Ion association and solvent interaction-conductance of alkali halides in chitosan solutions at four different temperatures

D.Moharatha[1],

Department of Physics Silicon Institute of Technology,
Bhubaneswar-751024,Odisha,India

G.S.Roy[2],

Bhubaneswar 751010 Odisha,India

U.N.Dash[3]

Bhubaneswar 751010 Odisha,India

Abstract

The conductance of halides of potassium, sodium and ammonium has been measured in the concentration range of 4 x 10^{-4} to 8 x 10^{-2} mol dm^{-3} in 0.1 mol HCl binary mixture containing chitosan (0.01,0.05 and 0.1%(w/w))at different temperatures (298.15 – 313.15 K). The conductance data in all the cases have been analysed by Shedlovsky equation to obtain Λ_m^0 and K_A. Based on the composition dependence of Walden product, the influence of the mixed solvent composition on the solvation of ions has been discussed. The values of association constants, K_A, are used to obtain various standard thermodynamic parameters for the association process in the solution.

Keywords: Binary chitosan solution ;Alkali halides; Association constants.

1.1 Introduction

Chitosan is derived from chitin a polysaccharide, which is also cellulose like polymer consisting mainly an unbranched chains of N-acetyl-D-glucosamine. Since chitosan finds wide applications in agriculture, horticulture, water filteration process, biomedical and industrial materials, the present work aims at determining the physico-chemical properties of the halides in chitosan solutions. Chitosan enhances the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable. Purified qualities of chitosan have occupied a separate area of

investigations by researchers due to its versatile pharmaceutical, biomedical and industrial applications. The studies on conductance of halides of potassium, sodium and ammonium in 0.01, 0.05, and 0.1% (w/v) chitosan in 0.1 molar HCl solutions(0.1 molar HCl solution is taken for the solubility of chitosan) are of importance in obtaining information on the behavior of ions in solutions and the interactions of water and chitosan with each other, and with the solute. The computed values of association constant are known to be composite quantity depending on specific and non-specific solute-solvent interactions and the separation of various interaction contributions is often very difficult. Since the composition of the solvents in a binary mixture is varied, in addition to the dielectric constant variation, there is also variation of solvent-solvent interaction in mixed solvents. Thus, studies in mixed solvent may provide information about both the specific and non-specific solvation effects on the ion-association phenomena. The aim of the present work is to study the role of ion- 0.1 mol.HCl soluble chitosan interactions characterizing the preferential solvation of the solute. In the present work, the molar conductance of halides of potassium, sodium and ammonium in 0.1 mol HCl and 0.1M HCl+chitosan mixtures have been measured at temperatures ranging from 298.15K to 313.15K at 5K intervals.

1.2 Experimental

All chemicals used were of G.R or B.D.H AnalaR grades. Alkali metal halides were heated at 120°C for 4hrs and kept along with ammonium chloride in vaccum desiccator over anhydrous calcium chloride until required. . Conductivity water (Sp.cond.~ 10^{-6} S cm^{-1}) was used for preparing 0.1 molar HCl solution.Since chitosan was not soluble in water the solution was prepared in 0.1 molar HCl solution and three different compositions of chitosan e.g. 0.1, 0.5 and 1.0 %,(w/v)) were prepared. The chitosan content in the mixed solvents was accurate within ±0.01%. The salt solutions were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression[1] considering the density data at the corresponding temperatures. Solutions were kept for 2hrs in a water thermostat maintained at the required temperatures accurate to within ±0.05K before use for conductivity measurements. Conductance measurements were made on a digital reading conductivity meter (Elico, CM 183) with a sensitivity of 0.1% and giving a conductance value of three digits. A dipping type conductivity cell with Platinized electrode (cell constants 1S cm^{-1}) was used. The measurements were made over the temperature range 298.15K – 313.15 K (± 0.05 K). The specific and molar conductances are expressed in S cm^{-1} and S cm^2 mol^{-1}, respectively. The ionic strengths of the solutions were kept as low as possible (~ 10^{-4} to 10^{-2} M). The experiment was repeated several times with different concentrations of the solutions (ranging from 1 x 10^{-2} to 7.5 x 10^{-4}M) in 0.1MHCl-water, and 0.01wt%, 0.05wt% and 0.1wt% chitosan in 0.1MHCl-water solutions. The conductance values of different concentrations of potassium, sodium and ammonium halides were measured several times making appropriate corrections for the conductance of the solvents concerned.

1.3 Results and Discussion

The experimental data of the conductance measurements for the halides of sodium, potassium and ammonium in water and three compositions of water + chitoan mixtures (as stated above), after solvent correction, were analyzed using Shedlovsky[2] and Fuoss-Kraus[3] extrapolation techniques as described elsewhere[4].As the limiting molar conductivity values, $\Lambda^{o}{}_{m}$ obtained by the two methods using values of ion-size parameter,$a_0=0$, q, and 2q are very close to each other, as in our previous studies[4], the values of $\Lambda^{o}{}_{m}$ for $a_0=q$ are given in Table 1 for the Shedlovsky method only, and so also the values of K_A, the association constant of the halide salts, in aqueous and in water+ chitosan mixed solvents at experimental temperatures. Table 1 also contains the values of Walden product, $\Lambda^{o}{}_{m} \eta_0$ for the salts at 25^0C only.

Since the conductance measurements of an ion depend upon mobility ,it is quite reasonable[5] to treat the conductance data similar to the one employed for the rate process taking place with the change of temperature, i.e.,

$$\Lambda^{o}{}_{m} = A e^{-E_s / RT}$$

Or

$$\log \Lambda^{o}{}_{m} = \log A - \frac{E_s}{2.303RT} \qquad (1)$$

where A is the frequency factor, R is the gas constant and E_s the Arrhenius activation energy of the transport process.

From the plot of $\log \Lambda^{o}{}_{m}$ vs.1/T, the E_s values have been computed from the

slope $(=-E_s/2.303R)$ and are shown in Table 2.
The standard free energy change, for the association process is calculated from Equation (2)[6]

$$\Delta G^0 = -RT \ln K_A \qquad (2)$$

The heat of association, ΔH^0 is determined from the slope of the plot of $\ln K_A$ vs. 1/T and the

entropy change, ΔS^0 from Gibbs-Helmholtz equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (3)$$

The values of the standard thermodynamic parameters are recorded in Table 2 at 25^0C only.

As observed, the decrease in Λ^0_m values with increase in chitosan content in mixed solvent for KCl, NaCl, and NH$_4$Cl (Table 1.) may be due to the fact that (i) with decrease in dielectric constant of the medium , the electrostatic attraction between the ions increases and hence , the dissociation of the solute into ions becomes less and (ii) with decrease in the extent of solvation , the distance of the closest approach becomes smaller resulting in poor dissociation. The Λ^0_m values in chitosan solution follows the order: potassium > ammonium> sodium which is the same order seen: in water + dextran mixtures[7].

The association constants, K_A of all the halides salts studied show an irregular trend with increase in temperature and also with increase in chitosan content (Table 1.). This may be attributed to the varying degree of exothermic ion-pair association caused due to difference in ionic stability, specific ion-solvent and solvent-solvent interactions.

The variation of the Walden product ($\Lambda^0_m\eta_0$) with composition at 298K is shown in Fig.1. In aqueous dextran solutions as studied earlier[7] the values in case of KCl , KBr, and KI increase almost linearly whereas in case of NaCl and NH$_4$Cl pass through minima. It is known that the variation of Walden product reflects the change of solvation[8]. The increase of the Walden product with increase of chitosan composition indicates weak solvation of ions. The observed minima in the plot of $\Lambda^0_m\eta_0$ vs composition, in case of NaCl and NH$_4$Cl indicates that there exists a region where the water structure remains more or less intact as the polymeric chitosan molecules are added into the cavities in this structure in the presence of Na$^+$ and NH$_4^+$ cations. Such results may be interpreted in terms of microheterogeneity[9] in the mixtures. It may be due to the electrochemical equilibrium between the ions and the solvent molecules on one hand and the selective solvation of ions on the other with the change of composition of the mixed solvent. In case of chitosan, the values of $\Lambda^0_m\eta_0$ (Fig.1.) decrease with increase in chitosan content in the solution. It might be due to increase in the effective ionic radii of the ions concerned. The variation in the values of Walden product with temperature as well as with solvent compositions indicate the variation in the ionic radii and mobility of the ions due to varying degree of ion solvation in solutions.

A perusal of Table 2. shows that the activation energy , E_s is positive for all the salts in all solvents. The free energy change, ΔG^0 values are negative for all the halide salts in all the solvent systems studied. This indicates that the association process is favoured over the dissociation process in all the mixed solvents. The positive values of ΔH^0 and ΔS^0 (excepting few cases) show that the association processes are endothermic in nature and more energy consuming.

Table 1. Values of Λ^0_m (cm^{2}mol^{-1}), K_A (dm^3 mol^{-1}) and $\Lambda^0_m \eta_0$ of halide salts in aqueous Chitosan solutions at different temperatures.

Chitosan(wt%)	Temp(K)	Λ^0_m	K_A	$\Lambda^0_m \eta_0$
1	2	3	4	5

Potassium Chloride

0.1MHCl	298.15	247.15±4.54	82.88±3.64	2027.5
	303.15	257.44±4.37	75.47±6.28	1921.5
	308.15	274.93±4.68	80.02±3.50	1874.9
	313.15	288.79±4.88	81.78±3.59	1759.7
0.01	298.15	202.31±3.18	57.50±2.37	1746.8
	303.15	215.46±3.25	56.57±2.32	1677.6
	308.15	236.07±4.14	73.78±3.21	1672.2
	313.15	261.53±5.21	100.74±4.45	1595.4
0.05	298.15	177.33±4.20	95.70±4.25	1502.8
	303.15	194.11±4.57	104.07±4.60	1487.3
	308.15	211.02±4.86	108.49±4.79	1480.6
	313.15	237.75±5.88	141.41±6.18	1458.7
0.1	298.15	152.83±4.66	138.30±6.04	1300.7
	303.15	161.99±4.64	127.51±5.62	1301.3
	308.15	183.81±5.27	151.97±6.52	1307.1
	313.15	208.30±6.06	179.19±7.59	1279.7

Sodium Chloride

0.1MHCl	298.15	182.45±5.01	25.61±2.74	1857.3
	303.15	234.78±3.65	61.83±2.61	1785.6
	308.15	249.02±4.18	71.80±3.12	1715.9
	313.15	262.19±3.38	52.96±2.12	1665.3
0.01	298.15	152.30±4.51	65.00±4.31	1569.1
	303.15	169.75±3.64	152.67±4.97	1497.8
	308.15	216.02±6.68	66.16±2.83	1546.6
	313.15	241.86±3.89	66.23±2.84	1543.4
0.05	298.15	137.12±0.20	631.50±0.62	1290.0
	303.15	134.48±4.74	52.02±4.34	1346.8
	308.15	187.82±3.88	79.88±3.50	1365.3
	313.15	217.80±4.97	108.78±4.83	1386.5

1	2	3	4	5
0.1	298.15	128.65±4.14	127.60±5.63	1106.4
	303.15	140.73±3.68	93.48±4.14	1178.2
	308.15	162.37±4.08	98.87±4.38	1221.2
	313.15	177.15±4.48	107.60±4.80	1171.9

Ammonium Chloride

0.1MHCl	298.15	227.79±3.29	55.34±2.27	1941.8
	303.15	239.64±3.54	58.30±2.44	1831.0
	308.15	254.99±3.99	65.55±2.81	1771.8
	313.15	284.27±5.29	89.12±4.08	1701.9
0.01	298.15	150.42±5.51	1.05±0.68	1642.9
	303.15	208.85±3.62	66.35±2.84	1602.5
	308.15	223.10±3.74	65.85±2.83	1597.0
	313.15	248.69±4.59	84.59±3.70	1549.7
0.05	298.15	139.42±2.97	61.18±2.83	1395.2
	303.15	184.07±4.46	103.70±4.60	1409.6
	308.15	199.19±4.29	90.07±3.98	1428.6
	313.15	218.46±4.79	100.93±4.48	1403.8
0.1	298.15	144.58±4.38	126.03±5.59	1244.0
	303.15	154.31±4.10	105.02±4.65	1273.6
	308.15	167.90±4.59	119.76±5.31	1230.1
	313.15	193.80±5.49	150.78±6.58	1220.9

Table 2. Values of thermodynamic parameters ΔG^0 (kJmol^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0

(J mol^{-1} K^{-1}) and E_S (kJ mol^{-1}) for alkali metals halides and ammonium

chloride in different chitosan compositions at 298.15K.

Chitosan (wt%)	ΔG^0	ΔH^0	ΔS^0	E_s
1	2	3	4	5

Potassium Chloride

0.1MHCl	-10.95±0.66	0.23±0.25	37.50±1.29	8.27±0.18
0.01	-10.04±0.50	30.07±2.49	134.55±4.65	13.35±1.76
0.05	-11.31±0.72	18.73±2.24	100.76±4.31	14.94±1.59
0.1	-12.22±0.87	14.66±2.11	90.16±4.18	16.35±1.49

Sodium Chloride

.1MHCl	-8.04±0.80	36.76±4.10	150.25±7.36	17.90±2.90
0.01	-10.35±0.79	-11.66±4.70	-4.42±8.49	25.28±3.32

| 0.05 | -15.98±0.04 | -76.68±4.29 | -203.58±7.85 | 26.65±3.03 |
| 0.1 | -12.02±0.84 | -7.27±1.39 | 15.93±2.03 | 17.12±0.98 |

Ammonium Chloride

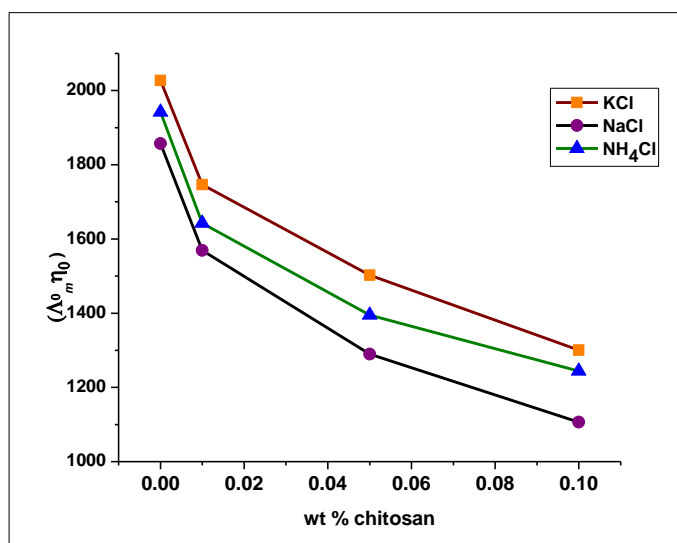| 0.1MHCl | -9.95±0.49 | 23.88±2.33 | 113.47±4.35 | 11.25±1.64 |
0.01	-0.11±0.95	206.47±5.06	692.86±9.10	24.55±3.58
0.05	-10.20±0.55	21.34±3.96	105.77±7.19	22.24±2.80
0.1	-11.99±0.84	10.18±1.74	74.35±3.54	14.91±1.23

Fig. 1   Plot of Walden product $\Lambda^0_m\eta_0$) *vs .*compositions of chitosan.

1.4 Conclusion:

The values of Λ^0_m of potassium chloride, sodium chloride and ammonium chloride have been determined in different composition of 0.1MHCl-chitosan solution at four different temperatures ranging from   298.15K to 313.15K. The values of Λ^0_m increase with increase of temperature for the three halides in all solvents but decrease with increase in chitosan content in 0.1MHcl solution. The values of Arrhenius activation energy are positive indicating the transport process spontaneous. The values of Walden product decrease with increase of chitosan content and temperature showing the variation of the ionic radii and mobility of ions due to varying degree of solvation in solutions. The negative values of ΔG^0 indicate that the association process is favoured over the dissociation process in all mixed solvent. The positive values of ΔH^0 and ΔS^0 are the indicative of the more energy consuming endothermic process.

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