GE-International Journal of Engineering Research
Vol. 5, Issue 1, January 2017 **Impact Factor- 5.613**
ISSN(O): 2321-1717, ISSN(P): 2394-420X

Website: www.aarf.asia Email : editor@aarf.asia , editoraarf@gmail.com

EFFECT OF SODIUM CHLORIDE ON EXCESS ENTHALPY OF N-BUTYLAMINE - WATER SYSTEM

Dr. A. Elango[1]., Dr. B. Karunanithi[2]
[1]Professor, Department of Chemical Engineering, Hindustan Institute of Technology & Science, Padur, Chennai, India.
[2]Professor, Department of Chemical Engineering, SRM University, Kattankulathur Chennai, Tamil Nadu, India.

ABSTRACT

Separation of liquid mixtures by the extractive distillation technique employing an inorganic or organic salt instead of the liquid separating agents, that are used conventionally, has the potential to yield higher separation efficiency with attendant advantages like lower energy requirements and lesser cost of equipments. The salt added plays an effective role by changing the Vapour-liquid equilibrium relationship in the view of the liquid phase turning into a solution of an electrolyte whose degree of dissociation becomes a function dependant on the relative proportions of the two volatile components. In this investigation the effect of sodium chloride on excess enthalpy of binary miscible Butylamine-Water system was studied with weight percentage 5%,10% and 15% of sodium chloride, it is found that the increase in the exothermic peak value of the system with increase in the salt concentration is due to the fact that the added salt favors association by acting as a polarizing medium.

Keywords:- Extractive Distillation, Exothermic, Model Parameter, Vapour liquid Equilibrium, Excess Enthalpy

Introduction

In the process of separation of liquid mixtures by the extractive and azeotropic distillation methods, the addition of a third component is a common technique. Such third components are added to alter the relative volatility or to alter or to eliminate azeotropes for the purpose of facilitating distillation. Recent studies have suggested that solid agents may also be used as separating agents in a dissolved form. Such three component systems consisting two liquids and one salt, have been encountered in various industrial processes. In many cases, distillation affords the most economical means of separating the liquid components. In the design of distillation equipment, the vapour liquid equilibrium relationship between the two components is of prime importance. Hence, any factors, affecting the equilibrium relationship, will in turn affect the separation efficiency. Here it may be noted that the presence of salt is one such factor which affects the equilibrium relationship .Although the exact nature of the action of the salt, dissolved in a liquid, is not certain, it is understood that the presence of salt alters the relative volatility of the liquid by lowering its vapour pressure. The extent of the change in volatility depends on the solubility of the salt in the liquid.In extractive distillation, the inorganic salt is added as an extractive agent to modify the relative volatility of the binary mixture. The selective effect that the salt can have on the volatilities of the two liquid components and hence on the composition of the equilibrium vapor comes about primarily through the effect exerted by salt ions and/or molecules on the structure of the liquid phase. In this investigation the effect of sodium chloride on excess enthalpy of binary miscible Butylamine-Water system was studied with weight percentage 5%, 10% and 15% of sodium chloride.

Literature Review

Rajendran et al [23,38] studied the effect of inorganic salts (Calcium chloride, Sodium chloride and Zinc Chloride) in vapor liquid equilibria and heat of mixing of the methanol-Ethyl acetate system. They found that the addition of calcium chloride brought about a significant enhancement in the heat of mixing while the salts sodium chloride and zinc chloride decrease the lateral shift. Rajendran et al [24,39] studied the effect of sodium chloride, calcium chloride and zinc chloride on excess enthalpy for systems methanol-water, methanol-benzene, pyridine-water . They found that for methanol-water system the salt sodium chloride decrease the exothermic value with increase in salt concentration while the calcium chloride found to shift the excess enthalpy to the endothermic side. They further found for the system methanol-benzene the salt calcium chloride and zinc chloride increased the endothermic excess enthalpy . Rajendran et al [21] Studied the effect of Sodium Chloride, Calcium Chloride and Zinc Chloride at the concentration 5wt% to 30 wt% on Liquid-Liquid Equilibria of the ternary system Ethyl acetate – 2.Proponal-Water and Vapor Liquid Equilibria of its constituent binary system (ie) Ethyl acetate-2-propanol, 2-Propanol-Water and ethyl acetate-water. The system 2-propanol-water had both positive and negative values of the excess enthalpy with exothermic behavior in propanal lean region. All the salts which were preferentially soluble in water were found to decrease the exothermic value steadily as their concentration was increased. In the case of 2.proponal –ethyl acetate system, the salt sodium chloride and zinc chloride had brought about a small change in the magnitude of heat of mixing, while the addition of calcium chloride had resulted in a decrease in the value of heat of mixing in ester rich region and increase in ester lean region. A shift in the peak value was observed when calcium chloride salt was added due to the possible formation of alcohol –salt complex. Rajendran et al [22,40,43] studied the effect of sodium chloride, calcium chloride and zinc chloride on heat of mixing of 2,proponal-Benzene system. They found that the salt sodium chloride and zinc chloride brought about an enhancement in heat of mixing values and the salt calcium found to produce the opposite effect. Frice et al [7] studied the excess enthalpies of methanol, ethanol, 1-propanol, 2-propanol and aqueous solution of NaCl, KCl values of excess enthalpy were measured using flow calorimeter at various Temperatures mixtures which are alcohols. The temperature at which the investigation was carried out are 285.65, 298.15, 308.15 and 323.15 K. Those with ethanol and propanol were additionally investigated at 338.15 K. The concentration of the salt water component was varied between 0 and 10% in water for 2-proponal + water system. That excess enthalpy of mixture of aqueous solution containing 7.5 weight percentage. NaCl at 308.15 K was reduced about one third compared to that of salt free system. For the mixture of ethanol, 1-prpoponol or 2-proponol with water the addition of KCl causes reduction of the exothermic effect by 13-16%.

Materials used

The solvents used in this investigation are obtained from E-Merck India Ltd. and also from British Drug House Labs India. The hydrocarbon are assayed by gas chromatography and exceeds 99.5% purity and some of the solvents are further purified by fractional distillation. Anhydrous grade salts are used and all salts are dried for about 24 hrs before use. The physical properties of solvents and salts are given in Tables 1 and 2.

Table 1 Physical Properties of the solvents used

Components	Boiling Point C		Density at 30^{o}C		Refractic Index at 30^{o}C	
	This work	Timmermans et al(1962)	This work	Timmermans et al (1962	This work	Timmermans et al(1962)
Butylamine	77.8	78.1	0.738	0.735	1.390	1.389
Water	100	100.10	0.9971	1.0102	1.3325	1.3330

Table 2 Physical properties of salt

Salt	Purity	Molecular weight	Specific gravity	Melting point ^{o}C	Solubility in water at 30^{o}C (gms/100cc)
Sodium Chloride	99.98	82.03	1.528	324	119

Experimental Calorimeter

The calorimeter is designed to operate isothermally so as to allow the excess enthalpy at a given temperature to be determined for the entire composition range of a system in two experimental runs. A temperature probe is used as the temperature sensing device and the isothermal conditions are easily maintained within ± 0.005^{o}C. The set temperature is readily reproduced within ± 0.002^{o}C. The calorimeter contains vapour space but and source of error due to condensation and vaporization are very negligible, operating procedure of the calorimeter are described in Rajendran et al [24,41,42]

Results and Discussion

linear plots of H^E/x_1x_2 vs x_1 and x_1x_2/H^E vs x_1 for salt free butylamine-water are shown in Figures 1 and 2 and the effect of NaCl on Butyl amine-water system is shown in Figure 3 and in the Table 3. The exothermic peak value of the system for 5wt% NaCl is -1816 J/mol obtained at 0.416 mol fraction of Butyl amine and for 10 wt% NaCl the exothermic peak value is -2268 J/mol obtained at 0.3827 mol fraction Butyl amine and for 15 wt% NaCl the exothermic peak value is -2406 J/mol obtained at 0.476 mol fraction Butyl amine. The increase in the exothermic peak value of the system with increase in the salt concentration is due to the fact that the added salt favors association by acting as a polarizing medium.

Table 3 Effect of NaCl on Excess Enthalpy of Butylamine(1)+Water(2) system

No Salt		5 wt % NaCl			10 wt % NaCl			15 wt % NaCl		
x_1	H^E	x_1	x_3	H^E	x_1	x_3	H^E	x_1	x_3	H^E
0.11	-900	0.11	0.0327	-960	0.109	0.0682	-1196	0.141	0.098	-1265
0.2	-1240	0.2	0.0252	-1459	0.196	0.0518	-1805	0.3	0.0589	-2114
0.25	-1400	0.251	0.0142	-1641	0.258	0.0429	-2075	0.38	0.0434	-2327
0.33	-1600	0.333	0.0106	-1801	0.3039	0.0376	-2196	0.476	0.0326	-2406
0.42	-1600	0.416	0.00782	-1816	0.3827	0.0296	-2268	0.568	0.0241	-2314
0.54	-1400	0.537	0.00512	-1629	0.479	0.0222	-2158	0.682	0.0159	-1986
0.65	-1000	0.649	0.0033	-1298	0.575	0.0613	-1881	0.763	0.0103	-1621
0.78	-600	0.7575	0.00205	-895	0.689	0.0107	-1407	0.854	0.00642	-1091
					0.777	0.00701	-986	0.952	0.0022	-389

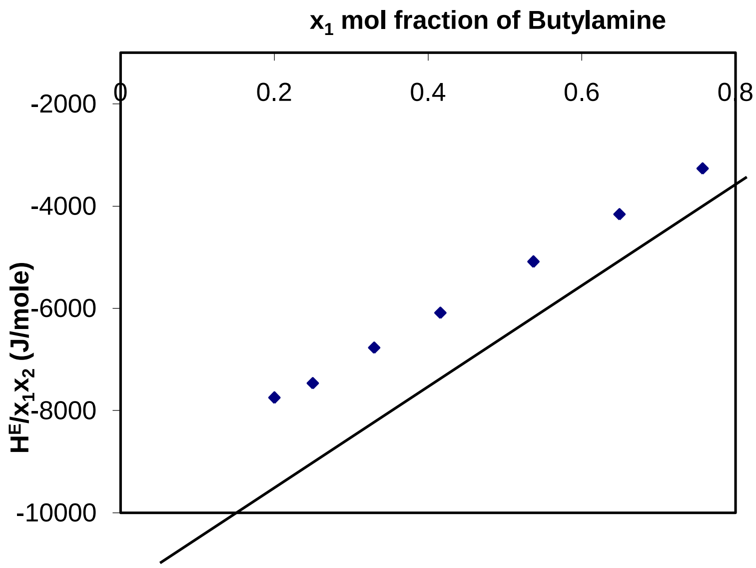

Figure 1 H^E/x_1x_2 vs x_1 for System Butylamine(1) + Water(2) at 30^oC

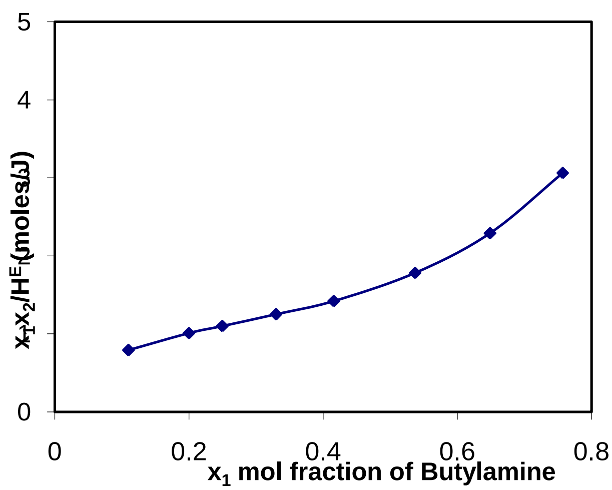

Figure 2 x_1x_2/H^E vs x_1 for System Butylamine(1) + Water(2) at 30^oC

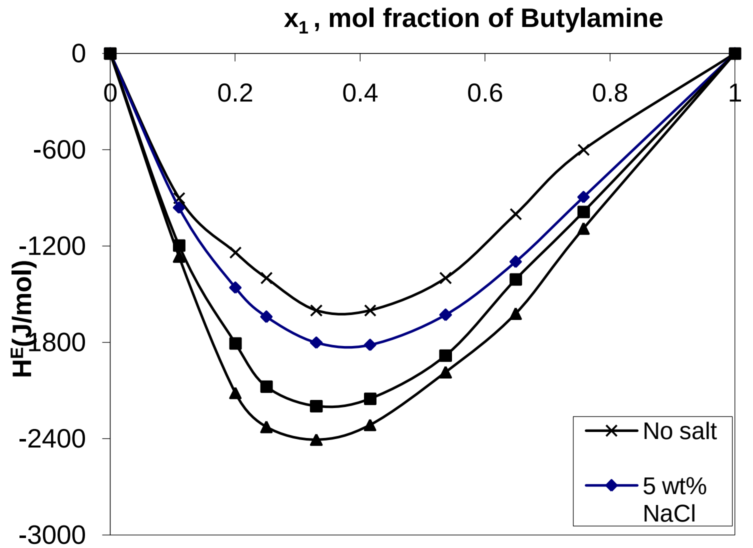

Figure 3 Effect of NaCl on Excess Enthapy of Butylamine(1)+Water(2) System at 30°C

CORRELATION OF EXPERIMENTAL EXCESS ENTHALPY DATA

The experimental data obtained in this investigation are fitted in the Redlich-Kister equation to obtain the parameters and to find the average deviation from the experimental results. The equation is given by

$$H^E/x_j(1-x_j) = \sum a_i (2x_j - 1)^i$$

where a_0, a_1, a_2, ... a_n are Redlich equation constants and **σ** is average deviation.

Table 4 Parameters of Redlich-Kister equation

Salt	Wt% of salt	a_0	a_1	a_2	a_3	a_4	σ
NaCl	-	-5526	2731	28.35	3.28	46.31	1.23
	5	-6834	3813	16.85	-21.36	-45.74	1.3
	10	-8439	4955	1.713	2.532	-2.08	1.56
	15	-9591	1191	7.75	-6.27	-16.49	1.75

Conclusion

The exothermic excess enthalpy of system N- Butylamine–Water increases with increase in concentration of sodium chloride. The results of this experiment-oriented investigation suggested that the salt in the dissolved form could bring about significant changes in the behavior of liquid mixtures which in turn are likely to have considerable influence on the economics of distillation and liquid extraction techniques.

List of symbols

a	-	constants of typical polynomial
f(x)	-	General form a typical fitting function
H^E	-	Excess enthalpy
i	-	Subscript of polynomial
m	-	Number of data points
n	-	Order of polynomial
x_1	-	Mol fraction of component 1
x_2	-	Mol fraction of component 2
x_3	-	Weight fraction of salt
x_i	-	Independent variable (typically mole fraction)
Σ	-	Summation symbol

References

1. Bevan Ott and Jadwiga Sipowska T. (1996), 'Applications of calorimetry to nonelectolyte solutions', J. Chem. Eng. Data. Vol.41, pp.987-1004.

2. Bockris J.O.M., Bowler Reed J. and Kichener J.A. (1951), 'Salt effect on Vapour Liquid Equlibria', Trans Faraday Soc, Vol.47, pp.184-187.

3. Butler J.A.V. (1929), 'The Mutual Salting-out of Ions', J. Phy. Chem. Vol.33, pp.1015-1023.

4. Ciparis J.N. (1966), 'Data of Salt Effect in VLE', Lithuanian Agricultural Academy', Kaunas, U.S.S.R.

5. Ding - Yu - Peng, George C. Benson (2000), `Excess enthalpies of 2, 2, 4 - Trimethyl penkane + Hexane + Octane at 298. 15 K', J. Chem. Eng. Data., Vol.45, pp.48-52.

6. Encina Calvo (1999), 'Heat capacities excess enthalpies and volumes of mixtures containing cyclic ehters', J. Chem. Eng. Data, Vol.44, pp.948-954.

7. Frice T., Schulz S., Ulbig P. and Wanger K. (1998), 'Effect of NaCl on excess enthalpies of binary liquid systems', Thermochemica. Acta., Vol.310, pp.87-94.

8. Frice T., Ulbig T., Schulz S. and Wagner K. (1999), 'Effect of NaCl, KCl on the excess enthalpies of Alkanol + water mixtures at various temperatures and salt concentrations', J. Chem. Engg. Data, Vol.44, pp.701-714.

9. Furter W.F. (1972), 'Salt Effect on Extractive Distillation', Amer Chem. Soc. Symp. Series, No.115, pp.35-39.

10. Furter W.F. (1976), 'In Thermodynamic Behavior of Electrolytes in Mixed Solvents', Advances in Chemistry Series 155; American Chemical Society: Washington, DC, pp.26-35.

11. Furter W.F. and Cook R.A. (1967), 'Salt Effect in Distillation - A Literature Review', Jl. H and Transfer, Vol.10, pp.23-36.

12. Klinkenberg, A. (1937), 'Predication of heat of mixing', Transaction Faraday Soc., Vol.33, pp.158-164.

13. Komolo Francescon (1986), 'Liquid-phase enthalpy of mixing for the system 1,3 dioxalane - chlorobenzene 288.15 K', J. Chem. Eng. Data, Vol. (31) pp.250-252.

14. Letcher T.M. and Koteswari Prasad (1991), 'Excess enthalpy and excess volume of (1,3,5-trimethyl benzene + an alk-l-yne) at the temperature 298.15 K', J. Chem. Thermodynamic, Vol.23, pp.643-646.

15. Letcher T.M. and Nirmala Deenadayalan (2000), 'Excess molar enthalpies and excess molar volumes for mixtures of 1,3-dimethyl-2-imidazolidinone and an alkanol and T=298.15', J. Chem. Eng. Data, Vol.45, pp.730-733.

16. Long F.A. and McDevit W.F. (1952), 'Activity Coefficients of Non-electrolyte Solutes in Aqueous Salt Solutions', Chemical Review, Vol.51, pp.119-169.

17. Long F.A. and McDevit W.F. (1952), 'The Activity Coefficient of Benzene in Aqueous Salt Solutions', Jl. Am. Chem. Soc., Vol.74, pp.1173-1777.

18. Mrazek, R.V. and Van ness, H.C. (1961), 'Heats of Mixing: alcohol-Aromatic binary systems at 25°, 35° and 45°C', A.I.Ch.E.J., Vol.7, pp.190-195.

19. Nowicka B., Osinska S.T. and Latha G.D. (1997), 'Enthalpies of solution of N-acetylamino acid amides in aqueous solutions of electrolytes at the temperature 298.15 K', J. Chem. Thermodynamics, Vol.29, pp.1017-1024.

20. Philip J.C. (1970), 'Hydration theory for liquid mixture', J. Chem. Soc. (London), Vol.91, pp.711-719.

21. Rajendran M., Renganarayanan S. and Srinivasan D. (1991), 'Salt Effect in Phase Equilibria and Heat of Mixing : Effect of Dissolved inorganic Salts on liquid-liquid equilibria of ethyl acetate –2-proponal-water system and heat of mixing of its constituent binaries', Fluid phase Equilibria, Vol. 70, pp. 65-106.

22. Rajendran M. and Srinivasan D. (1994), 'Salt effect in Heat of Mixing: Effect of dissolved salts on the heat of mixing of 2-propanol-Benzene system', Chem. Eng. Comm., Vol.128, pp.109-117.

23. Rajendran M., Renganarayanan S., Madhavan P.R. and Srinivasan D. (1988), 'Effect of dissolved inorganic salts on the Vapor-Liquid Equilibria and enthalpy of mixing of the Methanol-Ethylacetate system', Chem. Eng. Comm., Vol.74, pp.179-193.

24. Rajendran M., Renganarayanan S., Madhavan P.R. and Srinivasan D. (1989). 'Effect of dissolved salts on the heat of mixing of three binary systems', J. Chem. Engg. Data, Vol.34, pp.375-382.

25. Renon H. and Prausnitz J.M. (1968), 'Local composition in thermodynamic Excess functions for liquid mixtures', AIChE Journal, Vol.14, No.1, pp. 135-144.

26. Rezanova E.N., Kammerer K. and Lichtentnaler N. (2000), 'Excess enthalpies and volumes of ternary mixtures containing 1-propanol 1-butanol and ether (Diisopropyl ether or Dibutyl eter) and Heptane)', J. Chem. Eng. Data Vol.45, No.1, pp.124-130.

27. Sada E., Morisue T. and Miyahara K.J. (1975), 'Thermodynamics of Salt Effect on VLE', Jl. Chem. Eng. Data, 20, p.283.

28. Scatchart G., Ticknor C.B., Goots J.R. and McCarney E.R. (1952), 'Heat of mixing in some non electrolyte solutions', J. Am. Chem. Soc., Vol.74, pp.3721-3726.

29. Timmermans J. (1962), 'Physicochemical constants of pure organic compounds', Elsevier, Amsterdam.

30. Tomkins G.J. and Tomkins R.P.T. (1972), 'Non-aqueous Electrolytes Hand Book', Vol.I, Academic Press New York, 1972, Vol.II, 1973.

31. Tomkins R.P.T., Gerhardt G.M., Lichtenstein L.M. and Turner P.J. (1976), 'Heats of Solution and Dilution of Lithium perchlorate in Aqueous Acetonitrile', Adv. Chem. Series, Vol.155, pp.297-302.

32. Trevor M., Letcher (2000), 'Excess enthalpies and volumes for mixtures of (Acetonitrile + carboxylic acid) at 298.15 K', J. Chem. Eng. Data, Vol.45, pp.57-60.

33. Tsao C.C. and Smith J.M. (1953), 'Heats of mixing of liquids', Chem. Eng. Prog. Symp. Ser., Vol.49, pp.107-111.

34. Van Ness H.C. and Mrazek R.V. (1959), 'Treatment of Thermodynamic Data for Binary Systems', AIChE. Journal, Vol.5, pp.209-213.

35. Venkatesu P., Ramadevi R.S., Prabhakara Rao M.V. and Prasad D.H.L. (2000), 'Excess molar enthalpies of N-N-Dimethylformamide with chloroethanes and acetates at 298.15 K', J. Chem. Eng. Data, Vol.45, pp.515-517.

36. Viswanath.D.S.,Patel.H.R.,Sundaram.S.(1979),'Thermodynamic properties of the system Benzene-Chloroethane' J. Chem. Eng. Data, Vol.24,No:1 pp.45-47.

37. Wilson G.M. (1964), Vapour-liquid equilibrium: 'Excess enthalpies and volume for mixture of (Acetonitrile + A carboxylic acid) at 298.15 K', J. Chem. Eng. Data, Vol.45, pp. 57-60.

38. R. Rajesh, R. Raj Muhamed.,'Determination Thermodynamic Properties for

Hydrogen Bonded Complexes of Phenols with N-Methylaniline in N-Hexane Medium at Different Temperatures using Ultrasonic Technique'International Journal of ChemTech Research, Vol.9, No.02 pp 110-117, 2016.

39. M.C. Rao1 and K. Ramachandra Rao, 'Thermal Evaporated V2O5 Thin Films: Thermodynamic Properties' International Journal of ChemTech Research,Vol.6, No.7, pp 3931-3934, Sept-Oct 2014

40. K. Balwinder Saini, Ravi Sharma and R.C.Thakur. 'Thermodynamics and transport properties of L-Proline in water and binary aqueous mixtures of acetonitrile at 303.15' Journal of ChemTech Research Vol.8, No.12 pp 395-402, 2015.

41. K. Rajagopal. K, Johnson.J, 'Studies on volumetric and viscometric properties of lhistidine in aqueous xylose solution over temperature range (298.15 to 313.15)' International Journal of ChemTech Research ,Vol.8, No.1, pp 346-355, 2015 .

42. V.P.Gopika1,G.Havisha1, S.Muthu, M. Raja , R. Raj Muhamed,' Molecular structure, NBO, first order hyperpolarizability and HOMO-LUMO analysis of 7 Azathieno[2,3-c]cinnoline' International Journal of ChemTech Research,Vol.8, No.12 pp 721-733, 2015.

43. K.Rajagopal,G.Roy Richi Renold. 'Effect of Temperature on the Volumetric, Compressibility and Viscometric Properties of Paracetamol in Aqueous Methanol Solution' International Journal of PharmTech Research,Vol.8, No.8, pp 180-195, 2015.

44. Palani, G.Srinivasan and B. Geeta Lakshmi, 'Ultrasonic Studies on Molecular Interaction of Arginine in Aqueous Disaccharides at 298.15K.' International Journal of ChemTech Research Vol. 3, No.1, pp 284-289, Jan-Mar 2011.

45. Sonika, R.C.Thakur and Ravi Sharma, 'Effect of temperature on the partial molar volumes of some bivalent transition metal chlorides in water and binary aqueous mixtures of methanol' International Journal of ChemTech Research,Vol.7, No.5, pp 2222-2228, 2014-2015.

46. K.Rajagopal and J.Johnson, 'Intermolecular interaction studies of homologous α amino acids in aqueous fructose solution at 298.15 K' International Journal of PharmTech Research,Vol.8, No.3, pp 480-498, 2015.