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# Effect of temperature on the partial molar volumes of some bivalent transition metal chlorides in water and binary aqueous mixtures of methanol

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**Abstract:** Partial molar volumes of some transition metal chlorides, viz., manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride have been determined in water and in binary aqueous mixtures of methanol (5, 10, 15, 20 and 35% by weight of methanol) at one temperature with the help of density measurements. Effect of temperature on the partial molar volumes was also analysed in 5% methanol + water for these salts by taking five equidistant temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K). Magnesium chloride was taken as reference electrolyte in whole of the study. The density measurements were made by using Ward and Millero method and results have been analysed by Masson's equation. The experimental values of slopes and partial molar volumes of these transition metal chlorides have been interpreted in terms of ion-ion or ion –solvent interactions. The partial molar volumes vary with temperature as a power series of temperature. Structure making or breaking capacities of transition metal chlorides have been deduced by following the Hepler's criterion. In the present study transition metal chlorides have been found as structure maker in water and binary aqueous mixture of methanol.
**Key words:** Methanol+water, partial molar volumes, structure maker, transition metal chlorides.

## Introduction:

Partial molar volume is one of the important thermodynamic quantities which have been proved a very useful tool in elucidating the various types of interactions like ion-ion; ion - solvent and solvent –solvent interactions occurring in aqueous as well as non-aqueous solutions[1-10].These interactions are very helpful in determining the structure and properties of the solutions. Appreciable work has been done on thermodynamic properties of various electrolytes in different binary aqueous mixtures but studies are still lacking in case of transition metal chlorides in binary aqueous mixtures of methanol. Hence, the present studies seek an attempt to understand the interactions of transition metal chlorides in water and methanol+ water mixtures. Methanol is widely used as most of compounds are soluble in it with large freedom and also it is inexpensive. Transition metals and their compounds act as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. Partial molar volumes actually tell us about the interaction between the different components of the mixture and the local structure of the solvent. Particularly in water effects in the partial molar volume may be seen due to breaking of local water structure or even creating ice like structures ("iceberg model") around hydrophobic solutes.

There is a great need of accurate aqueous data over wide range of temperature, pressure and composition in many fields besides chemistry including geology, oceanography, boiler engineering and oil recovery systems. Due to the importance in geology, industrial and biological systems, a need has developed for accurate thermodynamic data for transition metal salts in aqueous solutions. Biologically transition metal ions

are important in different systems, like copper, iron and manganese are required for various purposes, while metals like nickel and cadmium can poison enzymes by substituting for their required metals. Transition metals are also important in geology because they are components of various minerals; on the other hand engineers are interested in these because of their role in corrosion processes.

## Experimental:

The reagents, manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride were taken of AR grade. All these reagents were used after drying over calcium oxide desiccator to keep them in dry atmosphere. Fresh triple distilled water was used as standard solvent for preparing binary methanol + water mixture. The density of methanol was found 0.7868gcm$^{-3}$ at 298.15 K, which is in good agreement with literature value of density of methanol (0.7865 gm$^{-3}$)[11].

The binary aqueous mixtures of methanol and seven different concentrations of above mentioned transition metal chlorides were prepared by weight and the conversion of molality, (m) into molar concentration(C) was done by using the standard expression:

$$C = \frac{md1000}{1000 + mM_2} \qquad (1)$$

Where, d is the density of solution and $M_2$ is the molecular weight of transition metal chloride salts.

The density was measured with the help of an apparatus similar to the one reported by Ward and Millero[12]. This apparatus consist of a glass float whi ch is suspended with nylon thread from a balance pan into a cylindrical sample container. The sample container has a bakelite top and placed in a water bath. The whole assembly of sample container and water-bath was placed in thermostat whose temperature was controlled with the help of an electronic relay. The fluctuation in temperature was within $\pm$ 0.01K.Density was calculated by using the relation $d = d_0 + (w_0 - w)/V_f$ where d and $d_0$ are densities of sample solution and water respectively, w and $w_0$ are the weights of float in the sample solution and water, and $V_f$ is float volume. The glass float of weight 28.8956g had a volume of 26.5148±0.0048 cm$^3$.The accuracy in the density measurements was 1 x 10$^{-4}$ gcm$^{-3}$.The apparent molar volumes ($\phi_v$) were calculated from the density data using the expression[13]

$$\phi_v = \frac{1000(d_0 - d)}{cd_0} + \frac{M_2}{d_0} \qquad (2)$$

where $d_0$ is the density of methanol + water as solvent and d is the density of solution; c is the molar concentration of chloride salts and $M_2$ is the molecular weight of transition metal chloride salts. The density measurements were carried out in a well stirred water bath with a temperature control of ± 0.01 K.

## Results and discussion:

The measured values of densities of aqueous solutions of transition metal chlorides in different compositions of methanol + water (5,10,15,20, 35%) at 303.15 K have been used to calculate the partial molar volumes $\phi_v^0$. The plot of $\phi_v$ verses $\sqrt{C}$ were found to be linear with positive slopes in different compositions of methanol + water. A sample plot for manganese chloride in different compositions of methanol +water at 303.15K is shown in fig.1. The partial molar volumes $\phi_v^0$ and experimental slopes ($S_v$) were calculated using Masson equation

$$\phi_v = \phi_v^0 + S_v C^{1/2} \qquad (3)$$

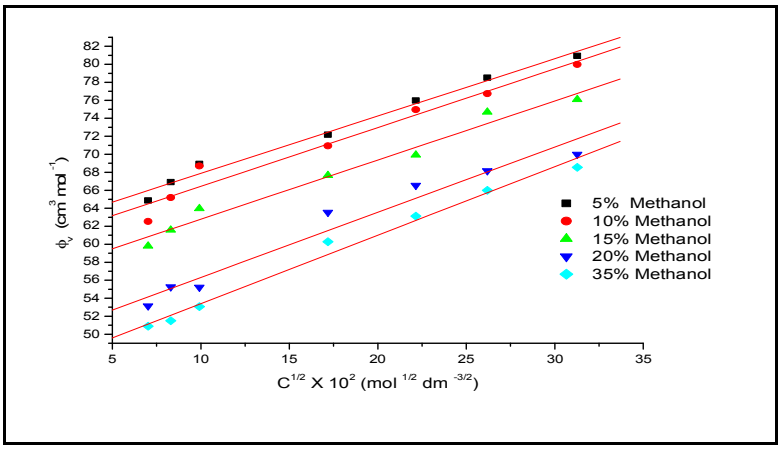


**Fig1: Plot of $\phi_v$ Vs $C^{1/2}$ of manganese chlorides in different compositions of methanol + water at 303.15K.**

**Table 1 Partial molar volumes ($\phi_v^0$), experimental slopes ($S_v$) and partial molar volumes of transfer ($\Delta V_{tr}^0$) for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in methanol + water mixtures at 303.15K**

| Methanol +Water | $\phi_v^0$ (cm$^3$ mol$^{-1}$) | $S_v$ (cm$^3$dm$^{3/2}$mol$^{-3/2}$) | $\Delta V_{tr}^0$ ((cm$^3$ mol$^{-1}$) |
|---|---|---|---|
| **Manganese chloride** | | | |
| 0(water) | 69.39 | 1.112 | ------- |
| 5 | 61.50 | 0.637 | -7.89 |
| 10 | 59.91 | 0.654 | -9.48 |
| 15 | 56.22 | 0.660 | -13.17 |
| 20 | 49.07 | 0.729 | -20.32 |
| 35 | 45.79 | 0.774 | -23.59 |
| **Cobalt chloride** | | | |
| 0(water) | 120.51 | 0.519 | ----- |
| 5 | 127.37 | 0.665 | 6.86 |
| 10 | 123.76 | 0.703 | 3.25 |
| 15 | 118.85 | 0.788 | -1.66 |
| 20 | 116.29 | 0.869 | -4.22 |
| 35 | 112.87 | 0.947 | -7.64 |
| **Nickel chloride** | | | |
| 0(water) | 83.88 | 0.865 | ---------- |
| 5 | 98.79 | 0.646 | 14.90 |
| 10 | 96.05 | 0.666 | 12.17 |
| 15 | 91.75 | 0.740 | 7.87 |
| 20 | 89.19 | 0.775 | 5.30 |
| 35 | 85.49 | 0.818 | 1.61 |
| **Copper chloride** | | | |
| 0(water) | 41.01 | 0.538 | ----- |
| 5 | 41.01 | 0.695 | 0.00 |
| 10 | 35.98 | 0.816 | -5.03 |
| 15 | 34.72 | 0.812 | -6.29 |
| 20 | 29.49 | 0.902 | -11.52 |
| 35 | 29.16 | 0.923 | -11.85 |
| **Cadmium chloride** | | | |
| 0(water) | 60.80 | 0.668 | ----- |
| 5 | 68.02 | 0.672 | 7.22 |
| 10 | 62.03 | 0.715 | 1.23 |
| 15 | 57.72 | 0.737 | -3.07 |
| 20 | 53.05 | 0.789 | -7.74 |
| 35 | 52.06 | 0.799 | -8.73 |

| Magnesium chloride | | | |
|---|---|---|---|
| 0(water) | 138.39 | 0.654 | ----- |
| 5 | 144.21 | 0.891 | 5.82 |
| 10 | 142.81 | 0.920 | 4.42 |
| 15 | 139.03 | 0.951 | 0.64 |
| 20 | 135.92 | 1.020 | -2.47<br>0.64 |
| 35 | 133.15 | 1.046 | -5.24 |

Table 1 shows the values of $\Phi_v^0$ and $S_v$, calculated in different compositions of binary aqueous mixture of methanol at 303.15 K. It is clear from table 1, that the values of slopes ($S_v$) are positive in water as well as in methanol+ water mixture at 303.15K in all the compositions. The positive slopes values of transition metal chlorides, indicates the presence of strong ion- ion interactions. Also, from Table 1, it is clear that the magnitude of $S_v$ values of transition metal chlorides increases with increase in the amount of methanol in water, which shows that ion-ion interactions are further, strengthened which trait to the decrease in solvation. Also from Table 1, it is clear that the $\Phi_v^0$ values are positive and decrease in magnitude, in all the compositions of methanol+ water at 303.15K for transition metals chlorides taken for study. The trend of $\Phi_v^0$ values, for each transition metal chloride, with the increase of methanol amount in water, shows that ion- solvent interactions decrease on the addition of methanol in water which indicates that solvent has more affinity for water. Also, on comparing the magnitudes of $\Phi_v^0$ values with the values of $S_v$ , $\Phi_v^0$ values are more in magnitudes than that of $S_v$ of the same transition metal chloride. This concludes that ion-solvent interactions dominate over the ion-ion interactions in methanol + water mixture at 303.15 K. The volume of transfer ($\Delta V^0_{tr}$) has been calculated by using the relation:

$$\Delta V^0_{tr} = \Delta \Phi_v^0(MS) - \Phi_v^0(W) \qquad (4)$$

Here $\Phi_v^0$ (MS) and $\Phi_v^0$ (W) are the partial molar volumes of transition metal chlorides in the mixture of methanol + water and water solvents respectively. The values of volume of transfer of transition metal chlorides were recorded in table1.It is clear from table 1 that the $\Delta V^0_{tr}$ values continuously decrease in magnitude with the increase in the content of methanol in water. The decrease in $\Phi_v^0$ and $\Delta V^0_{tr}$ may be trait to the increase in electrostriction in the presence of methanol. The electrostriction effect, which leads to the contraction in the volume of the solvent, is enhanced in the mixed solvents as compared to pure water. This electrostriction effect, again confirming the earlier conclusion of greater affinity of methanol for water. It is also clear that as $Cl^-$ ion is common in all transition metal chlorides and in magnesium chloride, the values of volume of transfer in a particular composition of methanol + water, the electrostriction for these cations follows the order as: $Ni^{2+} > Cd^{2+} > Co^{2+} > Mg^{2+} > Cu^{2+} > Mn^{2+}$.This trend indicates that $Mn^{2+}$ ion is highly solvated by methanol + water and $Ni^{2+}$ is least. So the solvation of these cations follows the trend: $Mn^{2+} > Cu^{2+} > Mg^{2+} > Co^{2+} > Cd^{2+} > Mn^{2+}$. Also; $\Delta V^0_{tr}$ values, for each transition metal chloride falls with the increase of methanol amount in water, which may be trait to the rise in solvent – solvent interactions between methanol + water.

Since the behaviour of the respective electrolyte was found to be linear and same in different composition of methanol + water at 303.15 K, only one composition system (5% w/w) has been selected for analyzing the effect of temperature. The experimentally determined values for the seven different concentrations of transition metal chlorides at different temperatures (298.15 – 315.15K) have been used to calculate the partial molar volume $\Phi_v^0$ of the salts. The plots of apparent molar volume $\Phi_v$ against the $\sqrt{C}$ were found to be linear with the positive slopes in water as well as in aqueous solution of methanol for all the salts and a sample plot is shown in fig. 2 for manganese chloride.

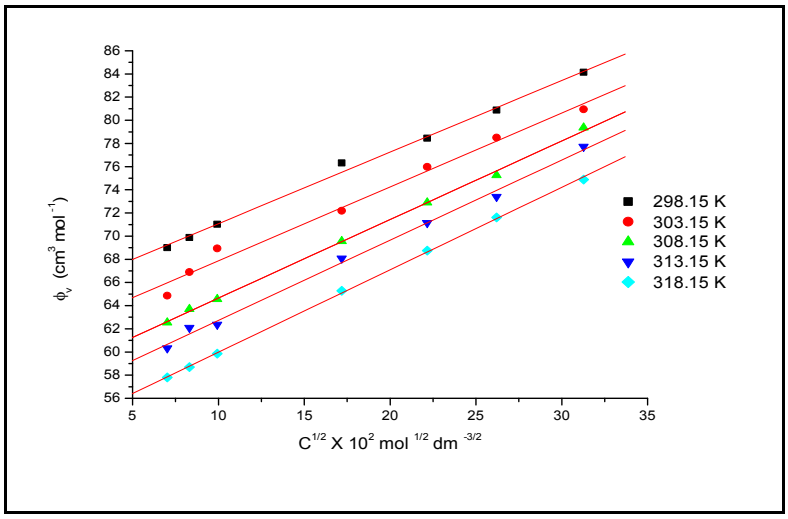


**Fig 2: Plot of $\phi_v$ Vs $C^{1/2}$ for manganese chloride in 5% binary mixture of methanol + water at different temperatures.**

**Table 2 Partial molar volumes ($\phi_v^0$), experimental slopes ($S_v$) and partial molar volume expansibilities ($\phi_E^0$) for transition metal chlorides in 5% methanol + water at different temperatures**

| Temperature (K) | $\phi_v^0$ (cm$^3$ mol$^{-1}$) | $S_v$ (cm$^3$dm$^{3/2}$mol$^{-3/2}$) | $\phi_E^0$ ( cm$^3$ mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| **Manganese chloride** | | | |
| 298.15 | 64.89 | 0.618 | -0.74 |
| 303.15 | 61.50 | 0.637 | -0.61 |
| 308.15 | 57.86 | 0.679 | -0.47 |
| 313.15 | 55.80 | 0.694 | -0.34 |
| 318.15 | 52.86 | 0.715 | -0.21 |
| **Cobalt chloride** | | | |
| 298.15 | 131.81 | 0.633 | -0.95 |
| 303.15 | 127.68 | 0.636 | -0.69 |
| 308.15 | 125.55 | 0.681 | -0.44 |
| 313.15 | 123.95 | 0.691 | -0.19 |
| 318.15 | 120.75 | 0.737 | 0.05 |
| **Nickel chloride** | | | |
| 298.15 | 104.61 | 0.680 | -1.61 |
| 303.15 | 96.83 | 0.691 | -1.49 |
| 308.15 | 93.87 | 0.717 | -1.38 |
| 313.15 | 87.21 | 0.724 | -1.27 |
| 318.15 | 84.09 | 0.763 | -1.16 |
| **Copper chloride** | | | |
| 298.15 | 43.16 | 0.585 | -0.48 |
| 303.15 | 40.89 | 0.681 | -0.42 |
| 308.15 | 37.27 | 0.710 | -0.37 |
| 313.15 | 35.53 | 0.726 | -0.31 |
| 318.15 | 33.29 | 0.735 | -0.26 |
| **Cadmium chloride** | | | |
| 298.15 | 73.56 | 0.498 | -1.10 |
| 303.15 | 68.13 | 0.541 | -1.06 |
| 308.15 | 63.37 | 0.688 | -1.01 |
| 313.15 | 58.38 | 0.699 | -0.97 |
| 318.15 | 53.66 | 0.812 | -0.93 |
| **Magnesium chloride** | | | |
| 298.15 | 64.89 | 0.618 | -2.10 |
| 303.15 | 61.50 | 0.637 | -1.49 |

| | | | |
|---|---|---|---|
| 308.15 | 57.86 | 0.679 | -0.88 |
| 313.15 | 55.80 | 0.694 | -0.27 |
| 318.15 | 52.86 | 0.715 | 0.33 |

It is evident from table 2 that the values of $S_v$ are positive for transition metal chlorides in 5% aqueous mixture of methanol at all temperatures. The positive values indicate the presence of strong ion-ion solvent interactions which are further strengthened with rise in temperature from 298.15 K to 318.15 K. Also ,it is clear from table 2 , that the values of $\Phi_v^0$ decrease with increase in temperature ,for the selected transition metal chlorides in methanol + water (5% w/w) ,thereby showing that ion – solvent interactions are weakened with increase in temperature. The decrease in $\Phi_v^0$ values may be trait to decrease in solvation of transition metal chlorides with rise in temperature.

The plot of $\Phi_v$ Vs √C at different temperature shows positive slopes indicating that transition metal chlorides taken in water are fully ionised but in methanol + water (5%w/w) composition are not completely ionized ,determine the absence of interionic penetration, which leads to positive slopes in plot of $\Phi_v$ vs √C.

It has been found that only $S_v$ is not only one parameter for determining the structure making or structure breaking nature of any solute. Partial molar volume expansibilities $\Phi_E^0$ is another parameter, which determines the making or breaking capacity of any solute in any of the solvent developed by Hepler[14].

The temperature dependence of $\Phi_v^0$ in 5% methanol + water for selected transition metal chlorides and magnesium chlorides can be expressed by the following relations:

$$\Phi_v^0 = 1468.37 - 8.66\,T + 0.01\,T^2 \text{ for manganese chloride} \quad (5)$$

$$\Phi_v^0 = 2664.80 - 16.03T + 0.02\,T^2 \text{ for cobalt chloride} \quad (6)$$

$$\Phi_v^0 = 1585.11 - 8.31T + 0.01\,T^2 \text{ for nickel chloride} \quad (7)$$

$$\Phi_v^0 = 663.80 - 3.68\,T + 5.37 \times 10^{-3}\,T^2 \text{ for copper chloride} \quad (8)$$

$$\Phi_v^0 = 793.92 - 3.72T + 4.39 \times 10^{-3}\,T^2 \text{ for cadmium chloride} \quad (9)$$

$$\Phi_v^0 = 6210.87 - 38.54\,T + 0.06\,T^2 \text{ for magnesium chloride} \quad (10)$$

Partial molar volume expansibilities $\Phi_E^0 = \left[\frac{\partial \Phi_v^0}{\partial T}\right]_P$ ,which is temperature dependence function of $\Phi_v^0$ , is calculated for transition metal chlorides by using relations (5) to (10) and are given in table 2. From table 2, $\phi_E^0$ values for transition metal chlorides at different temperatures are negative but increase in magnitude with rise in temperature showing that these transition metal chlorides behaving just like symmetrical tetra alkyl ammonium salts[15] and not like common salts[16, 17] because in the case of common electrolytes the molar volume expansibilities should decrease with the rise in temperature. The increase in the magnitude of $\phi_E^0$ values indicates the presence of "packing effect"[15]. The plot of $\phi^0_E$ verses temperature is found to be linear for all transition metal chlorides and magnesium chloride in 5% w/w methanol + water mixture as shown in fig.3.

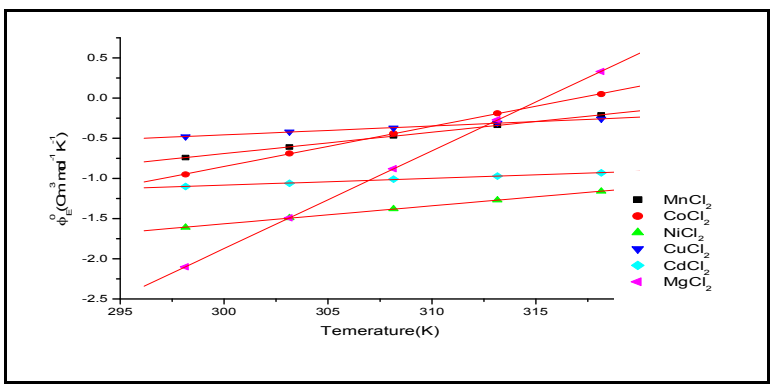


**Fig.3 Variation of $\phi_E^0$ with temperature for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in 5% methanol + water.**

In last few years back, It has been observed by the number of workers that $S_v$ is not the not the only criterion for determining the structure making or breaking nature of any solute.Hepler has given a method of finding the sign of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)p$ for different types of solutes in forms of long range structure making or structure breaking capacities of the solutes in aqueous solutions using the general thermodynamic relation[14]:

$$(\partial Cp)/\partial P) = -\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)p \qquad (11)$$

On the basis of equation (11), It has been found that the positive values indicates the structure making nature of solutes and negative values indicates the structure breaking nature of solutes. In our present study, it is found from equations (5) to (10), $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)p$ values are positive for transition metal chlorides in water 5% methanol + water suggests that the all the transition metal chlorides taken in present study act as structure makers in 5% methanol + water. This indicates that the addition of transition metal chlorides enhances the structure of methanol + water.

## References


1. Parmar M. L.and Banyal D. S., Effect of temperature on the partial molar volumes of some bivalent transition metal nitrates and magnesium nitrate in DMF + water mixtures, Indian J Chem., 2005,44A, 1582-1588.
2. Salabat A, Shamshiri L and Sahrakar F., Thermodynamic and transport properties of aqueous trisodium citrate system at 298.15 K, J Mol Liq., 2005,118, 67-70.
3. Man Singh, Study of apparent molal volume and viscosity of mutual citric acid and disodium hydrogen orthophosphate aqueous systems, J. Chem Sci., 2006, 118 , 269-274.
4. Malasane P.R and Aswar A.S., Thermodynamic and ultrasonic studies of adenosine in the presence of metal ions, Indian J Chem., 2005, 44A,2490-2494.
5. Warminska D, Krakowiak J and Grzybkowaski, Apparent Molar Volumes of Divalent Transition Metal Bromides in Dimethyl Sulfoxide Solutions, J Mol Liq., 2005, 116 , 61-65.
6. Parmar M .L.& Banyal D.S., Effect of temperature on the partial molar volumes of some bivalent transition metal nitrates and magnesium nitrate in the water-rich region of binary aqueous mixtures of dimethyl acetamide, Indian J Chem.,2009,48A,1667-1672
7. Zhao C.W., Ma P.S & Li J.D., Partial molar volumes and viscosity *B*-coefficients of arginine in aqueous glucose, sucrose and l-ascorbic acid solutions at $T$ = 298.15 K,J ChemThermodyn.,2005, 37,37-42 .
8. Swenson D.M & Wooley E.M, Apparent molar volumes and apparent molar heat capacities of aqueous KI, $HIO_3$, $NaIO_3$, and $KIO_3$ at temperatures from 278.15 K to 393.15 K and at the pressure 0.35 MPa, J Chem Thermodyn., 2008,40 ,54-66.
9. Parmar M.L & Attri S.C, A comparative study of partial molar volumes of some common, tetra-alkyl ammonium and multivalent electrolytes in aqueous and binary aqueous solutions of urea, J Mol Liq., 2007, 136 , 38-43.
10. Chemiselewska A, Wypych – Stasiewicz A & Bold A.,Viscosity of aqueous solutions of monocarboxylic acids J Mol Liq., 2007,130 ,42-47.
11. Covinton A.K & Dickison T., Physical Chemistry of Organic Solvent Systems, (Plenum, New York) 1973.
12. Ward G.K &Millero F.J., The effect of pressure on the ionization of boric acid in aqueous solutions from molal volume data, J Solution Chem., 1974,3 (6) 417-430.
13. Millero F.J., in structure and Transport Processes in water and Aqueous Solution, edited by R A Horne, (Wiley – inter science, New York) 1971, chap. 13, p 521.
14. Hepler L.G., Thermal expansion and structure in water and aqueous solutions, Can J Chem., 1969,47, 4613-4617.
15. Millero F.J, in structure and Transport Processes in water and Aqueous Solution, edited by R A Horne, (Wiley – inter science, New York) 1971, chap.15, p 622.
16. Millero F. J and W. Drost-Hansen, Apparent molal volumes of ammonium chloride and some symmetrical tetraalkylammonium chlorides at various temperatures, J. Phys. Chem., 1968,72 (5), 1758-1763.
17. Millero F.J.,The molal volumes of electrolytes. Chem. Rev., 1971, 71, 147-176.


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