MOLAR VOLUMES OF MAGNESIUM CHLORIDE AND MAGNESIUM SULPHATE IN AQUEOUS-SODIUM BICARBONATE SOLUTIONS

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The apparent molar volumes, ϕ_v of magnesium chloride and magnesium sulphate in aqueous-sodium bicarbonate (0.005, 0.01, 0.05 and 0.10 m $NaHCO_3$) at different concentrations and temperatures, have been estimated from the densities of the solutions measured by hydrostatic balance. The ϕ_v values vary linearly with square root of concentration. The limiting apparent molar volume, ϕ_v°, and the experimental slope, S_v have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. Structure making/breaking capacity of the electrolyte is inferred from the sign of $[\partial^2 \phi_v^\circ / \partial T^2]$ values. Both the electrolytes behave as structure makers/promoters and the behaviour is just like the symmetrical electrolytes rather than comon electrolytes. The molar expansibilities, at infinite dilution, have been found to be the same for both electrolytes at 306.4° K.

The determination of a thermodynamic property such as the partial molar volume of an electrolyte in a solution of another electrolyte has been of considerable value in establishing the theory of inter ionic attraction and extending our knowledge of ionic equilibria. Also the volumetric behaviour of solutes in solution can provide useful information about solute-solvent and solute-solute interactions.

Survey of literature showed that many molar volume studies have been carried out in mixed and simple electrolyte systems for 1:1 and 2:1 electrolytes [1,2], but little attention has been paid to the behaviour of 2:1 and 2:2 electrolytes in the presence of strong electrolyte solutions. This work was undertaken with an aim of learning more about the nature of solute-solvent interactions from the molar volume studies of magnesium chloride and magnesium sulphate in aqueous solutions of sodium bicarbonate, because sodium bicarbonate is an essential constituent [3] of all the artificial biological fluids and behaves as a strong electrolyte.

EXPERIMENTAL

Sodium bicarbonate, magnesium chloride and magnesium sulphate were of AnalaR grade were dried over P_2O_5 and used without further purification. Water of specific conductance of the order of 10^{-6} Ω^{-1} cm^{-1} was used for making the aqueous solutions of bicarbonate. The different compositions of aqueous-sodium bicarbonate, used as solvent, were made by weight. The solutions of the different electrolytes were also made by weight and conversion of molality to molarity was done by using the standard expression[4]

The density was measured with the help of apparatus similar to one described by Ward and Millero [5].

The glass sample cell had a bakelite top with a hole in the centre and was placed in a bath thermostatically controlled to ± 0.02°C. The weight of the glass float used was 29.085 g and it had a volume of 9.2159 Cm^3. Densities of the solutions were calculated with the help of following equation.

$$d - d^\circ = m^\circ - m/V_f$$

Where m° and m is the mass of the float in water and sample solution respectively, V_f is the volume of the float, d and d° are the densities of the sample and pure water respectively. The accuracy was checked by measuring the density of pure acetonitrile at 303° K. Our value of d = 0.77124 g cm^{-3} is in excellant agreement with the literature value [6] d = 0.77125 g Cm^{-3}.

RESULTS AND DISCUSSION

The densities have been measured for the various solutions of magnesium chloride and magnesium sulphate at 303 K in 0.005, 0.010, 0.050 and 0.100 molalities of sodium bicarbonate in order to estimate the effect of sodium bicarbonate on the various parameters.

The density of the various solutions of magnesium chloride and magnesium sulphate in the different compositions of sodium bicarbonate solutions can be represented by the following Root equation [7]

$$\frac{d - d^{\circ}}{C} = A - B\,C^{1/2} \qquad \text{------(1)}$$

where d° is the density of the solvent (binary aqueous-sodium bicarbonate), C, the molarity and A and B are the two constants of the Root equation. On plotting $(d-d^{\circ})/C$ vs $\sqrt{C}$, a straight

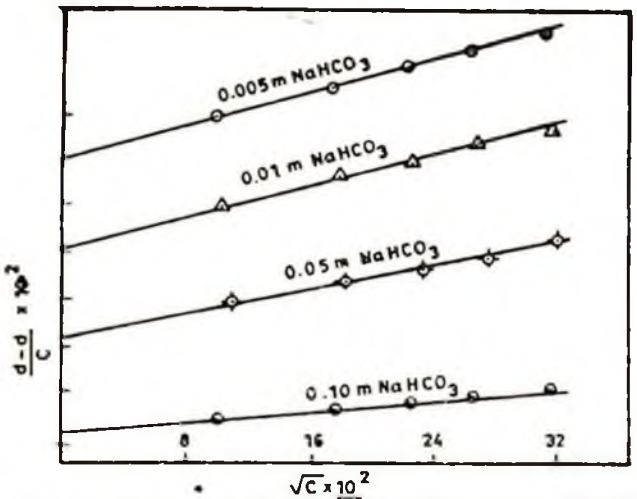


Fig.1 Plot of $\frac{d-d^{\circ}}{C}$ vs $\sqrt{C}$ for Magnesium Chloride in different compositions of sodium bicarbonate at 303° K.

line was obtained in each case as shown in Figs 1 and 2 for magnesium chloride and magnesium sulphate, respectively in the various compositions of aqueous sodium bicarbonate at of 303 K. The values of the parameters A and B evaluated from the intercepts and slopes of the parameters of the straight line plots respectively are given in Table 1.

The apparent molar volume, ϕ_v°, is calculated from the density data by using the following expression:

$$\phi_v = \frac{M_2}{d^{\circ}} + \frac{1000\ (d^{\circ} - d)}{C\ d^{\circ}} \qquad (2)$$

Where C is the molar concentration of the electroyte (magnesium chloride or magnesium sulphate), d the density of the electrolytic solution and d° is the density of the solvent (aqueous-sodium bicarbonate). M_2 is the molecular weight of the respective electrolyte.

The apparent molar volume has been found to vary linearly with the square root of the concentration of the electrolyte in all the com-

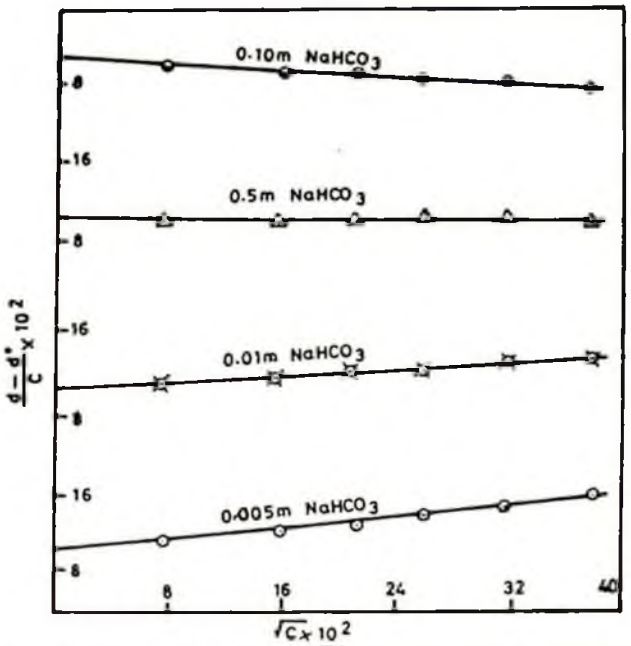


Fig.2 Plot of $\frac{d-d^{\circ}}{C}$ vs $\sqrt{C}$ for Magnesium Sulphate in different compositions of sodium bicarbonate at 303° K.

TABLE 1

VALUES OF PARAMETER A AND B OF ROOT EQUATION FOR MAGNESIUM CHLORIDE AND MAGNESIUM SULPHATE IN AQUEOUS-SODIUM BICARBONATE SOLUTIONS.

Conc. of $NaHCO_3$	Temp. (°K)	A (g mol^{-1} cm^{-3})	B ($g^{3/2}$ $mol^{-3/2}$ Cm^{-3})
	Magnesium Chloride		
0.005m	303	5.20	0.047
0.010m	303	3.20	0.108
0.050m	303	2.00	0.150
0.100m	303	1.80	0.143
	Magnesium Sulphate		
0.005m	303	10.00	0.050
0.010m	303	10.00	0.021
0.050m	303	14.80	- 0.050
0.100m	303	14.90	- 0.100
	Magnesium Chloride		
0.005m	298	4.50	0.190
	303	5.20	0.047
	308	4.80	0.330
	313	4.40	0.440
	Magnesium Sulphate		
0.005m	298	9.90	0.130
	303	10.00	0.050
	308	8.60	0.140
	313	7.60	0.160

positions of aqueous-sodium bicarbonate and the data can be represented by the following Masson's equation [8]

$$\phi_v = \phi^\circ_v + S_v \sqrt{C} \qquad \text{-----(3)}$$

Where ϕ°_v is the apparent molar volume at infinite dilution of the respective electrolyte (equal to partial molar volume V°_2) and S_v is the experimental slope.

In order to check the accuracy of the results, the studies were also carried out in pure water at 298 K. The values of the limiting apparent molar volume ϕ°_v and the experimental slope S_v, for magnesium chloride in case of pure water as obtained at 298 K are 15.20 Cm^3 mol^{-1} and 4.10 Cm^3 $liter^{1/2}$ $mol^{-3/2}$ respectively. The values of ϕ_v and S_v were found to be in excellent agreement with the literature [9] [15.30 Cm^3 mol^{-1} 4.26 Cm^3 $liter^{1/2}$ $mol^{-3/2}$ respectively].

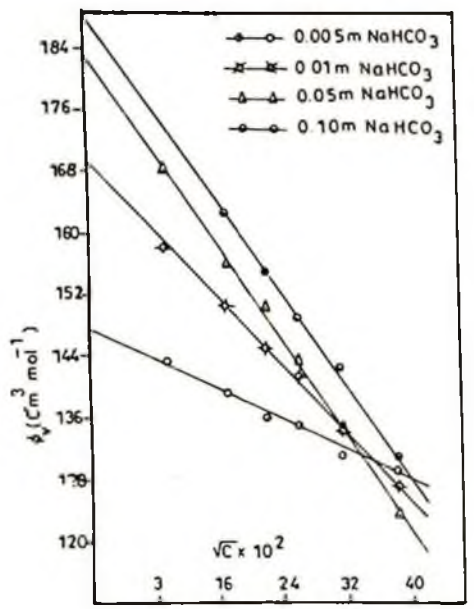


Fig. 3 Plot of ϕ_v vs $\sqrt{C}$ for Magnesium chloride in different compositions of sodium bicarbonate at 303°K.

Linear plots of ϕ_v versus $C^{1/2}$ have been obtained for magnesium chloride and magnesium sulphate in all the compositions of aqueous-sodium bicarbonate at 303 K as shown in Figures 3 and 4 respectively. The values of the limiting apparent molar volume ϕ°_v and the slope S_v for different systems are given in Table 2.

It is evident from Table 2 that the slope S_v in case of magnesium chloride in different aqueous-sodium bicarbonate at 303 K tends to be more and more negative whereas it is negative at lower concentrations of sodium bicarbonate and tends to be more and more positive in case of magnesium

TABLE 2

THE PARTIAL MOLAR VOLUME OF MAGNESIUM CHLORIDE AND MAGNESIUM SULPHATE IN AQUEOUS-SODIUM BICARBONATE AT INFINITE DILUTION AND EXPERIMENTAL SLOPE S_V AT VARIOUS TEMPERATURE

Conc. of $NaHCO_3$	Temperature (K)	ϕ°_v (Cm^3/mol^{-1})	$S_V \times 10^2$ (Cm^3 $]^{1/2}$ $mol^{-3/2}$)
		Magnesium Chloride	
0.005m	303	145.0	- 0.50
0.010m	303	169.6	- 1.13
0.050m	303	184.0	- 1.57
0.100m	303	188.4	- 1.52
		Magnesium Sulphate	
0.05m	303	146.8	- 1.00
0.010m	303	147.2	- 0.50
0.050m	303	98.6	0.77
0.100m	303	96.8	0.63
		Magnesium Chloride	
0.005m	298	153.5	- 2.00
	303	148.0	- 0.50
	308	155.0	- 1.75
	313	174.5	- 1.87
		Magnesium Sulphate	
0.005m	298	147.0	- 1.30
	303	151.2	- 1.18
	308	161.0	- 1.29
	313	173.0	- 1.65

sulphate with the increase in sodium bicarbonate content. Since S_v is a measure of solute-solute (or ion-ion) interactions [8] these results indicate that solute-solute interactions are quite weak in case of magnesium chloride and go on decreasing with the increasing content of sodium bicarbonate, whereas the solute-solute interactions are weak in 0.005 and 0.010 m aqueous-sodium bicarbonate but increase with the increase of sodium bicarbonate content for magnesium sulphate. Moreover S_V, changes sign in case of magnesium sulphate which may be attributed to the changes in structural aspect of the medium caused by magnesium sulphate.

It is clear from Table 2 that ϕ°_v values are positive and large for both the electrolytes indicating thereby the presence of strong solute-solvent interactions. In case of magnesium chloride the value goes on increasing with the increase of

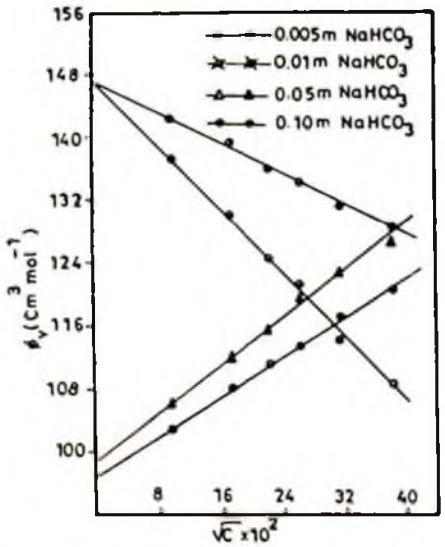


Fig. 4 Plot of ϕ_v vs $\sqrt{C}$ for Magnesium sulphate different compositions of sodium bicarbonate at 303°K.

sodium bicarbonate content thereby suggesting that the solute-solvent interactions go on increasing. Opposite is the case with magnesium sulphate, Further, since the value of ϕ_v^* at a particular composition of aqueous-sodium bicarbonate is higher for magnesium chloride than for magnesium sulphate, it suggests that the solute-solvent interactions are relatively more in case of magnesium chloride than magnesium sulphate. In other words chloride ion has more affinity for aqueous-sodium bicarbonate as compared to sulphate ion.

Effect of Temperature

Since the behaviour of magnesium chloride in different compositions of aqueous-sodium bicarbonate was found to be identical at 303° K, 0.005m of sodium bicarbonate was selected for studying the effect of temperature. The Root equation has also been verified at all the temperatures and the parameters A and B are also given in Table-1.

The linear plots of ϕ_v versus $\sqrt{C}$ have also been obtained at different temperatures (298, 303, 308 and 313 K) in 0.005 m sodium bicarbonate (Figs. 5 and 6). The values of the limiting apprent molar volume ϕ_v^* and experimental slope S_v at different tempratures are also recorded in Table 2.

It is evident from Table 2 that the value of S_v is negative and decreases with the increase of temperature in 0.005 m sodium bicarbonate thereby indicating that solute-solute interactions go on decreasing with the rise of temperature. In other words solute-solvent interactions increase with the increase of temperature. Also the maximum

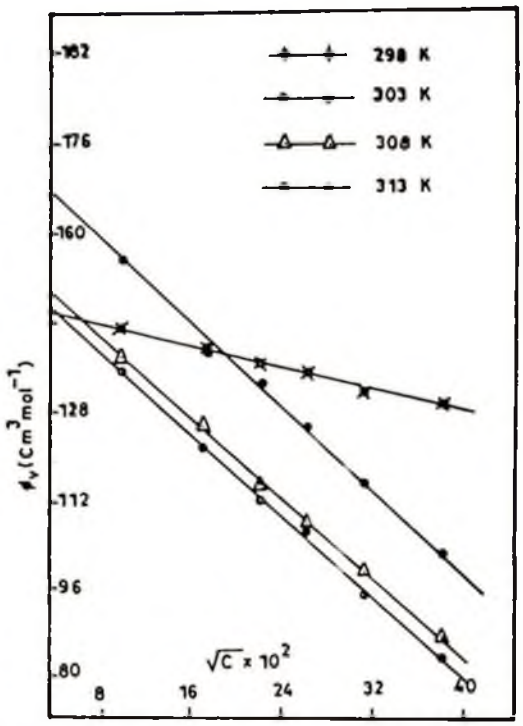


Fig. 5 Plot of ϕ_v vs $\sqrt{C}$ for Magnesium chloride at different temperatur in 0.005m sodium bicarbonate.

value of S_v at 303 K for both the electrolytes in 0.005 m sodium bicarbonate suggests that solute-solute interactions are lower at lower as well as

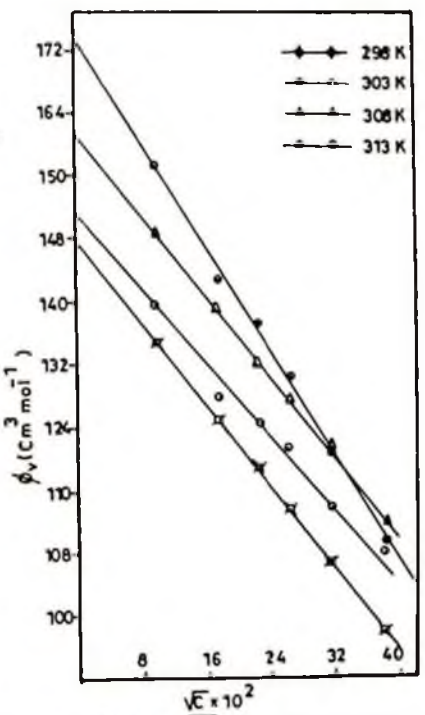


Fig. 6 Plot of ϕ_V vs $\sqrt{C}$ for Magnesium sulphate at different temperaturs in 0.005m sodium bicarbonate.

at higher temperatures.

It is also clear from Table 2 that a minima of ϕ_v° is observed at 303 K for magnesium chloride in 0.005 m sodium bicarbonate, which suggests that the solute-solvent interactions are higher at lower as well as at higher temperature, where as in case of magnesium sulphate, the value of ϕ_v° goes on increasing with the rise of temperature thereby indicating that solute-solvent interactions increase with the rise of temperature. These conclusions from ϕ_v° are in agreement with those derived from S_v data. The temperature dependence of ϕ_v° (T in Kelvin scale) in 0.005 m sodium bicarbonate can be expressed by the following equations :

$$\phi_v^\circ = 22122 - 145.24\ T + 0.24\ T^2 \qquad ---(4)$$

for magnesium chloride

$$\phi_v^\circ = 5878 - 39.20\ T + 0.067\ T^2 \qquad -----(5)$$

for magnesium sulphate

The increase in ϕ_v° of both the electrolytes with increasing temperature can be attributed to the increase in solvation. The apparent molar expansibilities $\phi_E^\circ = [\partial \phi_v^\circ / \partial T]$ calculated from (4) and (5) indicate that ϕ_E° increases with increase of temperature. The increase in magnitude per degrees temperature is positive indicating thereby that the behaviour of both the electrolytes is just like the behaviour of symmetrical tetra-alkyl ammonium salts [10] but not like the common electrolytes. The molar expansibility in the latter case should decrease with the increasing temperature [11,12].

The variation ϕ_E° of with temperature for both the electrolytes is linear as shown in Fig. 7. This positive increase of with increase of temperature can be ascribed to "Caging effect" [10]. These linear plots cross each other at 306.4° K and the molar expansibilities at this temperature are identical for the two salts and equal to 1.85 $Cm^3\ mol^{-1}\ K^{-1}$. Thus both the electrolytes have the same caging effect 0.005 m sodium bicarbonate solution at this temperatures.

During the past few years it has been reported that S_v is not the sole criterion for determining the structure making/breaking nature of electrolytes, so Hepler [13] has developed a technique of examining the sign of $[\partial^2 \phi_v^\circ / \partial T^2]$ for various solutes in terms of long range structure making and breaking capacity of the solute in aqueous solutions using the general thermodynamic equation

$$[\partial \bar{c}_p / \partial P]_T = -[\partial^2 \phi_v^\circ / \partial T^2]_p \qquad (6)$$

On the basis of this equation it has been deduced that structure making should have positive values whreas the structure breaking should have negative values. In the present study, $[\partial^2 \phi_v^\circ / \partial T^2]_p$ for both the electrolytes [from equation (4) and (5)]

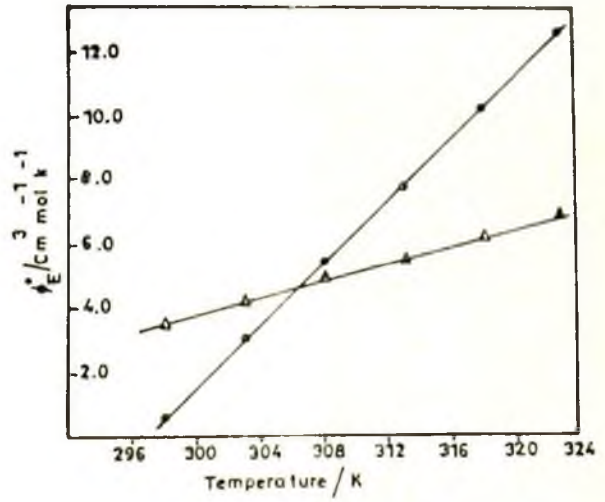


Fig. 7 Variation of ϕ vs temperature.

in 0.005 m sodium bicarbonate solution is positive indicating that both these electrolytes behave as structure makers/promotors.

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