2	1.5594	389.1
KI	327.6	1.6670	328.3
RbF	549.3	1.3960	548.3
RbCl	430.5	1.4936	418.8
RbBr	389.2	1.5528	384.4

Cont…

Compound	- ΔH°_{exp} (kJ/mol)	η	- ΔH°_{cal} (kJ/mol)
RbI	328.4	1.6474	329.8
CsF	530.9	1.4830	531.0
CsCl	433.0	1.6100	432.7
CsBr	394.6	1.6700	395.0
CsI	336.8	1.7876	336.9

Table 3: Polynomial numerical constants for different series of alkali halides

Compound	a	b	c
LiX	- 2668.1	2102.0	- 448.4
NaX	- 2262.0	1766.3	- 368.4
KX	- 3481.9	3309.4	- 850.4
RbX	- 6039.4	6530.0	- 1860.0
CsX	- 3505.4	3140.6	- 765.3

Moreover, it has also been observed from Tables 1 and 2 that the ionic character of bond decreases and refractive index increases, in a homologous series of alkali halides on varying the size of anion from F to I. Thus, the variation of refractive index obeys the negative correlation with ionic character of bond.

CONCLUSION

The values of standard enthalpy of formation of alkali halides have been correlated with the values of refractive index. These parameters have been discussed in the light of ionic character of metal-halogen bond. It has been observed that the negative values of standard enthalpy of formation decrease with increase of refractive index of compound in a homologous series, when electropositive element is kept constant. This is further associated with decrease in ionic character of metal-halogen bond and increase in size of halogen atoms.

An empirical second order polynomial equation has successfully been developed to calculate the standard enthalpy of formation of different alkali halides from the value of refractive index only.

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