C H A P T E R * VI

CHAPTER - VI

Compressibility studies of Tetraalkylammonium halides in DMSO and DMSO + H_2O mixtures (20, 40, 60 & 80% W/W) at 298.0 K

The role of solvents can hardly be explained in absence of complete knowledge of the nature of solvation of electrolytes and non-electrolytes. The subject has attracted considerable attention and the "solvation number" has been determined using well-known techniques. A good account of the aspect has been presented by Conway and Bockris and others[1-5].

However, in general, alarmingly large number of discrepant values of solvation numbers are obtained from different types of measurements. The apparent anomaly arises from different types of ion-solvent interactions and the capability of the different instruments to sense ion-solvent interactions.

To resolve the anomaly, Bockris[1,2] suggested that the term "Primary Solvation" be used to refer to the number of solvent molecules near to an ion which have lost their translational degrees of freedom and move as entity with the ion during the Brownanion motion. The term "Secondary Solvation" is used to refer to solvetn molecules not included in the solvation but which undergo electrostatic interaction with the primarily solvated ion sufficiently to affect solvation dependent quantities e.g. salting out. Thus, the primary solvation number is a definite quantity whilst numerical estimates of secondary solvation must depend on the phenomenon observed.

Of the different methods of determining solvation, we have adopted the compressibility method using ultrasonic interferometer. The method was utilised by Maiti, Chattopadhyay and Lahiri[6,7] in recent years.

The large tetraalkylammonium ions has attracted considerable attention due to their amphipathic nature of the electrolytes.

In view of the interesting physical properties of these salts received considerable attention and extensive studies have been made with these salts. However, anomalous behaviour of these salts have in no way been resolved. The nature of solvation of these tetraalkyl salts and the change in solvational characteristics in different DMSO + H_2O mixtures have been determined employing the compressibility method with an ultrasonic interferometer. The results are described in the present chapter.

Experimental details

The experimental details are given in Chapter - II. The measurements were taken at different percentages of DMSO + Water mixtures (20% - 80 wt% and 100 wt% in some cases. The measurements were carried out at different concentrations of the salts.

Results

The solvation number 'n' can be obtained by determining the compressibilities of the pure solvent (β_{solv}) and the ionic solutions (β_{soln}) from the relation :

$$n = \frac{n_s}{n_i}\left(1 - \frac{\beta_{solv}}{\beta_{solv}}\right)$$

where n, ni and ns represent the solvation number, number of moles of ions solvated and number of moles of solvent present in the system of volume V respectively.

The accoustic parameters are calculated as follows:

i) Adiabatic compressibility, $= \frac{1}{C^2\rho}$

ii) Specific acoustic impedance, $Z = C\rho$

iii) Intermolecular free length, $L_f = k\sqrt{\beta}$

where k is the temperature dependent constant. The value of k is taken to be 6.2206×10^{-4}.

The results are recorded in tables 1 and 2.

Discussion

The velocity of sound in air free distilled water at 298 K comes out to 1487 ± 3 m/sec which compares well with the value 1485.4 ± 2.3 m/sec at 298 K[8].

The velocity of sound C increases as the percentage of organic solvent increases and passes through a maximum at about 60 wt% of DMSO. Similarly, the adiabatic compressibility decreases and passes through a minima in the same region. This may be due to the fact that the interstitial spaces of water molecules are filled by the organic solvent molecules but beyond a certain limit. There cannot be any further accommodation of (solvent) molecules. However,

the compressibility behaviour may also be explained in terms of increase in the structure of water molecules due to the addition of DMSO initially followed by the formation of DMSO, $2H_2O$ complexes which would be maximum in the region ~ 70 wt% of DMSO. The DMSO, $2H_2O$ structure breaks down beyond this region[9-12]. The compressibility values of different electrolytes naturally show minima in this region.

It is likely that other acoustic parameters show a change in their behaviour in this region. It is but natural to associate the solvational behaviour of the electrolytes in mixed solvents with their structural properties.

It is found that the specific acoustic impedance, in general, decreases as we go from Me_4N^+ to Bu_4N^+ salts and the intermolecular bound length increases slightly. This is reasonable in view of increasing volume as we go from Me_4N^+ to Bu_4N^+ salts.

Curiously, we have tried to calculate the water association per DMSO molecule from the change in compressibility of DMSO + water mixtures assuming DMSO to be the solute. Each mole of DMSO is found to be associated with 2.43, 1.50, 0.84 and 0.69 moles of H_2O molecules, the rest of the water molecules may be regarded to be free. Though the result is not significants in view of the complicated nature of the problem, it can be assumed that dehydration of water molecules from DMSO gradually increases. But we do not attach much significance to these results.

In order to get the accurate solvation numbers, generally compressibility values are determined at various concentrations and extrapolated to zero dilution. We, therefore, carried out our

works in very dilute solutions so that we can determine the real solvation numbers of tetraalkyl ions. However, the works in dilute solution show that the solvation numbers of tetraalkylammonium ions are quite high. It is to be noted that the solvation number of ions changes with increasing concentrations due to cation-cation interactions[13]. In dilute solutions, the studies indicate that Pr_4N^+ and Bu_4N^+ ions increase the structure of water where Me_4N^+ ion diminishes the structure. The hydration numbers of Me_4N^+, Et_4N^+, Pr_4N^+ and Bu_4N^+ have been determined to be 16, 21, 27 and 32 respectively by Pottel and Lossen[14], whereas Hertz et al[15] assumed these numbers to be 25, 30, 35 and 40 respectively at 25° C. The solvation of tetraalkyl ions in dilute solutions are in conformity with these values.

However, the negative hydration have been observed for the electrolytes in 60-80 wt% of DMSO in general. The results indicate that these electrolytes behave as structure breakers in these solvent mixtures. The reasons may be that the addition of B_4NX to the solvent mixtures may lead to the preferential solvation of cations by water leading to a decrease in compressibility by decreasing the unbounded water and increasing electrostricted water. At the same time, the breakdown of DMSO, $2H_2O$ complex takes place which would increase the number of unbound DMSO molecules. Naturally, the compressibility would decrease.

One of the limitations of determining the solvation number in mixed solvents arise from the fact that DMSO + H_2O mixtures have been regarded to an assorted solvent, the total numbers of moles of

solvents have been calculated accordingly by simply summing the number of moles of water and DMSO respectively. But if we consider the solvent to be DMSO + $2H_2O$, the solvation number will change.

We also determined the solvation number of salts with reasonably high concentrations of the electrolytes and the results are given in Table 3. From Table 3, we have also calculated the single ion solvation numbers of tetraalkyl ions based on the solvation number of Bu_4NBPh_4 and apportioning it equally.

Thus, the solvation number of ions obtained are as follows:

	20%	40%	60%	80%
Bu_4N^+	1	0.5	-0.5	-0.5
BPh_4^-	1	0.5	-0.5	-0.5
Pr_4N^+	1-2	0.5-1.5	0.5-1.5	-0.5-0.5
I	1	0.5	0.5	1.5
Na^+	2	0.5	1.5	2.5
Br	0-1	0.5	0.5	1.5

We have not taken Me_4N^+ and Et_4N^+ into consideration as their concentrations were low.

However, in higher percentages, negative solvation of tetraalkyl ions are observed.

It is apparent that the accurate compressibility data of different electrolytes may be of great help in determining the solvation number of ions in solution.

Table - 1

Accoustic Parameters of Tetraalkylammonium halides in DMSO and DMSO + Water mixtures at 298 K

Wt% DMSO	ρ/g cm^{-3}	Velocity (m/sec)	$\beta \times 10^{12}$ (cm^2/dyne)	$Z \times 10^{-5}$ (Rayl)	L_f (Å)	n
			Me_4NI (C = 0.05 M)			
20	1.02731	1640	37.55	1.654	0.3835	9.0
40	1.05622	1678	34.64	1.732	0.3606	17.0
60	1.08574	1624	30.92	1.803	0.3676	+37.0
80	1.10248	1640	33.72	1.808	0.36119	- 6.0
100	1.09684	1510	39.91	1.659	0.3929	9.0
			Et_4NI (C = 0.05 M)			
20	1.02607	1624	36.95	1.656	0.3781	15
40	1.05678	1680	33.53	1.775	0.3602	9
60	1.08538	1632	34.59	1.771	0.3658	-34.0
80	1.10115	1644	33.60	1.810	0.3606	- 6.0
100	1.09778	1520	39.43	1.669	0.3905	11.0
			Pr_4NI (C = 0.05M)			
20	1.02637	1628	38.94	1.663	0.3780	23
40	1.05622	1684	33.39	1.778	0.3594	9
60	1.08518	1652	33.77	1.792	0.3615	-25
80	1.10035	1646	33.54	1.811	0.3602	-22
100	1.09723	1492	40.94	1.637	0.3980	6

Contd..

Table - 1 (Contd..)

Bu_4NI (C = 0.05M)

20	1.02641	1636	36.40	1.679	0.3753	30
40	1.05638	1678	33.70	1.770	0.36108	5
60	1.03415	1660	33.47	1.800	0.3599	-22
80	1.09967	1648	33.48	1.812	0.3599	- 5
100	1.09458	1506	40.28	1.648	0.3948	8

Me_4NBr (C = 0.05M)

20	1.02546	1604	37.90	1.645	0.3829	12
40	1.05878	1664	34.23	1.756	0.3639	- 1
60	1.08851	1588	32.36	1.830	0.3538	-11
80	1.10093	1636	33.94	1.801	0.3624	- 8
100	1.09662	1544	39.47	1.657	0.3908	11

Et_4NBr (C = 0.05 M)

20	1.02585	1616	37.34	1.657	0.38008	18
40	1.05506	1692	33.11	1.785	0.35791	12
60	1.08402	1548	33.97	1.786	0.36253	-27
80	1.10061	1640	33.78	1.805	0.36151	- 7
100	1.09586	1544	38.21	1.693	0.38448	15

Contd..

Table - 1 (Contd..)

Pr_4NBr (C = 0.05 M)

20	1.02496	1620	37.18	1.660	0.37927	20
40	1.05464	1680	33.56	1.772	0.36073	6
60	1.08327	1656	33.66	1.794	0.36087	-24
80	1.09984	1642	33.73	1.805	0.36124	- 7
100	1.09526	1488	41.77	1.630	0.39958	5

Bu_4NBr (C = 0.05 M)

20	1.02461	1628	36.82	1.668	0.37742	25
40	1.05421	1668	34.09	1.758	0.36316	0
60	1.08278	1660	33.51	1.797	0.36006	-22
80	1.09935	1644	33.66	1.807	0.36087	- 6
100						

Me_4NCl (C = 0.05 M)

20	1.02356	1628	36.85	1.666	0.37763	24
40	1.05746	1672	33.98	1.760	0.36258	2
60	1.08259	1676	32.88	1.814	0.35666	-16
80	1.09975	1652	33.01	1.817	0.35737	- 1

Contd..

Table - 1 (Contd..)

Et_4NCl (C = 0.05 M)

20	1.02562	1636	36.43	1.678	0.37542	29
40	1.05646	1680	33.64	1.769	0.36076	6
60	1.08250	1668	33.36	1.866	0.35926	-21
80	1.09959	1646	33.57	1.810	0.36038	- 5

NaI

20	1.02689	1600	38.04	1.643	0.38363	10
40	1.05850	1604	36.72	1.697	0.37691	-31
60	1.08746	1664	33.21	1.810	0.35845	-20
80	1.10412	1640	33.67	1.811	0.36092	- 6

$NaBPh_4$

20	1.02661	1604	37.66	1.646	0.38272	12
40	1.05544	1608	36.64	1.697	0.37650	-29
60	1.08370	1668	33.17	1.808	0.35823	-19
80	1.09988	1648	33.48	1.813	0.35990	- 5

Table - 2

Acoustic Parameters of DMSO + Water mixtures (W/W) at 298 K

Wt% of DMSO	ρ gm cm^{-3}	Velocity m/s	B x 10^{12} cm^2/dyne	Z Rayl	$L_g(A^o)$
0	0.99707	1485	45.45	1.481	0.41933
20	1.02347	1600	38.16	1.638	0.38423
40	1.05357	1668	34.20	1.775	0.36375
60	1.08256	1718	31.30	1.860	0.34799
80	1.09805	1666	32.81	1.829	0.35628
100	1.09410	1482	41.62	1.621	0.40127

Table - 3

Acoustic Parameters of Tetraalkylammonium halides in DMSO + Water Mixture (v/v) at 298 K

Molar concentrations of solutions C = 1(M)

Salts	ρ/gm cm^{-3}	Velocity (m/sec)	B x 10^{-12} (cm^2 /dyne)	G x 10^{-5} (Rayl)	$L_f(\lambda^o)$	n
			20% DMSO			
Me_4NI*	1.02731	1610	37.55	1.654	0.38353	9
Et_4NI*	1.02730	1602	37.93	1.646	0.38317	3
Pr_4NI	1.03454	1605	37.52	1.660	0.38100	2
Bu_4NI	1.03456	1608	37.38	1.664	0.38029	2
Me_4NBr	1.03111	1610	37.41	1.660	0.38044	2
Et_4NBr	1.03095	1612	37.32	1.662	0.37998	3
Pr_4NBr	1.02917	1610	37.68	1.657	0.38079	2
Bu_4NBr	1.02779	1605	37.77	1.650	0.38226	1
NaI	1.03503	1612	37.15	1.672	0.37865	3
$NaBPh_4$	1.03530	1600	37.73	1.659	0.37922	3

Contd..

Table - 3 (Contd..)

Salts	ρ/gm cm^{-3}	Velocity (m/sec)	$\beta \times 10^{-12}$ (cm^2/dyne)	$Z \times 10^{-5}$ (Rayl)	$\log(\lambda^{o})$	n
			40% DMSO			
Me_4NI*	1.05622	1678	33.61	1.772	0.36060	7
Et_4NI*	1.05678	1674	33.77	1.769	0.36146	5
Pr_4NI	1.06478	1672	33.59	1.780	0.36649	2
Bu_4NI	1.06631	1669	33.70	1.778	0.36103	1
Me_4NBr	1.06105	1678	33.47	1.780	0.35985	2
Et_4NBr	1.06108	1675	33.59	1.777	0.36049	2
Pr_4NBr	1.05918	1673	33.73	1.772	0.36124	1
Bu_4NBr	1.05738	1670	33.11	1.766	0.36220	1
NaI	1.07342	1677	33.12	1.800	0.35796	1
$NaBPh_4$	1.06202	1670	33.76	1.774	0.36140	1

Contd..

Table - 3 (Contd..)

Salts	ρ/gm cm^{-3}	Velocity (m/sec)	B x 10^{-12} (cm^2/dyne)	K x 10^{-5} (Ray l)	L_f(A^o)	n
			60% DMSO			
Me_4NI*	1.08574	1728	30.84	1.876	0.34542	5
Et_4NI*	1.08539	1724	30.99	1.871	0.34526	3
Pr_4NI	1.09194	1720	30.96	1.878	0.346091	1
Bu_4NI	1.08828	1718	31.13	1.870	0.34704	0
Me_4NBr	1.08966	1727	30.77	1.882	0.34503	1
Et_4NBr	1.08994	1723	30.91	1.878	0.34581	1
Pr_4NBr	1.08519	1720	31.14	1.867	0.34710	0
Bu_4NBr	1.08336	1719	31.24	1.862	0.34765	0
NaI	1.09341	1731	30.82	1.893	0.34362	2
$NaBPh_4$	1.08502	1729	30.83	1.860	0.34464	1

Contd..

Table - 3 (Contd..)

Salts	ρ/gm cm^{-3}	Velocity (m/sec)	B x 10^{-12} (cm^2/dyne)	Z x 10^{-5} (Rayl)	L_f(A^o)	n
			80% DMSO			
Me_4NI *	1.10248	1685	31.94	1.858	0.35153	7
Et_4NI *	1.10115	1684	32.02	1.854	0.35197	6
Pr_4NI	1.10624	1681	31.99	1.860	0.35180	2
Bu_4NI	1.10301	1673	32.39	1.845	0.35399	1
Me_4NBr	1.10846	1684	31.81	1.867	0.35103	2
Et_4NBr	1.10721	1682	31.92	1.862	0.35142	2
Pr_4NBr	1.10446	1680	32.08	1.855	0.35230	1
Bu_4NBr	1.10268	1675	32.32	1.847	0.35301	1
NaI	1.11898	1688	31.36	1.889	0.34832	4
$NaBPh_4$	1.10407	1684	31.94	1.859	0.35147	2

*Concentration is = 0.05 (M)

R E F E R E N C E S

1. B.E. Conway and J.O'M Bockris in Modern Aspects of Electro-Chemistry, Vol. I, Ed. J.O'M Bockris, Butterworth's Publication Inc. London, 1954, Chapter II.

2. J.O'M. Bockris and A.K.M. Reddy, Modern Electrochemistry, Vol. I, Plenum Press (1970), Chapter II.

3. J. Padova, J. Chem. Phys., 40, 391, 1964.

4. A. Weissberger, Techniques of Organic Chemistry, Vol. 7, Interscience Publisher Inc. New York, 1959.

5. S. Prakash, N. Prasad and O. Prakash, J. Chem. Engng. Data, 22, 51, 1977.

6. B.K. Maiti, A.K. Chattopadhyay and S.C. Lahiri, Electrochim. Acta, 25, 1487, 1980.

7. A.K. Chattopadhyay and S.C. Lahiri, Electrochim. Acta., 27, 269, 1982.

8. A.B. Wood, A Text Book of Sound, 3rd Ed.n, J. Bell, London, 1960, p. 51 and 577.

9. J.J. Lindberg and J. Kentemma, Soumen. Kem. B33, 104, 1960.

10. M.R.J. Dock, Chemical Society Reviews, 4, 211, 1975.

11. C.C.Deb, D.K. Hazra and S.C. Lahiri, Bull. Soc. Chim Belges, 93, 621, 1984.

12. Chapters 4 and 5 of the present dissertation.

13. Wen-Yang Wen in Water and Aqueous Solutions : Structure, Thermodynamics and Transport Processes, Ed. R.A. Horne, Chapter 15.

14. R. Pottel and C. Lossen, Ber. Bunsenges, Physik. Chem., 71, 135, 1967.

15. H.G. Hertz, Ber. Bunsenges, Physik. Chem., 68, 907, 1964.