Solvation Enthalpies of Some Univalent Ions in n-Butanol

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Solubilities of alkali metal and ammonium halides and nitrates have been determined in n-butanol at 25°C, 30°C and 35°C. Solubilities of all the salts increase with the increase in temperature. Plots of logarithms of thermodynamic solubility product versus reciprocal of temperature are linear over the temperature range studied. Heats of solution of the electrolytes have been determined from the slopes of those plots. By combining the heats of solution with the lattice energies of the electrolytes, solvation enthalpies of the electrolytes have been evaluated. Ionic solvation enthalpies have been calculated and found to decrease in n-butanol with the increase in the size of the ions. Solvation enthalpies of anions are larger than those of cations of comparable sizes which shows the protic nature of this solvent.

Though ion-solvation enthalpies are of fundamental importance for understanding ion/solvent interactions in solvent yet such investigation are completely lacking in n-butanol. In continuation to our studies concerning solute-solvent interaction[1-3], the solubilities of some uni-univalent electrolyte at temperatures of 25°C, 30°C and 35°C are reported in this solvent. The data of temperature dependance of solubility have been used to evaluate solvation enthalpies of electrolytes. Ionic-solvation enthalpies have been computed using modified method of Latimer.

EXPERIMENTAL

Solvent was purified as described by Gardam and Evans[4] and the electrolyte were purified by the method reported by Paul et al[5].

Solubilities and solvate formation of the electrolytes have been determined essentially by the method reported by Abraham et al[6]. Freshly distilled solvent was used in each experiment.

RESULTS AND DISCUSSION

Solubilities of alkali metal and ammonium halides and nitrates have been determined in n-butanol at 25°C, 30°C and 35°C. All the relevant data are listed in Table-1. Solubilities of all these salts increase with increase in temperature. Table-1 reveals that the solubilities of alkali metal salts decrease with the decrease in the sizes of the anions at all the temperature. This is in accordance with the findings in various solvents[6-8].

Heat of solution of the electrolytes (ΔH°_{solv}) is related to the thermodynamic solubility product (K_{sp}) of the electrolyte at temperature T by the following relationship[9]:

$$\log K_{sp} = -\frac{\Delta H^\circ_{solv}}{2.303\,RT} + C \qquad \ldots(1)$$

Where C is the integration constant. Thermodynamic solubility products of the electrolytes have been computed as reported earlier[1].

The values of association constant are reported for some of the salts[4] and that of the other salts have been estimated[6]. Precise conductance studies[10-11] reveals that the value of distance

TABLE 1

Solubilities of some Uni-Univalent Electrolytes in n-Butanol at various Temperatures

Electrolyte	Solubility (moles/1000g of solvent) 25°C	30°C	35°C
LiCL	2.91	3.39	4.09
NaCL	2.8×10^{-4}	3.3×10^{-4}	3.7×10^{-4}
NaI	1.59	1.70	1.83
$NaNO_3$	5.2×10^{-3}	7.2×10^{-3}	8.3×10^{-3}
KCl	2.5×10^{-4}	2.8×10^{-4}	3.0×10^{-4}
KBr	2.5×10^{-3}	2.7×10^{-3}	3.0×10^{-3}
KI	2.4×10^{-2}	2.61×10^{-2}	1.70×10^{-2}
KNO_3	8.3×10^{-4}	9.1×10^{-4}	1.0×10^{-3}
CsCl	4.4×10^{-3}	5.1×10^{-3}	5.6×10^{-3}
NH_4Cl	1.6×10^{-2}	1.77×10^{-2}	1.95×10^{-2}
NH_4Br	5.43×10^{-2}	5.88×10^{-2}	6.51×10^{-2}
NH_4NO_3	10.6×10^{-2}	11.7×10^{-2}	13.9×10^{-2}

of closest approach is constant for various electrolytes in a solvent. In n-butanol[4] this value is 5.6 ± 0.004 A°. Literature records that the slight variation in the values of these parameters do not affect the value of thermodynamic solubility product and heat of solution significantly[1,6] .

Heats of solution of the elctrolytes have been calculated from the slopes of the linear plots of log K_{So} versus 1/T (equation(1)). All the relevant data are listed in Table 2.

TABLE 2

HEATS OF SOLUTION ($\Delta H°_{soln}$) LATICE ENERGIES ($\Delta H°_{lat}$) AND SOLVATION ENTHALPIES ($\Delta H°_{solv}$) OF SOME ELECTROLYTES IN n-BUTANOL

Electrolytes	$\Delta H°_{soln}$ (Kcal $mole^{-1}$)	$-\Delta H°_{lat}$ (Kcal $mole^{-1}$)	$-\Delta H°_{solv}$ (Kcal $mole^{-1}$)
LiCl	8.40	205.09	197.50
NaCl	10.05	188.10	176.05
NaI	4.05	167.90	163.85
$NaNO_3$	11.21	184.97	173.76
KCl	6.78	171.40	164.62
KBr	6.64	164.70	158.06
KI	5.52	154.50	148.98
KNO_3	6.58	165.13	158.55
CaCl	7.31	157.60	150.29
NH_4Cl	4.61	161.60	156.99
NH_4Br	2.34	152.20	149.86
NH_4NO_3	2.37	153.14	150.77

Enthalpies of solvation ($\Delta H°_{solv}$) of the electrolytes have been determined by combining the heats of solution with the lattice energies of the electrolytes. Lattice energy of the electrolytes have either been taken from literature[12] or calculated from Kaputinski's equation[13] . All the relevant data are recorded in Table 2.

Persual of Table 2 reveals that the enthalpies of solvation of the elctrolyte increase with the decrease in the size of the ions. This is in accord with the findings in various solvents[14-16]

Ion-solvation enthalpies ($\Delta H°_{solv}$ (±)) of various ions in n-butanol have determined using the method suggested by Paul et al[12] which is a modification of the model of Latimer et al[17] . Plots of solvation enthalpies of electrolytes with common cation of anions versus reciprocal crystallographic radii ($1/r_i$) of the anions or cations respectively are not linear. However, by adding a correction factor (δ) of 0.1A° and 0.4A° to the crystallographic radii of anions and cations respectively, these plots become linear. Extrapolation of these plots of zero value of $1/(r_i+\delta)$ gives the value of solvation enthalpy of the common cation of anion.

The values of 81.1 k cal $mole^{-1}$ and 84.1 k cal $mole^{-1}$ have been obtained as the enthalpies of solvation of potassium and chloride ions respectively from these plots. Sum of these two values is quite close to the solvation enthalpy of potassium chloride which shows the applicability of this modol in n-butanol. Solvation enthalpies of the other ions in this solvent have been calculated on the basis of the enthalpy of solvation of potassium and chloride ions (solvation enthalpy of ions being the additive property). All the relevant data are listed in Table 3.

TABLE 3

ION-SOLVATION ENTHALPIES ($\Delta H°_{solv}(\pm)$ OF VARIOUS IONS IN n-BUTANOL

Ion	$-\Delta H°_{solv}$ (±) (Kcal $mole^{-1}$)
Li^+	113.9
Na^+	91.9
K^+	81.1
Cs^+	66.2
NH_4^+	72.9
Cl^-	84.1
Br^-	76.9
I^-	67.9
NO_3^-	77.5

Table 3 reveals that the solvation enthalpies of the ions decrease with the increase in the size of the ions and follow the order:

$$Li^+ > Na^+ > K^+ > NH_4^+ > Cs^+$$
$$Cl^- > Br^- > I^-$$

This order is in accord with the one reported in various solvents and also with the solvation number of the ions in n-Butanol[2]

Persual of Table 3 reveals that the solvation enthalpies of anions are more than those of cations of comparable size. In other solvents also, the solvation enthalpies of anions are more than that of cations[14-16,18,19] However, the differences of the solvation enthalpies between the cations and anions are more in this solvent as compared to that in other solvents. This may be because of the fact that in this solvent the anions-solvents interactions are supplemented by hydrogen bond formation.

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