

Molecular interactions of Niacin in binary aqueous solutions of KCl and FeCl₃ at different temperatures: Volumetric Approach

R.C.Thakur*, Ravi Sharma, Veerpal Kaur, Harpreet Kaur

Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara 144411, Punjab, India.

*E-mail: drthakurchem@gmail.com

Keywords: Partial molar volume, ion-ion interactions, ion – solvent interactions, structure maker /structure breaker.

Abstract

Molecular interactions of niacin in aqueous medium, aqueous solutions of KCl and FeCl₃ were analyzed and various thermodynamic parameters like partial molar volumes and limiting molar expansibilities of Niacin were analyzed in water and binary aqueous mixtures of KCl and FeCl₃ at different temperatures. Masson's equation and Hepler's criterion have been used to infer various types of interactions and in the present study niacin was found structure promoter in water and structure breaker in mixtures of KCl and FeCl₃ in water respectively.

1.Introduction

When any of the solute is added in water or any of the solvent system, different types of molecular interactions occur in the solvent systems which include ion-ion, ion-solvent and solvent – solvent type of interactions but primarily our interest always lies in ion-solvent/ion-solvent interactions. There are many thermodynamic and transport parameters which help us in analyzing these type of interactions and as a result of these studies we are able to understand the nature of solute as well as its behavior in the one or the solvent mixtures [1-6] in terms of structure making/breaking. The literature shows that many workers have already worked on the thermodynamics of many biomolecules to understand their behavior in different solvent systems but very few studies are available on vitamins like Niacin (Nicotinic Acid) in electrolytic solutions such as binary aqueous solutions of KCl and FeCl₃ [7-16]. Niacin which is vitamin B3 and is water soluble plays a major role in genetic material repairing and steroid hormones creation in the adrenal gland. Also, it has wide applications in food and cosmetics industries. Potassium is one of the mineral essential for beating of our heart. Potassium chloride is used in preventing or treating hypocalcaemia. Iron (III) chloride is used in drinking water production and sewage treatment. The over cropping of an animal's claws in veterinary practice are treated by FeCl₃. As it is clear that all three chemicals used in the study have a great biological and industrial

application so it was necessary to elucidate the type of molecular interactions existing between these molecules.

2. Experimental details

All the reagents Niacin ($C_6H_5NO_2$, M.W. 123.11g), potassium chloride (KCl M.W 74.5513g) and ferric chloride ($FeCl_3$, M.W. 162.20g) were of AR grade and the specifications with the procurement details are given in Table 1.

Table 1: Specification of chemical samples.

Chemical name	Molecular weight (gm/mol)	Provenance	Mass Fraction purity
Niacin	123.11	S.D Fine-Chem Limited	>0.99
KCl	74.55	S.D Fine-Chem Limited	>0.98
$FeCl_3$	162.20	Loba Chemie	>0.99

The de-ionized and distilled water was used for the preparation of all the solutions. In the present study all the chemicals were used after drying for more than 24 hours over CaO. All the solutions of Niacin in different solvent systems were prepared by weight.

Molarity was calculated by using the expression:

$$C = \frac{\rho \cdot 1000}{1000 + m \cdot M} \quad (1)$$

where ρ , is the density, m is the molality and M is the molecular mass of the Niacin.

The density was measured with the help of apparatus shown in fig. I as used by Ward and Millero [17] and by Thakur and others [18]. In the present study 33.813g float (A) of volume 25.066cm^3 at 303.15K was used and volume of float was determined with the help of following equation:

$$V_f = \frac{W_{\text{air}} - W_{\text{water}}}{d_0} \quad (2)$$

Where W_{air} is weight of float in air and W_{water} is weight of float in water and d_0 is the density of water at a particular temperature T . To obtain the W_{water} the sample container was filled with water (after suspension of float in it) so that level of water come upto fixed mark on the container.

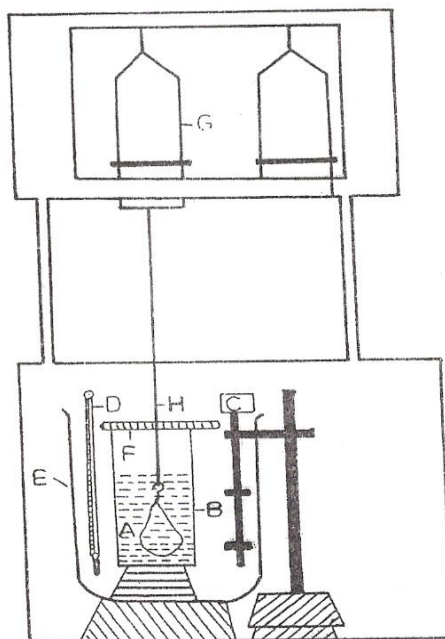


Fig. 1. APPARATUS FOR MEASUREMENT OF DENSITY

The densities of solution are then calculated by using the relationship.

$$d - d_0 = \frac{W_0 - W}{V_f} \quad (3)$$

where d is the density of solution under study and d_0 is density of pure solvent at particular temperature, W is weight of float in solution (under study) and W_0 is the weight of float in water, V_f is the volume of float. While performing experiment every care was taken so that suspension thread did not touch any part of equipment. The calibration of the apparatus was done by determining the density of pure water at 303.15K and our value of density was found of 1.0227 gcm^{-3} which was in good agreement with the literature value of pure water at the same temper i.e 1.02230 gcm^{-3} .

3. Results and discussion:

3.1. Partial molar volumes

The apparent molar volumes, ϕ_v of niacin in water and different mixtures of KCl / FeCl_3 in water at 303.15K have been measured by using the following equation

$$\phi_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{C\rho_0} \quad (4)$$

where C represents the moarity of the solution, M represents the molecular weight of solute, ρ_0 and ρ are the densities of the solvent and solution respectively. Values of apparent molar volumes for niacin were positive and found to escalate with increase in the content of KCl and FeCl_3 in water at 303.15K and a sample plot is shown in fig.2 for KCl in water (different compositions) at 303.15K

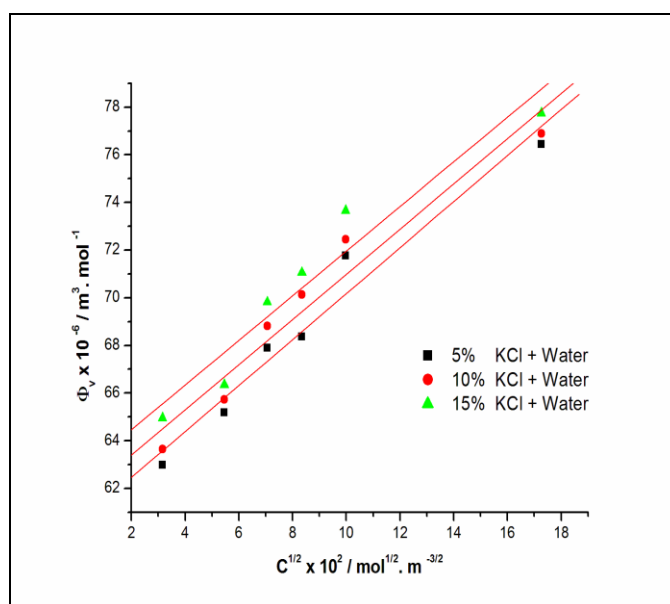


Figure 2: Variation of ϕ_v with concentration of niacin in KCl +Water (different compositions) at 303.15K

Table 2: Values of partial molar volumes (ϕ_v^0) and their corresponding experimental slopes (S_v^*) of niacin in different compositions of KCl + water and FeCl_3 + water mixture at 303.15 K.

Composition (wt.%)	$\phi_v^0(\text{m}^3\text{mol}^{-1})$	$S_v^*(\text{m}^3\text{L}^{1/2}\text{mol}^{-3/2})$	$\phi_v^0(\text{m}^3\text{mol}^{-1})$	$S_v^*(\text{m}^3\text{L}^{1/2}\text{mol}^{-3/2})$
	KCl + Water		FeCl_3 + Water	
5	60.52	0.950	104.8	0.737
10	61.50	0.920	108.0	0.689
15	62.59	0.895	109.5	0.675

The values of limiting apparent molar volumes (ϕ_v^0) were determined using least square fitting method to the plots of ϕ_v Vs $C^{1/2}$ which is represented by following equation:

$$\phi_v = \phi_v^0 + S_v^* C^{1/2} \quad (5)$$

where ϕ_v^0 is the intercept and S_v^* is the experimental slope.

From table 2 it is observed that values of slope S_v^* were found positive and decrease with the increase in concentration of KCl and FeCl₃ in water indicating the specific ion-ion interactions which are further reduced with increase in concentration of KCl and FeCl₃ in water. On the other hand ϕ_v^0 represents the magnitude of ion –solvent interactions and with the increase in content of KCl and FeCl₃ in water values of ϕ_v^0 were found increasing indicating the increase in ion – solvent interactions i.e solvation of niacin is enhanced with increase in increase in concentration of KCl and FeCl₃ in water.

Effect of temperature

From the experimental observations it was found that similar trends were found in water and different compositions of KCl and FeCl₃ in water at one temperature so in order to analyze the effect of temperature lowest composition of KCl and FeCl₃ in water have been taken for the experimental study. Five equidistant temperatures 298.15 K to 313.15 K were taken for the entire study at the lowest composition of KCl and FeCl₃ in water

Table 3: Limiting apparent volumes (ϕ_v^0) and their corresponding experimental slopes (S_v^*) for niacin in water and in 5% KCl in water and 5% FeCl₃ + water at different temperatures

T/K	298.15K	303.15K	308.15K	313.15K
Water				
$(m^3 mol^{-1})\phi_v^0$	67.01 (±0.961)	65.79 (±1.200)	64.93 (±0.926)	63.87(±0.856)
$(m^3 L^{1/2} mol^{-3/2})S_v^*$	0.985 (±0.099)	1.049(±0.124)	1.068 (±0.096)	1.091(±0.089)
5% KCl + Water				
$(m^3 mol^{-1})\phi_v^0$	50.60(±0.741)	60.52(±0.909)	63.94(±0.812)	66.96(±0.997)
$(m^3 L^{1/2} mol^{-3/2})S_v^*$	0.964(±0.0759)	0.950(±0.092)	0.945(±0.083)	0.930(±0.102)
5% FeCl₃ + Water				
$(m^3 mol^{-1})\phi_v^0$	97.89(±0360)	104.80(±0.676)	106.50(±0.434)	111.00(±0.117)
$(m^3 L^{1/2} mol^{-3/2})S_v^*$	0.755(±0.036)	0.737(±0.069)	0.697(±0.044)	0.497(±0.012)

Table 3, shows that the S_v^* values were found positive in water , KCl + water and FeCl₃ +water systems for the entire temperature range indicating the presence of strong ion- ion interactions[19-22].The values of S_v^* were found to increase in magnitude in water with increase in temperature and on the other hand values were found to decreases in magnitude with rise in the temperature in KCl + water as well as in FeCl₃ + water systems, indicating that ion –ion interactions are strengthened in water which trait to the decrease in solvation in water whereas ion –ion interactions are weakened in KCl + water as well as in FeCl₃ + water systems with the increase in temperature justifying the

increased solvation in binary compositions of KCl and FeCl₃. On the other hand the ϕ_v^0 values for niacin were found positive in water and decrease with increase in temperature indicating decrease of ion-solvent interactions whereas values of ϕ_v^0 were found to increase with temperature in different compositions of KCl and FeCl₃ in water, showing that ion - solvent interactions are further strengthened with the addition of KCl and FeCl₃ indicating that molecules of niacin are highly solvated

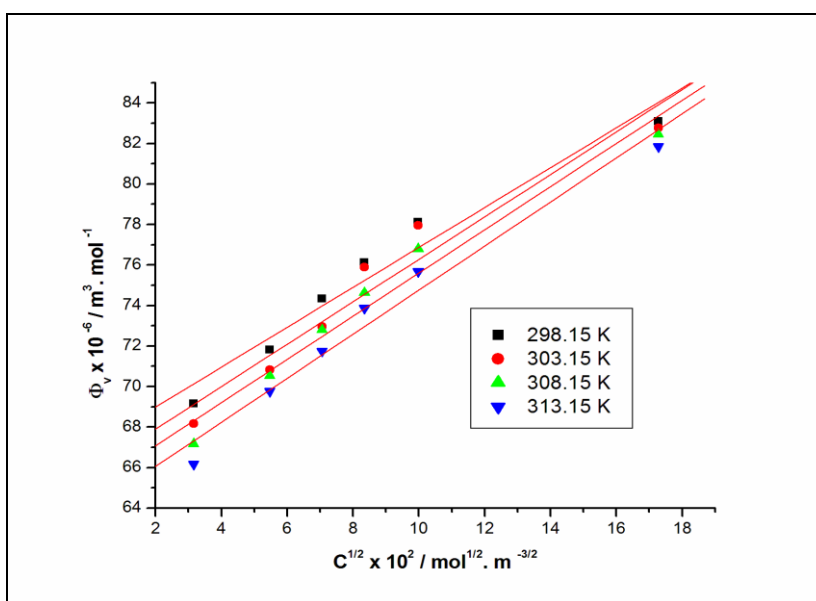


Figure 3: Variation of apparent molar volume with conc. for Niacin in water at different temperatures.

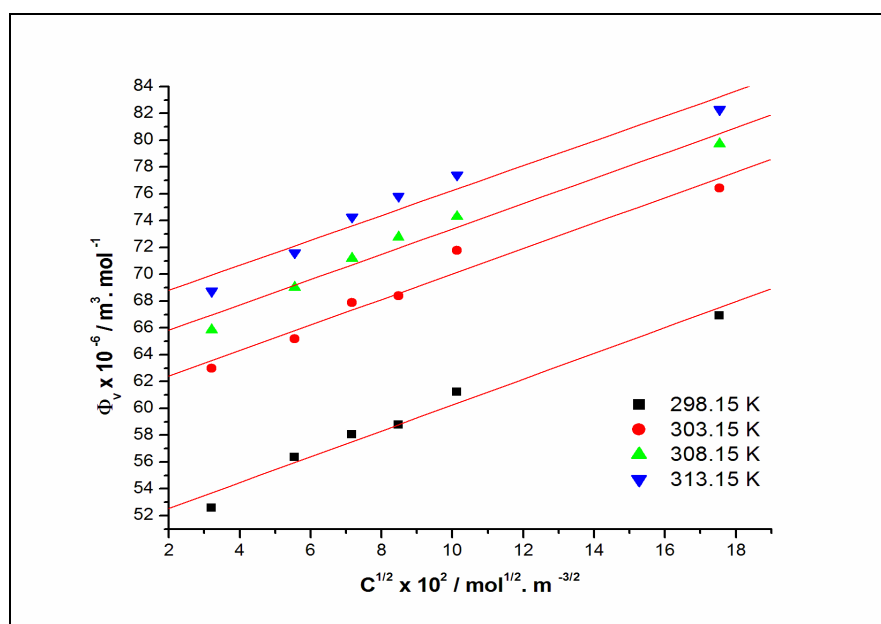


Figure 4: Variation of apparent molar volume with conc. for niacin in binary aqueous mixtures of 5% KCl at equidistant temperatures

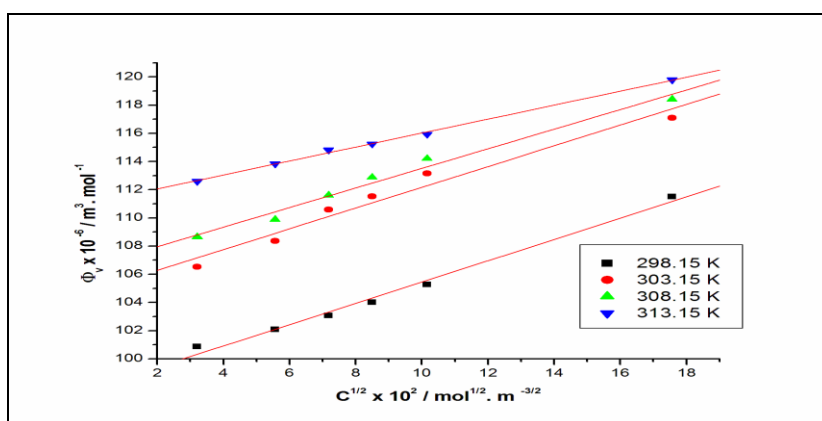


Figure 5: Variation of apparent molar volume with conc. for niacin in binary aqueous solution of 5% FeCl₃ at different temperatures.

Variation of apparent molar volume with $C^{1/2}$ for Niacin in water and in binary aqueous solutions of KCl and FeCl₃ are shown in figs. 3,4 and 5 respectively.

3.2. Partial molar expansibilities

In order to analyse the performance of niacin in terms of structure making and breaking in the present solvent systems, the partial molar expansibilities, ϕ_E^0 and the molar heat capacities were determined [23] in water and for the lower compositions of KCl and FeCl₃ and temperature dependence equations of partial molar volumes in water , 5% KCl in water and 5% FeCl₃ in water for niacin can be expressed by the following relations. Partial molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T} \right]_p$, has been calculated for

niacin in water , 5% KCl + water and 5% FeCl₃ + water by using equations 6 to 8.

$$\phi_v^0 = 284.34 - 1.206T + 0.00016T^2 \quad \text{in water} \quad (6)$$

$$\phi_v^0 = -6776.33 + 43.47T - 0.069T^2 \quad \text{in 5\% KCl + water} \quad (7)$$

$$\phi_v^0 = -2491.42 + 15.87T - 0.024T^2 \quad \text{in 5\% FeCl}_3 \text{ + water} \quad (8)$$

Table 4: Variation of partial molar expansibilities (ϕ_E^0) for niacin in water, 5% KCl + water and 5% FeCl₃ + water at different temperatures (K).

T/K	Water	5% KCl +water	5% FeCl ₃ + water
$(m^3 \text{ mol}^{-1} \text{ K}^{-1})\phi_E^0$			
298.15	-0.252	2.320	1.499
303.15	-0.236	1.630	1.258
308.15	-0.220	0.940	1.017
313.15	-0.204	0.250	0.776

From the table 4, it was found that values of partial molar expansibilities for Niacin were found increasing in water with the increase in temperature where as these values were found decreasing in 5% KCl+ water and 5% FeCl₃+ water indicating that niacin is behaving like symmetrical tetra alkyl ammonium salts [22] in water and behaving like common salts [24] in 5% KCl+ water and 5% FeCl₃+ water because the limiting apparent molar volume expansibilities decreases with the increase in temperature for a common salt. The increase in magnitude of partial molar expansibilities is ascribed to presence of “packing effect”[23] in water where as it is absent in 5% KCl+ water and 5% FeCl₃+ water. A sample plot for niacin in binary aqueous mixtures of FeCl₃ is shown in fig. 6.

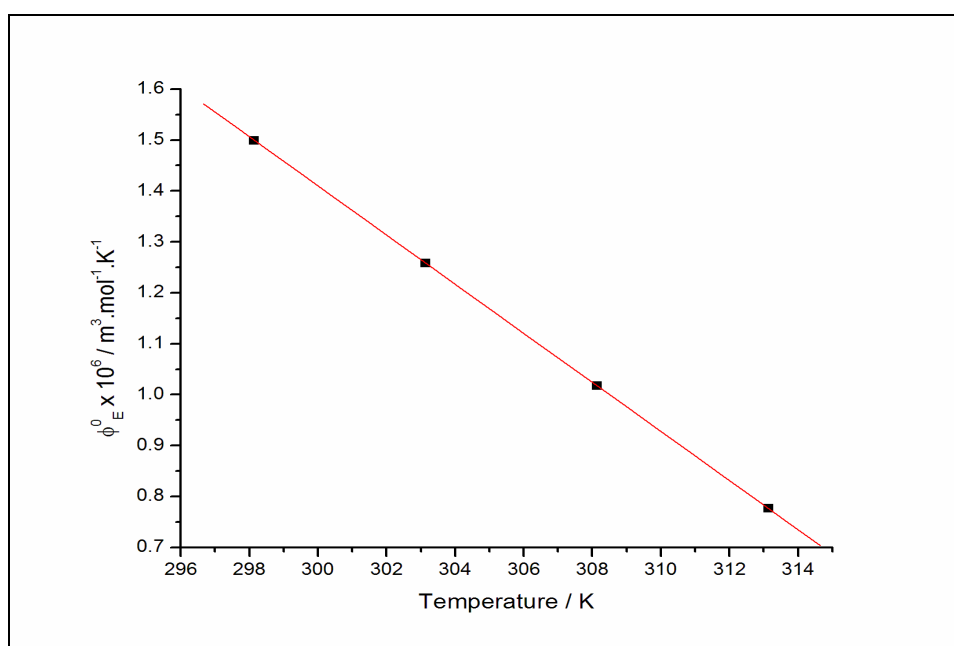


Figure 6: Variation of ϕ_E^0 with temperature for niacin in 5% FeCl₃ +Water

Partial molar heat capacities are expressed by the general equation:

$$(\partial C_p / \partial P)_T = -T (\partial^2 \phi_v^0 / \partial T^2)_P \quad (7)$$

From relations (4 to 6) sign of the values of $(\partial C_p / \partial P)_T$ were found negative indicating the structure making behavior in water and positive values of $(\partial C_p / \partial P)_T$ for the solutions of niacin in binary aqueous mixtures of KCl and FeCl₃ showing the structure breaking behavior. Predictable molecular interactions existing between niacin and aqueous KCl solutions are represented in figure 6.

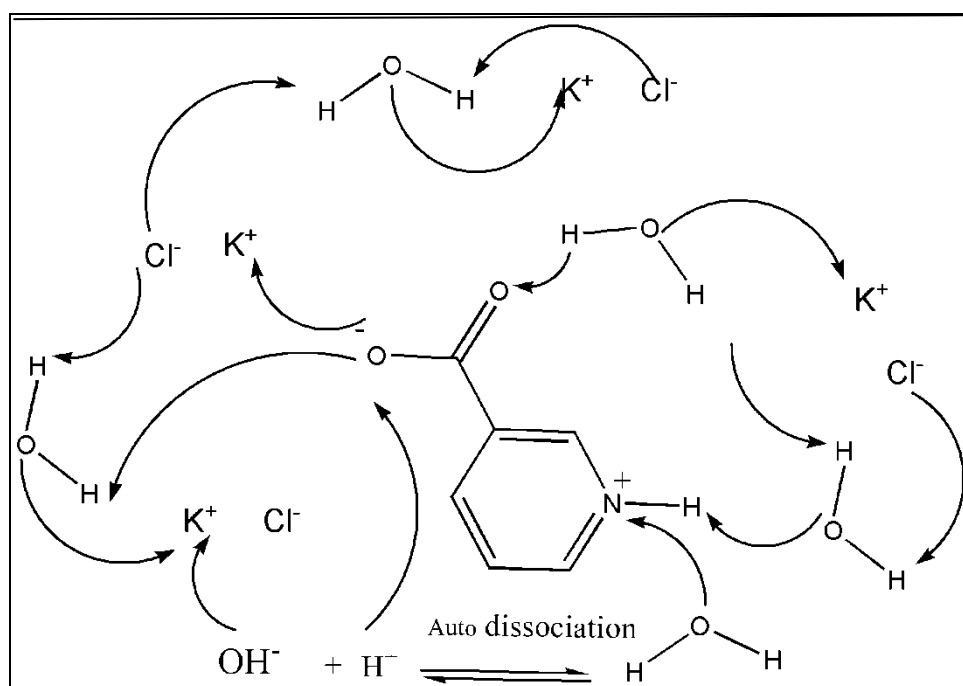


Figure 6: Molecular interactions existing between niacin and aqueous KCl solution.

Conclusion

Present study ascribed the behavior of Niacin in different solvent systems of KCl and FeCl₃ and it was found that Niacin is behaving differently in water and in binary aqueous mixtures of KCl and FeCl₃ in terms of structure making and breaking nature. The increase in values of partial molar expansibilities is ascribed to presence of “packing effect” in water where as it was found absent in 5% KCl+ water and 5% FeCl₃+ water

References

1. M.L Parmar and R.C.Thakur, “Effect of temperature on the partial molar volumes of some divalent transition metal sulphates and magnesium sulphate in binary aqueous mixtures of diethylene glycol”, Proc. Nat. Acad. Sci. India, vol. 76(A), pp.183, 2006.
2. M.L Parmar and R.C.Thakur, “Effect of Temperature on the partial molar volumes of some divalent transition metal sulphates and magnesium sulphate in the water-rich region of aqueous mixtures of ethylene glycol”, J. Mol. Liq, vol. 128, pp. 85-89, July 2006.
3. R.C. Thakur, Ravi Sharma, Ashish Kumar and M.L. Parmar, “Thermodynamic and transport studies of some aluminium salts in water and binary aqueous mixtures of tetrahydrofuran, J. Mater. Environ. Sci., vol. 6 (5) pp.130-1336, May 2015.
4. R.C.Thakur and Sonika, “Effect of Temperature on Partial Molar Volumes of Some Bivalent Transition Metal Chlorides and Magnesium Chloride in the Water-Rich Region of Binary Aqueous Mixtures of Ethanol” , Research J. Pharma, Bio. and Chem. Sci., vol. 5(6), pp.1298-1305, Dec. 2014.
5. R.C.Thakur, Ravi Sharma, Ashish Kumar, Sanjay Kumar and M.L.Parmar, “Partial Molar Volumes of Aluminium Chloride, Aluminium Sulphate and Aluminium Nitrate in Water-rich Binary Aqueous Mixtures of Tetrahydrofuran” Oriental J. Chem.,vol. 30 (4), pp.2037-2041, 2014.

6. R.C.Thakur, Ravi Sharma, Meenakshi and Ashish Kumar,” Thermodynamic Study of Copper Sulphate and Zinc Sulphate in Water and Binary Aqueous Mixtures of Propylene Glycol” Orient. J. Chem.,vol. 31(1) pp. 363-369, 2015.
7. R.C. Thakur, Ravi Sharma and Manju Bala, “Partial Molar Volumes of Cobalt Nitrate and Nickel Nitrate in Water and Binary Aqueous Mixtures of DMSO at Different Temperatures”, J. Mater. Environ. Sci.,vol. 7(9), pp. 3415-3420, 2016.
8. R. C. Thakur, Ravi Sharma and Vishali Gill, “Effect of Temperature on the Volumetric Studies of some Thiocyanates in Water”, Rasayan J.Chem., vol. 9 (1), pp. 44-51, March 2016.
9. Ravi Sharma, R. C. Thakur, Balwinder Sani and Harsh Kumar, “Properties of L-Ascorbic Acid in Water and Binary Aqueous Mixtures of D-Glucose and D-Fructose at Different Temperatures”, Russian Journal of Physical Chemistry A, vol. 91(12), pp.2389-2396, 2017.
10. Agnita Kundu and Nand Kishore, “Apparent Molar Heat Capacities and Apparent Molar Volumes of Aqueous Nicotinamide at Different Temperatures”, J. Solution Chem., vol. 32, pp.703-717, Aug. 2003.
11. Guler Ayranci, Melike Bilgi, Erol Ayranci, “Volumetric properties of ascorbic acid (vitamin C) and thiamine hydrochloride (vitamin B1) in dilute HCl and in aqueous NaCl solutions at (283.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K”, The Journal of Chemical Thermodynamics, vol. 39(12), pp.1620–1631, Dec. 2007.
12. Zoya Orekhova, Meyrav Ben-Hamo, Emanuel Manzurola and Alexander Apelblat, “Electrical Conductance and Volumetric Studies in Aqueous Solutions of Nicotinic Acid”, J. Solution. Chemistry, vol. 34, pp. 687-700, Jun. 2005.
13. Hui-Ping Pan, Tong-Chun Bai Xuan-Dong Wang, “Density, Viscosity, and Electric Conductance of a Ternary Solution of (Nicotinic Acid + Polyethanol + Water)”, J. Chem. Eng. Data., vol. 55(6), pp.2257-2262, Nov. 2009.
14. A Pal, B Kumar, “ Volumetric and Acoustic Properties of Binary Mixtures of the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate [bmim][BF₄] with Alkoxyalkanols at Different Temperatures” J. Chem. Eng. Data ,vol. 57 (30), pp. 688-695, Feb. 2012.
15. Vickramjeet Singh, Dharmendra Singh and Ramesh L. Gardas, “Effect of DBU (1,8-Diazobicyclo[5.4.0]undec-7-ene) Based Protic Ionic Liquid on the Volumetric and Ultrasonic Properties of Ascorbic Acid in Aqueous Solution, Ind. Eng. Chem. Res, vol. 54, 7, pp. 2237-2245, Feb. 2015.
16. Ravi Sharma, R. C. Thakur & Harsh Kumar, “ Study of viscometric properties of L-ascorbic acid in binary aqueous mixtures of D-glucose and D-fructose” , Physics and Chemistry of Liquids, vol. 57, pp.139-150, Feb. 2018.
17. Gary K. Ward and Frank J. Millero, “The effect of pressure on the ionization of boric acid in aqueous solutions from molal-volume data” vol. 3, pp. 417–430, Jun. 1974.
18. Ravi Sharma and R. C. Thakur, “Molecular Interactions of Pyridoxine Hydrochloride in Aqueous Mixtures of D-Glucose, D-Fructose and D-Lactose at Different Temperatures; Russian Journal of Physical Chemistry A”, vol. 92(13), pp. 76–83, 2018.
19. F.J.Millero and J.H. Knox,” Apparent molal volumes of aqueous sodium fluoride, sodium sulfate, potassium chloride, potassium sulfate, magnesium chloride, and magnesium sulfate solutions at 0.deg. and 50.deg”J. Chem. Eng. Data, vol. 18,pp.407-411, Oct.1973.
20. Mohammad Arif Cheema, Pablo Taboada, Silvia Barbosa, Emilio Castro, Mohammad Siddiq, Víctor Mosquera,” A comparative study of the thermodynamic properties at the air–water interface and in the bulk of structurally related phenothiazine drugs aqueous solutions” The Journal of Chemical Thermodynamics, vol. 40(2), pp.298-308, Feb. 2008.
21. Franks Felix, “Water a Comprehensive Treatise - Aqueous Solutions of Amphiphiles and Macromolecule”, Vol. 6: Recent Advances, Plenum Press, New York, 1975.
22. Carmen M Romero, and Faustino Negrete, “Effect of temperature on partial molar volumes and viscosities of aqueous solutions of α -dl-Aminobutyric acid, dl-Norvaline and dl-Norleucine”, , Phys. Chem. Liq., vol. 42, pp.261-267, Aug. 2006.
23. L.G.Hepler, “Thermal expansion and structure in water and aqueous solutions”, Can. J. Chem., vol. 47(24) pp.4613-4617, 1969.
24. F.J.Millero and W Drost Hansen, “Apparent molal volumes of ammonium chloride and some symmetrical tetraalkylammonium chlorides at various temperatures” J. Phy. Chem., vol. 72, 5, pp.1758-1763, 1968.