

CHAPTER VI

Ultrasonic Velocities and Isentropic Compressibilities of Electrolytes in 2-Methoxyethanol in the Temperature Range 288.15 to 308.15 K

It is well recognised that ultrasonic velocity and isentropic compressibilities of liquids, electrolyte solutions, and liquid mixtures provide information on ion-ion, ion-solvent and solvent-solvent interactions.¹ Very useful and often interesting results are obtained while investigating the variation of ultrasonic velocities of electrolyte solutions as a function of concentration and temperature. The relative magnitudes of the limiting apparent molar isentropic compressibilities (κ_{ϕ}°) would enable us to gather information about the strengths of interactions between ions and solvent molecules.

In the previous chapter we reported our conductance and FT-Raman spectral studies of solutions of lithium tetrafluoroborate (LiBF_4), sodium tetrafluoroborate (NaBF_4), tetraphenylphosphonium chloride (Ph_4PCl), tetraphenylphosphonium bromide (Ph_4PBr), and tetraphenylarsonium chloride (Ph_4AsCl) in 2-methoxyethanol. In this chapter we present the ultrasonic velocity measurements on the same set of electrolyte solutions in 2-methoxyethanol as functions of temperature ($288.15 \leq T/\text{K} \leq 308.15$). An attempt has been made to unravel the nature of various types of interactions prevailing in these solutions.

Apparent molar isentropic compressibilities (κ_{ϕ}) of these electrolytes were derived from the measured ultrasonic velocity data, supplemented with their densities. Infinite dilution partial molar isentropic compressibilities (κ_{ϕ}°) were obtained by

extrapolation from the plot of κ_ϕ against the square-root of the molarity. The κ_ϕ^0 values of the electrolytes were split into approximate limiting ionic compressibilities ($\kappa_\phi^0 \pm$) on the basis of the assumption that $\kappa_\phi^0(\text{BF}_4^-) = 0$. The results have been interpreted in terms of specific constitutional and structural factors of the solvent molecules and of the solute ions.

6.1 EXPERIMENTAL SECTION

6.1.1 Materials:

Tetraphenylarsonium chloride (Ph_4AsCl), tetraphenylphosphonium chloride (Ph_4PCl), tetraphenylphosphonium bromide (Ph_4PBr), lithium tetrafluoroborate (LiBF_4), and sodium tetrafluoroborate (NaBF_4) were prepared and purified as reported in Chapter 3. The purified ME had a density of $0.96002 \text{ g cm}^{-3}$ and a coefficient of viscosity of 1.5414 mPa s , at 298.15 K .

6.1.2 Apparatus and Procedure:

Sound velocities were measured with an accuracy of $\pm 0.3 \%$ using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz and the procedure has been described in Chapter 3.

Isentropic compressibility coefficients (κ_s) were derived from the relation

$$\kappa_s = 1/(u^2\rho) \quad (1)$$

where ρ is the solution density and u is the sound velocity in the solution.

The apparent molar isentropic compressibility (κ_ϕ) of liquid solutions was calculated from the relation

$$\kappa_\phi = [(1000/m\rho\rho_o)(\kappa_s\rho_o - \kappa_s^\circ \rho)] + \kappa_s M/\rho_o \quad (2)$$

where m is the molality of the solution and the other symbols have their usual significance.

6.2 RESULTS AND DISCUSSION

The molal concentration (m), density (ρ), the sound velocity (u) and the apparent molar isentropic compressibility (κ_ϕ) of the solutions of LiBF_4 , NaBF_4 , Ph_4AsCl , Ph_4PCl , and Ph_4PBr at 288.15, 293.15, 298.15, and 308.15 K are given in Table 1.

The limiting apparent molar isentropic compressibilities (κ_ϕ°) were obtained² by extrapolating the plots of κ_ϕ versus the square root of the molal concentration of the solute to zero concentration by the method of least squares:

$$\kappa_\phi = \kappa_\phi^\circ + S_k \sqrt{m} \quad (3)$$

where S_k is the experimental slope. The κ_ϕ° values along with the experimental slopes (S_k) are listed in Table 2.

Ionic additivity can usually give some idea of the reliability of results. The differences between LiBr^3 and LiBF_4 and between NaBr^3 and NaBF_4 are respectively -43.82 and $-43.85 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ which gives an indication of the reliability and internal consistency of our data.

For all of these electrolytes, the apparent molar isentropic compressibilities have been found to have large negative values at all the temperatures investigated. The possible effects which the solutes can exert on the solvent structure and their role on solvent compressibility have been explained as follows:

- i) the smaller ions e.g., Li^+ , Na^+ , Cl^- , and Br^- are known to be largely solvated by the electrostriction of solvent molecules around them in ME.⁴ This results in a loss of compressibility of ME in solution compared to the pure solvent. The BF_4^- ion, on the other hand, has been shown to remain unsolvated in ME⁵; moreover, it has too small an intramolecular free space to have any significant intrinsic compressibility. This ion, therefore, does not influence the compressibility of the medium to any significant extent.
- ii) most of the interpretations of κ_ϕ^0 in terms of solvation effects⁶⁻¹⁰ assume that κ_ϕ^0 of unsolvated ions is negligible, although Conway and Verral recognized that large organic ions (here Ph_4P^+ and Ph_4As^+) could have some intrinsic compressibility due to the intramolecular free space which makes the solution more compressible.

- iii) Another effect that is possible for large organic ions is the penetration of the solvent molecules into the intramolecular space. This is the result of the interaction of the positively charged phosphorus/arsenic atom of the tetraphenyl ions with the neighbouring solvent molecules. This is essentially an electrostriction effect and causes constriction in the solution volumes resulting in a more compact and hence less compressible medium.
- iv) Infrared spectral studies indicate^{11,12} that intramolecular hydrogen bonding exists in ME molecules in the liquid state. While solvating smaller ions like, Li^+ , Na^+ , Cl^- , and Br^- , some of the intramolecular hydrogen-bonds are broken down making the solution less compressible.

The interplay of the above four factors actually controls the compressibility of the solution.

For LiBF_4 and NaBF_4 solutions, the negative κ_ϕ^0 values can be ascribed to the effects (i) and (iv). Here Li^+ and Na^+ ions are primarily responsible for the loss of compressibility in solution. LiBF_4 solutions are found to be less compressible than NaBF_4 solutions in the temperature range investigated. The charge density on the Li^+ ion is greater than that on the Na^+ ion, and hence effective electrostatic pressure should be larger in solutions of lithium salt than in those of the sodium salt. One can thus expect that compressibility of the lithium salt solution to be less than that of the sodium salt at any given concentration.

The negative κ_{ϕ}° values of the Ph_4PCl , Ph_4PBr , and Ph_4AsCl solutions can be attributed to the predominance of the effects (i), (iii), and (iv) over the effect (ii).

The κ_{ϕ}° values for Ph_4PBr solutions are always a little bit more negative than those for Ph_4PCl solutions indicating that the loss of the compressibility of the medium is less in the presence of Ph_4PBr .

From the experimental values of the limiting apparent molar isentropic compressibilities of Ph_4PCl and Ph_4AsCl solutions, it is clear that the presence of Ph_4P^+ ions makes ME more compressible than the presence of Ph_4As^+ ions. These observations can give an important insight into the structures of these ions in ME. Both Ph_4P^+ and Ph_4As^+ ions should have almost equal intramolecular free space. But, since the positively charged arsenic atom has a greater tendency to attract the ME molecule¹³, penetration will be more in Ph_4As^+ ion than in Ph_4P^+ ion. This makes the former ion less compressible than the latter.

The variation of the κ_{ϕ}° values of the salt solutions with temperature is quite interesting. While the alkali metal salts LiBF_4 and NaBF_4 exhibit a regular decrease of κ_{ϕ}° values with temperatures, for the other three tetraphenyl salts e.g., Ph_4PCl , Ph_4PBr , and Ph_4AsCl , a maximum in the κ_{ϕ}° vs. temperature curve is observed at 298.15 K.

On raising the temperature of the system, the alkali metal ions lose some solvent molecules from their first coordination sphere progressively which is expected to increase the compressibility. But at higher temperatures, a breakdown of the intramolecular hydrogen-bonds in ME also takes place more effectively resulting in a loss of compressibility. Thus, it may be concluded that for LiBF_4 and NaBF_4 solutions, the latter effect is growing faster and overriding the former as far as the present temperature range is concerned.

In Ph_4PCl , Ph_4PBr , and Ph_4AsCl solutions, the halide ions are gradually desolvated with the rise in temperature. The Ph_4P^+ and Ph_4As^+ ions also release some solvent molecules from inside their intramolecular spaces. The release of solvent molecules should render these solutions more compressible. Moreover, the larger organic ions are becoming more and more compressible at elevated temperatures due to the availability of the space in between the phenyl groups which was earlier occupied by solvent molecules at lower temperatures. The desolvation effects must predominate up to ~ 298.15 K in these salt solutions where κ_ϕ° values reach maxima. Beyond this temperature, solutions become less compressible as a result of the predominance of the other effects e.g., breaking down of intramolecular hydrogen-bonds of solvent molecules over the desolvation effects. With increasing temperature, the effect of desolvation becomes smaller and smaller and we believe that at least one ion in these salts gets fully desolvated when a maximum in κ_ϕ° vs. temperature is reached.

There are no reliable methods of dividing κ_{ϕ}° into ionic components. Millero¹⁴ has suggested dividing the partial molar volumes of $\text{Ph}_4\text{As}^+\text{Ph}_4\text{B}^-$ into ionic components but such a method cannot be used here since we do not know the ratio of the compressibilities of the pure (solid or gaseous) ions. The extrapolation method as suggested by Conway *et al.*¹⁵ can also not be used for the division of κ_{ϕ}° values. The method¹⁶ used in acetonitrile assuming $\kappa_{\phi}^{\circ}(\text{Ph}_4\text{B}^-) = 0$ is also not appropriate as the Ph_4B^- ion is large (0.535 nm) and therefore its compressibility contribution cannot be taken as zero.

Under these circumstances and also in view of the compressibility behaviour of the BF_4^- ion in ME, the assumption that $\kappa_{\phi}^{\circ}(\text{BF}_4^-) = 0$ seems to be the best choice at the moment. Ionic κ_{ϕ}° values based on this assumption are given in Table 3 which seem to fit quite well with the discussion made above on the basis of the κ_{ϕ}° values of the salts as a whole.

References

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Table 1. Molal concentration ($m/\text{mol kg}^{-1}$) density ($\rho/\text{g cm}^{-3}$), ultrasonic velocity ($u/\text{m s}^{-1}$) and apparent molar isentropic compressibility ($\kappa_{\phi}/\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$) of the electrolyte solutions in 2-methoxyethanol at different temperatures.

m	ρ	u	$10^4 \kappa_{\phi}$	m	ρ	u	$10^4 \kappa_{\phi}$
T = 288.15 K							
LiBF₄				NaBF₄			
0.01060	0.97025	1382.28	-81.8	0.02075	0.97158	1382.09	-64.2
0.03101	0.97147	1383.48	-69.8	0.03113	0.97225	1382.63	-61.2
0.05165	0.97271	1384.31	-61.0	0.06232	0.97463	1383.46	-54.5
0.07273	0.97397	1384.81	-54.0	0.07766	0.97665	1384.45	-51.9
0.09323	0.97518	1385.11	-48.1	0.09319	0.97665	1384.45	-49.6
0.11811	0.97666	1385.16	-41.7	0.12491	0.97918	1384.52	-45.1
Ph₄PCl				Ph₄PBr			
0.01068	0.97043	1383.65	-78.9	0.01559	0.97198	1384.71	-109.5
0.03185	0.97273	1387.26	-62.3	0.02598	0.97345	1386.63	-121.1
0.04198	0.97382	1388.78	-56.7	0.03663	0.97484	1388.68	-130.9
0.06351	0.97612	1391.72	-46.4	0.04712	0.97684	1390.65	-139.0
0.08454	0.97825	1394.23	-38.1	0.05314	0.97689	1391.83	-143.1
0.10953	0.98096	1396.83	-29.5	0.05916	0.97759	1392.99	-147.3
PhAsCl							
0.00516	0.97085	1382.44	-83.2				
0.01207	0.97165	1383.79	-68.7				
0.01901	0.97245	1384.98	-57.9				
0.02598	0.97325	1386.06	-48.9				
0.03416	0.97418	1387.19	-39.4				
0.04152	0.99511	1388.19	-31.2				
0.05066	0.97605	1389.08	-24.1				

Contd....

Table 1 contd..

T = 298.15 K

LiBF₄				NaBF₄			
0.01047	0.96156	1353.41	- 114.3	0.02096	0.96249	1353.69	- 84.3
0.03144	0.96281	1355.23	- 100.1	0.03670	0.96363	1354.63	- 80.6
0.04193	0.96344	1355.98	- 95.4	0.05246	0.96477	1355.47	- 77.6
0.06294	0.96469	1357.24	- 86.9	0.08357	0.96694	1356.70	- 72.3
0.08397	0.96594	1358.23	- 79.6	0.10461	0.96946	1357.90	- 68.2
0.10505	0.96719	1358.98	- 73.2	0.13720	0.97114	1358.48	- 65.8
Ph₄PCl				Ph₄PBr			
0.01047	0.96164	1353.92	- 67.0	0.01057	0.96138	1352.38	- 80.1
0.03159	0.96348	1357.75	- 52.2	0.03164	0.96413	1356.00	- 70.1
0.04225	0.96438	1359.53	- 46.7	0.04228	0.96548	1357.76	- 66.5
0.06375	0.96621	1362.81	- 37.6	0.05298	0.96682	1359.48	- 63.4
0.08552	0.96805	1365.83	- 30.0	0.06388	0.96808	1361.32	- 60.3
0.11138	0.97020	1369.06	- 22.0	0.07887	0.96999	1363.49	- 56.5
Ph₄AsCl							
0.00523	0.96134	1353.52	- 71.1				
0.01223	0.96221	1354.64	- 57.6				
0.01925	0.96309	1355.63	- 47.5				
0.02630	0.96397	1356.51	- 39.0				
0.03516	0.96509	1357.45	- 30.2				
0.04407	0.96622	1358.26	- 22.2				
0.05301	0.96735	1358.96	- 15.3				

Contd....

Table 1 contd...

T= 308.15 K

LiBF₄				NaBF₄			
0.01070	0.95481	1318.43	- 164.1	0.01078	0.95439	1318.12	- 96.2
0.03173	0.95622	1321.05	- 153.7	0.03151	0.95583	1319.48	- 89.3
0.05276	0.95765	1323.38	- 146.3	0.05268	0.95751	1320.40	- 84.8
0.07383	0.95905	1325.56	- 140.5	0.07389	0.95899	1321.47	- 80.4
0.09450	0.96042	1327.53	- 135.3	0.09470	0.96047	1322.36	- 77.1
0.12389	0.96237	1330.08	- 129.3	0.11597	0.96201	1323.12	- 74.1
Ph₄PCl				Ph₄PBr			
0.01074	0.95488	1319.95	- 89.3	0.01600	0.95622	1320.62	- 91.7
0.03169	0.95670	1324.18	- 78.3	0.03716	0.95848	1324.30	- 82.6
0.05325	0.95865	1328.08	- 70.1	0.04797	0.96020	1326.32	- 79.1
0.07507	0.96057	1331.85	- 64.0	0.05886	0.96143	1328.31	- 75.9
0.08365	0.96132	1333.27	- 61.6	0.08054	0.96409	1331.78	- 70.4
0.11036	0.96365	1337.52	- 55.4	0.09430	0.96584	1333.81	- 67.2
Ph₄AsCl							
0.00738	0.95390	1319.28	- 77.1				
0.01082	0.95445	1319.66	- 70.0				
0.01581	0.95525	1320.14	- 61.4				
0.02119	0.95610	1320.62	- 53.2				
0.02646	0.95693	1321.02	- 46.9				
0.03848	0.95837	1322.39	- 34.0				
0.05151	0.95990	1323.69	- 29.9				

Table 2. Limiting apparent molar isentropic compressibilities (κ_ϕ°) and the experimental slopes (S_k) together with the standard deviations (σ) for the electrolyte solutions at different temperatures in 2-methoxyethanol.

Electrolyte	T / K	$10^4 \kappa_\phi^\circ$ ($\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$)	$10^4 S_k$ ($\text{cm}^3 \text{mol}^{-3/2} \text{kg}^{1/2} \text{bar}^{-1}$)	σ
LiBF ₄	288.15	-99.09 ± 0.11	169.86	0.09
	298.15	-133.33 ± 0.09	189.34	0.07
	308.15	-178.69 ± 0.14	144.16	0.10
NaBF ₄	288.15	-77.31 ± 0.08	92.65	0.06
	298.15	-99.17 ± 0.20	92.09	0.14
	308.15	-106.00 ± 0.20	96.13	0.15
Ph ₄ PCl	288.15	-101.73 ± 0.07	224.81	0.06
	298.15	-87.30 ± 0.06	202.57	0.05
	308.15	-109.15 ± 0.18	141.51	0.13
Ph ₄ PBr	288.15	-109.72 ± 0.20	145.04	0.10
	298.15	-93.93 ± 0.17	137.07	0.11
	308.15	-109.15 ± 0.06	141.51	0.04
Ph ₄ AsCl	288.15	-111.54 ± 0.27	397.61	0.22
	298.15	-99.00 ± 0.14	365.21	0.11
	308.15	-110.95 ± 0.25	404.83	0.20

Table 3. Ionic standard apparent molal isentropic compressibilities in 2-methoxyethanol at 298.15 K

Ion	$10^4 \kappa_{\phi}^{\circ \pm}$ ($\text{cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$)	Ion	$10^4 \kappa_{\phi}^{\circ \pm}$ ($\text{cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$)
Li^+	-133.33	Cl^-	-37.20
Na^+	-99.17	Br^-	-43.83
Ph_4P^+	-50.10	BF_4^-	0.00