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Abstract

Polymers having many ionizable groups in their molecular structure are called Polyelectrolytes. They are extensively used in industries like papermaking, food processing, medicine and pharmaceuticals, water purification, oil field exploration, cosmetic formulation etc. In spite of wide applicability its current status of knowledge is precursory due complexity of their behavior in solution as well as at interface. Solution properties of polyelectrolytes are extensively studied in last 40 years to understand their behavior. The activity is important thermodynamic property. From activity we can get most of thermodynamic properties like interaction parameter, free energy of dilution of the polyelectrolyte, degree of dissociation of polyelectrolytes etc.

Several models of Polyelectrolytes thermodynamics have been proposed. Two general approaches have been used to model Polyelectrolytes thermodynamics, spherical and cylindrical (chain) models. Two of the successful models to explain and predict commonly measured properties of polyelectrolytes such as osmotic coefficient and counterion activity coefficients have been proposed by Manning and Oosawa. Most of these models are applicable at infinite dilution only may be due to weak inter chain interactions. An Excess Gibb's free energy model can predict properties at finite concentrations of polyelectrolytes, which is combination of Manning model and Local composition model.

Vapor pressure osmometry and isothermal Titration Microcalorimetry are experimental methods to determine the thermodynamic properties of polymer solvent system. Osmometry helps to understand the thermodynamics of polymer solutions as it determines the value of osmotic pressure, which in turn gives the value of thermodynamic parameters**.** Isothermal Titration Microcalorimetry gives the heat of dilution directly from which we can calculate activity of the solution.

The osmotic coefficient and activity of water in aqueous NaPSS solution are found out using Vapor pressure osmometry and Isothermal titration calorimeter at different temperatures. The results are compared with result obtained by an excess Gibb's free energy model. Measured data show good agreement with available literature data at that temperature.

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Nomenclature

A	Debye-Hukel parameter
a_w	Actvity of water
e	Electronic charge
Ge	Excess Gibbs free energy
h	Partial molar enthalpy
I	Ionic strength.
L	**The contour length of polyelectrolyte**
χ	Flory Huggins parameter
$\Delta_{sol}H$	Enthalpy of vaporization
ΔH_v	Enthalpy of vaporisation
ΔS_m	Entropy of mixing
ΔG	Change in Gibbs energy
Kcal	Calibation constant
M	Molecular weight of solvent
m	Molality
P	Pressure
R	Gas constant
ΔS^0	Standard change in entropy
T	Absolute temperature
Vm	Molar volume of solvent
Xi	Effective local mole fraction
z_i	The valance of the ith species

GREEK LETTERS

π	Osmotic pressure
ϕ	Osmotic coefficient

χ	Interaction parameter
φ_1	Volume fraction of solvent
α	Degree of dissociation
α_{ji}	Non-randomness factor
β	Uniform charge density
ρ	Density
γ	Activity coefficient
κ	The inverse of Debye length
μ	Chemical potential
ξ	Charge density parameter
τ	NRTL model parameter

Chapter 1

Introduction

1.1 Polyelectrolytes

Polyelectrolytes are long-chain molecules carrying a large number of ionizable groups. Polyelectrolytes contain ionizable groups at levels ranging from few to 100 mole% of repeating units. Polyelectrolytes could be a polyacid, a polybase, or a polyampholyte depending upon whether the ionizable groups are all anionic, all cationic or a mixture of acidic and basic groups reside in the polymer chain. The molecules could be synthetic or naturally occurring. Examples are polymeric acids such as poly(vinyl sulfonic acid), poly(acrylic acid), polymeric bases such as poly(vinyl amine), poly(vinyl pyridine) and many naturally occurring proteins, polysaccharides, and nucleic acids.

Solution properties of polyelectrolytes differ considerably from uncharged macromolecule or electrolyte. Origin of this difference in properties lies in the combination of properties derived from long chain molecule with properties derived from the charge interaction. In solution, polyelectrolytes are dissociated into polyvalent macroions (polyions) and a large number of small ions of opposite charge (counterions).

Polyelectrolyte solutions are generally electroneutral in thermodynamic sense. The high charge on macroion produces a strong ionic field, which attract counterions. This strong ionic interaction between polyvalent macroion and the counterions is the source of the characteristic properties of polyelectrolytes. Most of the macroions are long, flexible chains having a large extension in solution. Their size and shape depends on the charge and interactions with the counterions. With increasing the charge, the flexible chain changes its shape from a contacted, random coil to a fully extended one.

Polyelectrolytes are extensively used in industries like papermaking, food processing, medicine and pharmaceuticals, water purification, oil field exploration, cosmetic formulation etc. Due to various applications the study of thermodynamic proprieties of polyelectrolyte solution becomes more importance.

1.2 Objective of study

The main objective is to study thermodynamics of polyelectrolyte solutions using Vapor pressure osmometer (VPO) and Isothermal titration calorimeter (ITC) and compare data obtained by VPO and ITC. To determine osmotic coefficient and activity of the water in NaPSS solution using VPO and ITC at different temperatures and compare them. The experimental values to be compared with the available model. The activity of the solvent is an important property. From activity we can get most of thermodynamic properties like interaction parameter, free energy of dilution of the polyelectrolyte, degree of dissociation of polyelectrolytes etc.

First experiments are done using VPO at different concentrations of NaPSS at three different temperatures. The VPO has been designed to exactly measure the total osmolality of physical fluids and to determine the average molecular mass of polymers in aqueous or organic solutions. From osmolality, the osmotic pressure, osmotic coefficient and activity coefficient can be calculated.

ITC is the calorimetry of small samples, specifically microgram samples with micro level heats measurements. With help of ITC, it is possible to measure very small heat flows down to nanoWatt regions. Using heat data, the heat of dilution of sample, partial molar enthalpy, interaction parameter and activity of solvent can be determined.

1.3 Organization of report

This report contains overview of the thermodynamic of polyelectrolyte solutions. In the second chapter model used for the prediction of osmotic properties of the polyelectrolytes are described in detail**.** Various experimental techniques have been used for the study of osmotic properties of polyelectrolyte solution. These techniques include freezing point depression, boiling point elevation, dynamic and static vapor pressure measurement, osmotic pressure measurement and the isopiestic method. The VPO and ITC techniques are explained in chapter three. Chapter four included literatures review. In chapter five all experiment details are given and results are discussed. Lastly chapter six give conclusion and future scope for work.

Chapter 2

Thermodynamic models of Polyelectrolytes

Several models of Polyelectrolytes thermodynamics have been proposed. Two general approaches have been used to model a polyelectrolyte, spherical and cylindrical (chain) models. In the former approach, the coiled polyions are treated as spherical with the charge density distributed within the sphere. This approach predicts smaller electrostatic potentials and larger polyions sizes than the experimentally measured. These discrepancies primarily arise from that assumption of smeared charge distribution in the poly-ion region, whereas the potential around the polyion actually varies strongly with distance from the polyion.

Most realistic and currently accepted theories of polyelectrolyte solution are based on the analyses of the properties of an infinitely long cylinder with the electric charge uniformly distributed along its surface. Two of the successful models to explain and predict commonly measured properties of polyelectrolytes such as osmotic coefficient and counterion activity coefficients have been proposed by Manning and Oosawa.

In this chapter starting from PB equation, Debye-Hükel limiting law is discussed. Then Manning model and excess Gibbs free energy model is given.

2.1 Poisson-Boltzman equation

Coulomb's law determines interaction between two ionic species, if there are no other charges. However, in case of polyelectrolytes, counterions are also present, hence the interaction can not be determined by the Coulomb's law only. The method to determine electrostatic potential is described by Poisson-Boltzman (PB) equation.

Considering a system of several ionic species the local charge density and local ion concentration is relates by

$$r(r) = e \sum_i z_i n_i (r) \tag{2.1}$$

Where, sum goes all over the ionic species, z_i is the valance of the i^{th} species and n_i is local composition.

Due to requirement of electroneutriality,

$$\sum z_i n_i(0) = 0 \tag{2.2}$$

Ignoring the fluctuations of local potential that is replacing the by its time averaged value, in mean field approximation the local concentration is expressed as a Boltzman distribution.

$$n_i\,(r) = n_i(0)\,\exp[-\frac{z_i e\psi(r)}{kT}] \tag{2.3}$$

We have Poisson equation,

$$\nabla^2\psi = -\frac{\rho(r)}{\varepsilon\varepsilon_0} \tag{2.4}$$

Hence from equations (1), (3), and (4)

$$\nabla^2\psi = -\frac{e}{\varepsilon\varepsilon_0}\sum_i z_i n_i(0)\exp(-z_i e\psi(r)/kT) \tag{2.5}$$

PB equation is of fundamental importance for the study of electrolytes as well as polyelectrolytes.

Debye and Hükel who suggested approximating the non-linear form of PB equation by a linearized form and introduced some simplifications made one of the essential steps in development of the theory of electrolytes in solution in 1923.

2.2 Debye-Hükel (DH) approximation

Debye-Hükel approximated nonlinear PB to linearized form, which is correct at weak potentials that is $\psi(r) << \frac{kT}{z_i e}$, linear PB becomes

$$\nabla^2\psi = \frac{e^2}{\varepsilon\varepsilon_0 kT}\sum_i z_i^{\,2} n_i(0)\psi(r)$$

$$\nabla^2\psi = \kappa^2\psi(r) \tag{2.6}$$

Above equation is Debye-Hükel Equation. The inverse of Debye length κ

is defined as,

$$\kappa^2 = \frac{e^2}{\varepsilon\varepsilon_0 kT}\sum_i z_i{}^2 n_i(0)$$

Introducing ionic strength, I , given by

$$I = \frac{1}{2}\sum_i z_i c_i$$

κ Can be expressed as

$$\kappa = \left(\frac{2e^2 I}{\varepsilon\varepsilon_0 kT}\right)^{\frac{1}{2}}$$

The electrostatic potential around a point charge is given by (solution of equation (2.6)),

$$\psi(r) = \frac{z_i e}{4\pi\varepsilon\varepsilon_0 r}\exp(-\kappa r) \qquad (2.7)$$

Many experimental data on simple salt have been successfully interpreted by Debye-Hükel theory. For PELs, however, some assumptions made for deriving Debye-Hükel potential are very quationable. Near poly-ion where many charges are bundled together, the potential is not necessarily weak and linearization can fail. Despite of these problems most of the theoretical and simulation studies of polyelectrolytes in solution apply the Debye-Hükel potential for the modeling the interaction between charged chain segments.

2.3 Debye-Hükel Limiting Law

The long range and strength of Coulombic interactions between ions means that it is likely to be primarily responsible for the departure from the ideality in ionic solutions and to dominate all other contributions to non ideality. This domination is the basis of Debye-Hükel theory of ionic solution.

Oppositely charged ions attract each other. As a result, cations and anions are not uniformly distributed in the solution: anions are more likely to be found near cations and viceversa. Overall solution is electrically neutral but near any given ion there is an excess of counter-ions, the ions of the oppositely charge. Averaged over time, counter-ions are more likely to be found by any given ion. This time averaged, spherical haze, in which counter-ions out number ions of the same charge as the central ion, has a net charge equal in magnitude but opposite in sign to that on the central ion and is called its ionic atmosphere. The energy and therefore the chemical potential of any given central ion is lower as the result of its electrostatic interaction with its ionic atmosphere. This lowering of energy appears as difference of Gibbs energy and ideal Gibbs energy of the solution.

The model lead to result at low concentration, activity coefficient is given by,

$$\log \gamma_{\pm} = -|z_{+} z_{-}| A I^{\frac{1}{2}} \tag{2.8}$$

A=0.509 for aqueous solution at 25 °C and I= ionic strength.

DH Limiting law is corrected for some concentration range called extended DH limiting Law, given by,

$$\log \gamma_{\pm} = \frac{-|z_{+} z_{-}| A I^{\frac{1}{2}}}{1 + B I^{\frac{1}{2}}} \tag{2.9}$$

Where, B is adjustable parameter.

2.4 Debye-Hükel prediction of osmotic coefficient

Debye-Hükel theory also can be used to obtain limiting law expressions for the activity of the solvent. This is usually done by expressing activity of solvent in terms of practical osmotic coefficient. For an electrolyte solution, it is defined in general way as,

$$\phi = -\frac{\ln a_1}{M_1 \sum_{k} \nu_k m_k} \tag{2.10}$$

Where, ν_k = Number of moles of the ions produced by a solute 'k', m_k = Molality of solute, M_1= molecular weight of solvent.

For single electrolyte, (that is k=1)

$$\phi = -\frac{\ln a_1}{M_1 \nu m} \tag{2.11}$$

The osmotic coefficient is often used as the measure of the activity of solvent instead of a_1 because a_1 is nearly unity over the concentration range where activity coefficient is changing and many significant figures are required to show effect of solute concentration on activity. The activity coefficient also becomes one at infinite dilution but deviates more rapidly with concentration of solute than activity of solvent.

The osmotic coefficient and activity coefficient of solute is related in a simple manner through Gibbs-Duhem equation. Writing the Gibbs-Duhem equation in the form of activities as

$$n_1 d\ln a_1 + n_2 d\ln a_2 = 0 \qquad (2.12)$$

For binary solution containing,

$n_2 = m$ Moles of solute.

$n_1 = \frac{1}{M_1}$ Moles of solvent.

Above equation becomes,

$$\frac{1}{M_1} d\ln a_1 + m d\ln a_2 = 0 \qquad (2.13)$$

Substituting for a_1 and a_2

For solvent,

$$\ln a_1 = -M_1 \nu m \phi$$

$$d\ln a_1 = -M_1 \nu (m d\phi + \phi dm) \qquad (2.14)$$

For solute,

$$d\ln a_2 = \nu d\ln \gamma_\pm + \nu d\ln m \qquad (2.15)$$

Combining equations (2.13), (2.14),(2.15) , we get

$$d\ln \gamma_\pm = d\phi + \frac{\phi - 1}{m} dm$$

Integrating above equation between

m=0, where $\phi = 1 \text{and} \gamma_\pm = 1$

m=m, where, $\phi = \phi \text{and} \gamma_\pm = \gamma_\pm$.

$$\ln \gamma_{\pm} = \phi - 1 + \int_{0}^{m} \frac{(\phi - 1)}{m} dm \qquad (2.16)$$

This is the relation between activity coefficient and osmotic coefficient.

Knowing practical osmotic coefficient we can determine activity coefficient of solute.

2.5 Manning model

Manning has constructed a series of plausible and well-motivated assumptions, which leads to formulas for colligative properties of PEL solution (G.S.Manning, 1969). These formulas are considered as ”limiting laws” in the sense that they are derived specially for the solution of low concentration of PELs. Although it was unlikely that formulas would be generally valid as the Debye-Hükel limiting laws, which is accepted as exact for simple electrolyte solutions at low concentrations, it was hope that they would serve similar purpose to distinguish effects which dominates at low concentration from that effect which become prominent only with increasing concentration.

Following are assumptions involved in this model.

1.The real polyelectrolyte chain is replaced by an infinite line charge with density β given by equation (2.17).

2. Interaction between two or more poly-ions are neglected regardless of the ratio of polyelectrolyte concentration to that of added salt.

3.The dielectric constant is taken as that of the pure bulk solvent.

4.For dilute solution, a sufficient number of the counterions will condense on polyion to lower charge density parameter ξ to its critical value $\xi_c = \frac{1}{Z_p Z_i}$

5.Uncondensed mobile ions may be treated in the Debye-Hükel approximation.

If the contour length of polyelectrolyte is L, and if chain bears m charged groups of valance Zp, the uniform charge density is given by

$$\beta = \frac{Z_p e}{b} \qquad (2.17)$$

Where, $b = \frac{L}{m}$

For the discussion of the fourth assumption, Onsager has observed the statistical-mechanical phase integral for in infinite line charge model diverges for all values β of greater than its critical value. If ‘y’ denotes distance from line charge, then the electrostatic energy of mobile ion of valance Zi for sufficiently small values of the y, say $y \le y_0$, is given by the unscreened Coulomb interaction,

$$U_{ip} = -\frac{2Z_i e\beta}{4\pi\varepsilon\varepsilon_0}\ln y \qquad y \le y_0 \tag{2.18}$$

The contribution $A_i(y_0)$ to phase integral of the region in which ith mobile ion is within a distance y_0 of the line charge, while all other mobile ions are at a distance greater than y_0, thereby contributing finite factor $f(y_0)$, is given by,

$$A_i(y_o) = f(y_o)\int_0^{y_o}\exp(-\frac{U_{ip}(y)}{kT})2pydy = 2pf(y_0)\int y^{1+2Z_iZ_px}\,dy \tag{2.19}$$

Where,

$$x = \frac{e^2}{4pee_0kTb}$$

If ion is counterion, so that $Z_iZ_p < 0$, the integral (2.19) diverges at the lower limit for all x such that,

$$x \ge \frac{1}{Z_iZ_p} \tag{2.20}$$

In Manning model, attention is restricted to monovalent charged groups and mobile ions, so condition (2.20) becomes

$$x \ge 1 \tag{2.21}$$

The physical interpretation of divergence of the phase integral for the values of x greater than unity is that the system characterized by such values are unstable: sufficiently many counterions will condense on the line charge to reduce x to a value just less than one.

Manning’s result can be obtained by considering two separate cases, depending on whether the value of charge density parameter x is less than or greater than its critical value.

Case1 $x \leq 1$

According to the fifth assumption, the case $x \leq 1$ may be treated in the Debye-Hükel approximation. The potential $y(y)$ at distance y from the line charge (taken along the z-axis) is given by a superposition of screened Coulomb potential from infinitesimal segment of length dz.

$$y(y) = \frac{b}{4pee_0} \int_{-\infty}^{\infty} \frac{\exp(-k(y^2 + z^2)^{1/2}}{(y^2 + z^2)^{1/2}} dz$$

$$= \frac{2b}{4pee_0} \int_{1}^{\infty} \frac{\exp(-kyt)}{(t^2 - 1)^{1/2}} dt = \frac{2b}{4pee_0} K_0(ky) \qquad (2.22)$$

Where, $K_0(ky)$ is zeroth-order modified Bessel function of the second kind. If the two species, cations and anions both monovalent are present, the inverse Debye length is given by

$$k^2 = l(n_+ + n_-)$$
$$where,\ l = \frac{e^2}{ee_0 kT} \qquad (2.23)$$

The function $K_0(ky)$ has asymptotic behavior

$$K(ky) \sim -\ln ky \qquad ky \to 0$$

So that the y is allow tending zero in (2.22) the potential $y'(0)$ at the position of the line charge due to mobile ions is seen to be

$$y'(0) = -\frac{2b}{4pee_0} \ln k \qquad (2.24)$$

The term proportional to lny is the potential due to the line charge itself. The excess free energy associated with the segment dz of the line charge, can be found as

$$f_e dz = -\frac{\beta^2}{4\pi\varepsilon\varepsilon_0} \ln \kappa dz \qquad (2.25)$$

The total excess free energy F_e of the solution volume V is set equal to $N_p \int_{-\infty}^{\infty} f_e dz$ where Np is the number of polyions in the solution so that, when equation (2.17) used for β (with $|z_p| = 1$).

$$\frac{F_e}{VkT} = -\xi n_e \ln \kappa \tag{2.26}$$

Where the equation (2.19) of ξ has been used, and $b^{-1}\int_{-\infty}^{\infty} dz$ has been given the obvious interpretation as the number m of charged groups on the each polyions; equivalent concentration is

$$n_e = \frac{mN_p}{V} \tag{2.27}$$

Having obtained an expression for the excess Helmoltz free energy, the activity coefficients of the mobile ions give by

$$\ln \gamma_i = \left(\frac{\partial(F_e / VkT)}{\partial n_i}\right)_{T,V,n_{j\neq i}} = -\frac{1}{2}\xi\lambda n_e \kappa^{-2} \tag{2.28}$$

Since from (2.23), $\frac{\partial\kappa}{\partial n_i} = \frac{\lambda}{2\kappa}$. The counterion and coion concentrations can be written as

$$n_+ = n_e + n_s \tag{2.29}$$

Where n_s is the concentration of monovalent salt added to polyelectrolyte solution.

$$X = \frac{n_e}{n_s}$$

Equation (2.28) becomes

$$\ln \gamma_i = -\frac{\xi X}{2(X+2)} \qquad \text{Where} \qquad \xi \le 1 \tag{2.30}$$

The mean activity coefficient of mobile ion given by

$$\ln \gamma_\pm = (\ln \lambda_+ \ln \lambda_-)^{1/2} = -\frac{\xi X}{2(X+2)} \qquad \xi \le 1 \tag{2.31}$$

The osmotic coefficient is calculated from (2.26) with the help of the derivative ($n_i = \frac{N_i}{V}$) where N_i is number of species i)

$$\left(\frac{\partial\kappa}{\partial V}\right)_{N_i} = -\frac{\kappa}{2V} \tag{2.32}$$

Since osmotic coefficient ϕ is defined in terms of the excess part of the osmotic pressure π_e,

$$kT(\phi - 1)(n_+ + n_-) = \pi_e = -\left(\frac{\partial F_e}{\partial V}\right)_{T,N_p N_i} \tag{2.33}$$

One gets expression for osmotic coefficient as

$$\phi = 1 - \frac{\xi X}{2(X+2)} \tag{2.34}$$

Where, $\xi \le 1$

For salt free case, $n_s = 0 \text{and} X \to \infty$, the equations becomes,

$$\ln \gamma_i = \ln \lambda_\pm = -\frac{1}{2}\xi \qquad \xi \le 1 \tag{2.35}$$

$$\phi = 1 - \frac{1}{2}\xi \qquad \xi \le 1 \tag{2.36}$$

Case2 $\xi > 1$

According to the fourth assumption when the real value of the ξ is greater than unity, its effective value will be equal to one since condensed counter-ions will neutralize the fraction $(1 - \xi^{-1})$ of the poly-ion charge. Similarly, while real (stoichiometric) concentration of the counter-ions is $(n_e + n_s)$, the effective value (uncondensed counter-ions) is $(\xi^{-1} n_e + n_s)$. The stoichiometric and effective concentrations of the co-ion have the same value n_s.

The osmotic pressure of the solution is given by

$$\frac{\pi}{kT} = \phi(n_+ + n_-) = \phi(n_e + 2n_s) \tag{2.37}$$

On the other hand, since the effective concentration of mobile ions is $(\xi^{-1} n_e + 2n_s)$ and the effective charge density of poly-ion corresponds to $\xi = 1$.

$$\frac{\pi}{kT} = \phi(1, \xi^{-1} n_e)(\xi^{-1} n_e + 2n_s) \tag{2.38}$$

Where, $\phi(1, \xi^{-1} n_e)$ is the osmotic pressure of a solution whose polyelectrolytes having charge density one and equivalent concentration $\xi^{-1} n_e$, whose concentration of salt is same value n_s. The Debye-Hükel approximation to this quantity is obtained from equation (2.34) with $\xi = 1$ and $X = n_e / n_s$ replaced by $\xi^{-1} X$.

$$\phi(1, \xi^{-1} n_e) = 1 - \frac{\xi^{-1} X}{2(\xi^{-1} X + 2)} \tag{2.39}$$

Combining equation (37) and (39),

$$\phi = \frac{\frac{1}{2}\xi^{-1} X + 2}{X + 2} \tag{2.40}$$

Stoichiometric activity of the counter-ions a_+ is given by

$$a_+ = \gamma_+ n_+ = \gamma_+ (n_e + n_s) \tag{2.41}$$

Another expression for a_+ in terms of effective quantities is

$$a_+ = \gamma_+ (1, \xi^{-1} n_e)(\xi^{-1} n_e + n_s) \tag{2.42}$$

Where, $\gamma_+ (1, \xi^{-1} n_e)$ has meaning analogous to the corresponding osmotic coefficient in equation (2.37) and is obtained from (2.40),

$$\gamma_+ (1, \xi^{-1} n_e) = \exp\left[-\frac{1}{2} \frac{\xi^{-1} X}{(\xi^{-1} X + 2)} \right]$$

It follows that,

$$\gamma_+ = \frac{\xi^{-1} X + 1}{X + 1} \exp\left[-\frac{1}{2} \frac{\xi^{-1} X}{(\xi^{-1} X + 2)} \right] \tag{2.43}$$

The activity coefficient of the co-ions is given by

$$\gamma_- = \exp\left[-\frac{1}{2} \frac{\xi^{-1} X}{(\xi^{-1} X + 2)} \right] \tag{2.44}$$

The mean activity coefficient of mobile ion is given by

$$\gamma_{\pm} = \frac{\xi^{-1}X+1}{X+1}\exp\left[-\frac{1}{2}\frac{\xi^{-1}X}{(\xi^{-1}X+2)}\right] \tag{2.45}$$

For the salt free solution.

$$\gamma_{+} = \xi^{-1}e^{-1/2} \tag{2.46}$$

$$\gamma_{-} = e^{-1/2} \tag{2.47}$$

And

$$\phi = \frac{1}{2\xi} \tag{2.48}$$

Manning model results are in quantitative agreement with experimental measurements. Comparison of the model value with experiment is shown in figure (2.1).

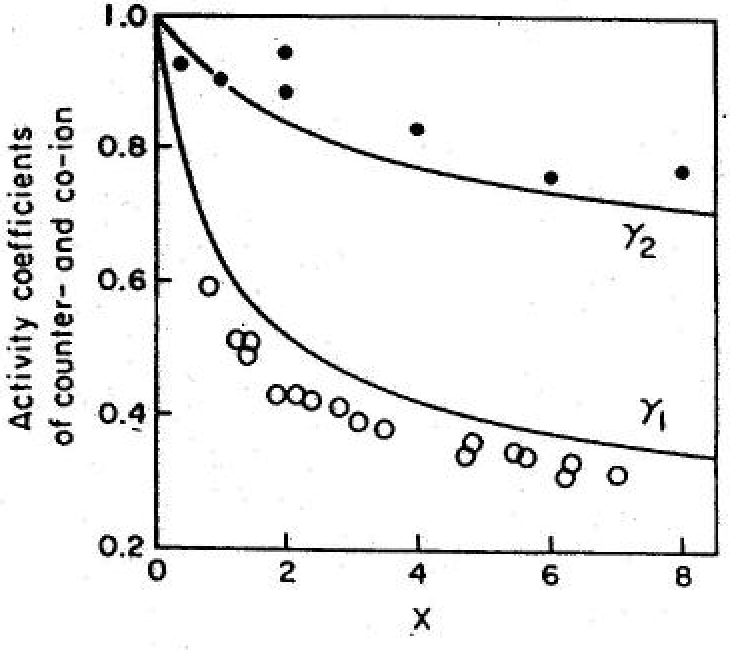


Figure 2.1.Comparision of counter ion and co-ion activity coefficient with experimental data

Manning model assumes that the polyion is in maximum extension at infinite dilution and distance between the adjacent charged groups is calculated on basis of this assumption. But as the concentration of added salt is increased, flexibility of polymer chain increases. So Manning model does not provide the correct limit for added salt systems. Hence the formulas, which contains no adjustable parameters, are “limiting laws” but in a restricted sense and the agreement of the model with experiment is usually found to be quantitative.

2.6 An excess Gibbs free energy model

Nagvekar and Danner have (M. Nagvekar and R.P.Danner, 1989) developed an excess Gibbs free energy model for polyelectrolyte solutions. The key feature of the model is to express the excess Gibbs free energy as the sum of the contributions from long rang and short range interactions. The limiting laws of Manning are used to account long-range interactions and a local composition model of the Non-Random Two Liquid (NRTL) type is used for short-range interactions. This type of approach has been used previously for simple electrolyte solutions. Chen used the non-random two-liquid (NRTL) model for the short-range interactions (Chen *et al.*, 1982).

Thus the molar excess Gibbs free energy is given by

$$\frac{G_e^*}{RT} = \frac{G_e^{L*}}{RT} + \frac{G_e^{S*}}{RT} \qquad (2.49)$$

Where, superscript L refers to the long-range interaction contribution from Manning model and superscript S for the short –range contribution from NRTL model. The asterisk indicates that the model is an unsymmetrical model. For activity coefficient it becomes,

$$\ln\gamma^* = \ln\gamma^{L*} + \ln\gamma^{S*} \qquad (2.50)$$

Nagvekar and Danner have been used same approach used by Chen and Evas for simple electrolyte systems.

The underlying assumption of any local composition mode is that, because of the specific interactions between the various species in a given system, the local concentration of any species is different from its bulk concentration. Thus, the first step in development of the model is establishment of some form of relationship between the local and bulk concentrations. For electrolyte and polyelectrolytes, it is also necessary to define an effective overall concentration before defining local compositions.

The effective mole fraction for species i is defined as $X_i = x_i Z_i$ where x_i is the overall mole fraction, Z_i is the absolute value of the valance for ionic species and unity for molecules. The effective local mole fraction, X_{ij} and X_{ii}, of species j and i around a central species i is related by

$$\frac{X_{ji}}{X_{ii}} = \frac{X_j}{X_i} G_{ji} \tag{2.51}$$

Where,

$$G_{ij} = \exp(\alpha_{ji} \tau_{ji}) \tag{2.52}$$

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT} \tag{2.53}$$

Here, α_{ji} is the non-randomness factor while g_{ji}, g_{ii} are the energies of the interaction between the j-i and i-i pairs of species. Similarly, the effective local mole fraction of the species j and k around a central species i is related by,

$$\frac{X_{ji}}{X_{ki}} = \frac{X_j}{X_k} G_{ji,ki} \tag{2.54}$$

$$G_{ij,ki} = \exp(\alpha_{ji,ki} \tau_{ji,ki}) \tag{2.55}$$

$$\tau_{ji,ki} = \frac{(g_{ji} - g_{ki})}{RT} \tag{2.56}$$

For a polyelectrolytes system with no salt added, three different species can be identified-the solvent molecule, the counterions, and the repeating units on the polyelectrolyte chain. In what follows, m refers to the solvent, 1 refers to the counterion, and p refers to the charged repeat unit on the polyelectrolyte.

As shown in figure (2.2), there are three types of cells in this system. The first type consists of a solvent molecule (m) as the central species surround by other solvent molecules, counterion (1), and the polyelectrolyte repeat units (p).

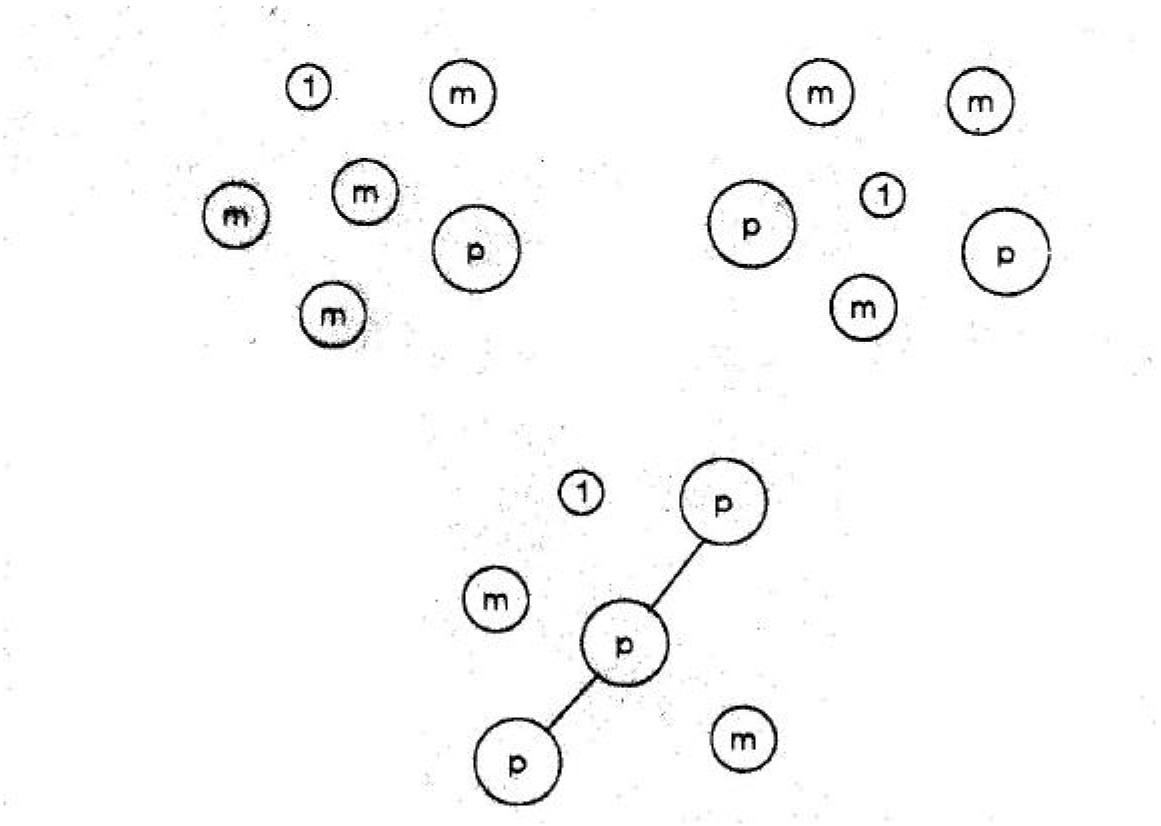


Figure (2.2). Three types of cells in polyelectrolyte solutions without added salts

On second type of cell consist of a counter ion as the central species surround by solvent molecules, and polyelectrolyte repeat units but no counterions due to like ion repulsion. Similarly, a cell with a repeat unit as the central species would be surrounded by the solvent molecules, the counterions, and the two adjacent repeat units from other polyelectrolyte chains. For a simple electrolyte, Chen and Evans have assumed that for the cells with the central solvent molecule the distribution of cations and anions around the solvent molecule is such that the net local ionic charge is zero (Chen *et al.*, 1982). But this assumption has not been used in the Nagvekar and Danner for two reasons. First, in the case of polyelectrolyte with a large number of charges, it appears to be too strict. Second, the number of parameters is halved since the binary parameters for cations and anions are equal as a consequence of this assumption.

For the local composition model, Nagvekar and Danner found the symmetric excess Gibbs free energy expression, which is for the completely generalize case of multicomponent system with one or more solvent and any number of polyelectrolyte and simple salts. The expression can be normalized to infinite dilution Reference State, which result in the expression for the unsymmetric excess Gibbs free energy as follows,

$$\frac{G_e^{S*}}{RT} = \frac{G_e^{S}}{RT} - \sum_c \ln \gamma_c^{s\infty} - \sum_a \ln \gamma_a^{s\infty} \tag{2.57}$$

Where, $\gamma_c^{s\infty}$ and $\gamma_a^{s\infty}$ are the infinite dilution activity coefficient of cations and the anions. These can be determined from the definition of the activity coefficient,

$$\ln \gamma_i = \frac{\partial(n_T G_e / RT)}{\partial n_i} \tag{2.58}$$

Using the condition that the concentration of solvent tends to unity while the concentration of all ionic species tends to zero.

Nagvekar and Danner determined the expression for the activity coefficient and the osmotic coefficient for polyelectrolytes with and without added salt.

2.6.1 Polyelectrolyte solution without added salt

The counterion activity coefficient is given by

$$\ln \gamma_1^{s*} = \frac{X_m^2 G_{1m}\tau_{1m} + X_m X_p G_{1m} G_{1p}(\tau_{1m} - \tau_{1p})}{(X_1 G_{1m} + X_p G_{pm} + X_m G_{mm})} + \frac{X_m G_{m1,p1}\tau_{m1,p1}}{(X_p + X_m G_{m1,p1})} - \frac{X_m X_p G_{mp,1p}\tau_{mp,1p}}{(X_1 + X_m G_{mp,1p})^2}$$
$$- G_{1m}\tau_{1m} - \tau_{m1,p1} \tag{2.59}$$

Above equation is only due to the short-range interactions. The contribution due to long range is given by Manning model and depends upon the value of charge density parameter,

Hence

For $\xi < \xi_c$

$$\ln g_1^{s*} = -\frac{1}{2}|Z_1|x + \frac{X_m^2 G_{1m} t_{1m} + X_m X_p G_{1m} G_{1p(t_{1m}-t_{1p})}}{(X_1 G_{1m} + X_p G_{pm} + X_m G_{mm})} + \frac{X_m G_{m1,p1} t_{m1,p1}}{(X_p + X_m G_{m1,p1})} \quad \text{For } \xi > \xi_c$$
$$- \frac{X_m X_p G_{mp,1pt_{mp,1p}}}{(X_1 + X_m G_{mp,1p})^2} - G_{1m} t_{1m} - t_{m1,p1}$$

(2.60)

$$\ln g_1^{s*} = -\frac{1}{2} - \ln|Z_1|x + \frac{X_m^2 G_{1m} t_{1m} + X_m X_p G_{1m} G_{1p(t_{1m}-t_{1p})}}{(X_1 G_{1m} + X_p G_{pm} + X_m G_{mm})} + \frac{X_m G_{m1,p1} t_{m1,p1}}{(X_p + X_m G_{m1,p1})} \tag{2.61}$$
$$- \frac{X_m X_p G_{mp,1pt_{mp,1p}}}{(X_1 + X_m G_{mp,1p})^2} - G_{1m} t_{1m} - t_{m1,p1}$$

The osmotic coefficient of a solution is related to activity of solvent through osmotic pressure. In general:

$$\pi = \phi RT \sum \nu_i m_i = \frac{RT}{V_m} \ln \gamma_m \tag{2.62}$$

Thus osmotic coefficient is given by

$$\phi = -\frac{1}{V_m \sum_i \nu_i m_i} \ln \gamma_m \tag{2.63}$$

Where, γ_m is the activity coefficient of the solvent, V_m is the molal volume of the solvent.

Hence osmotic coefficient is given by

$$\phi = \phi^L - \frac{1}{V_m \sum_i \nu_i m_i} \ln \gamma_m \tag{2.64}$$

ϕ^L is the osmotic coefficient from the Manning model.

Thus for $\xi \le \xi_c$

$$\phi = 1 - \frac{1}{2}|Z_1|\xi - \frac{1}{V_m \sum_i \nu_i m_i} \ln \gamma_m \tag{2.65}$$

For $\xi > \xi_c$

$$\phi = \frac{1}{2}|Z_1|\xi - \frac{1}{V_m \sum_i \nu_i m_i} \ln \gamma_m \tag{2.66}$$

With the solvent activity coefficient from local composition model given by

$$\ln \gamma_1^{S*} = \frac{X_1 G_{1m} \tau_{1m} + X_p G_{pm} \tau_{pm}}{(X_1 G_{1m} + X_p G_{pm} + X_m G_{mm})} - \frac{X_m X_1 G_{1m} \tau_{1m} + X_p X_m G_{pm} \tau_{pm}}{(X_1 G_{1m} + X_p G_{pm} + X_m G_{mm})^2} + \frac{X_1 X_p G_{m1,p1} \tau_{m1,p1}}{(X_p + X_m G_{m1,1p})^2}$$
$$+ \frac{X_1 X_p G_{mp,1p} \tau_{mp,1p}}{(X_1 + X_m G_{mp,1p})^2}$$

2.6.2 Polyelectrolyte solution with added salt

The short-range interactions are described by the local composition model, but for the long-range interactions the Manning model cannot be used in the simple electrolyte solutions. Since the local composition model does not assume the local electroneutriality around the central solvent molecule, the interaction parameter of the Chen *et al.*, cannot be used. Thus, before applying the model to polyelectrolyte solution with added salts, it is necessary to obtain the interaction parameters for electrolyte systems. In this model original Debye-Hükel model was chosen to account the long-range interaction. This choice made primarily to be consistent with Manning model for polyelectrolyte solutions as one of the assumptions of the Manning model is that the uncondensed mobile ions are treated in the Debye-Hükel approximation.

For the dilute solutions containing a single solvent and single electrolyte, the Debye-Hükel model gives the following expression for the long-range interaction activity coefficient either of the ionic species in the solution.

$$\ln \gamma_+^{L*} = \ln \gamma_-^{L*} = -A \,|\, Z_- Z_+ \,|\, \sqrt{I} \qquad (2.67)$$

Where A is the Debye-Hükel parameter and I is the ionic strength of polyelectrolyte solution. Thus, after accounting for short-range interaction, the activity coefficient of cationic species is given by

$$\ln g_+^* = -A \,|\, Z_+ Z_- \,|\, \sqrt{I} + \frac{X_m^2 G_{1m} t_{1m} + X_m X_p G_{1m} G_{1p(t_{1m} - t_{1p})}}{(X_1 G_{1m} + X_p G_{pm} + X_m G_{mm})} + \frac{X_m G_{m1,p1} t_{m1,p1}}{(X_p + X_m G_{m1,p1})}$$
$$- \frac{X_m X_p G_{mp,1p t_{mp,1p}}}{(X_1 + X_m G_{mp,1p})^2} - G_{1m} t_{1m} - t_{m1,p1} \qquad (2.68)$$

The local composition model has four binary interaction parameters per polyelectrolyte solution. These parameters were obtained from experimental data for electrolyte-solvent and electrolyte-polyelectrolyte systems. Non randomness factor was set equal to 0.20 or 0.33.The results of correlation for osmotic coefficient and activity coefficient were compared with experimental measurement of the NaPSS. The model has been used to correlate the data for poly-vinyl sulfate, polystyrene sulfonate, and polymethylstyrene sulfonate with number of monovalant and divalent cations as counterions. Hence it is general model in the sense that it can correlate data for multi-component system with one or more solvents and any number of polyelectrolyte and simple salt.

The model cannot be used as a predictive model for polyelectrolyte solution with added salt based on interaction parameters obtained from polyelectrolyte and simple electrolyte solution only. Additional interaction parameters must be determined from the data for polyelectrolyte solution with added electrolytes.

Chapter 3

Vapor Pressure Osmometer and Isothermal titration calorimeter.

In this chapter we have discussed the overview of the vapor pressure osmometry and isothermal titration calorimeter.

3.1.1 Osmosis

If two solutions of different concentration are separated by a semi-permeable membrane which is permeable to the smaller solvent molecules but not to the larger solute molecules, then the solvent will tend to diffuse across the membrane from the less concentrated to the more concentrated solution. This process is called osmosis. Osmosis is a reversible thermodynamic process. That is, the direction of water flow through the membrane can be reversed at any moment by proper control of the external pressure on the solution.

3.1.2 Osmolality and Osmotic Pressure

Osmolality is a concentration scale to express total concentration of solute particles directly related to any of the four colligative properties. To calculate osmolality it is the total particle concentration that matters. It depends on solute dissociation. It is dependent of temperature variation. It also depends on interaction between the dissolved particles or to be more precise depends on the non-ideality of the solution. Osmotic concentration or osmolality is, by definition, an expression of the total number of solute particles dissolved in one kilogram of solvent without regard for particle size, density, configuration, or electrical charge. Osmotic pressure (π) is a colligative property of a solution, and thus depends on molar concentration of the solute but not directly on the size of the molecules for a specified molar concentration. The underlying principle is that small molecules of solvent can pass through the pores of the semi permeable membrane, which separate the solution of the polymer from the pure solvent. The membrane is impenetrable by the molecules of the polymer. Thus, if allowed to, solvent will pass through the membrane from the pure solvent to dilute the solution. This dilution continues until the increased pressure in the solution compartment counterbalances the tendency toward further dilution. At this point, the chemical potential of the solvent is the same in both compartments and the pressure difference between the compartments is the osmotic pressure, π. So the osmotic pressure is defined as the difference in hydrostatic pressure between the solvent side and the solution side at which the net solvent flow is zero. Osmotic pressure is a common way to measure the chemical potential of polymer solution. The osmotic pressures were measured by different ways:

(i) Measured directly by determining the pressure required on the solution side of a semipermeable membrane to prevent water flow into that solution.

(ii) Measured through the vapor pressure of the solutions using a vapor pressure osmometer.

(iii) Measured using light scattering.

3.2 Vapor Pressure Osmometry

3.2.1 Design and Measurement Principle

The vapor pressure osmometer has been designed to exactly measure the total osmolality of physical fluids and to determine the average molecular mass of polymers in aqueous or organic solutions.

Two thermistors are part of a Whetstone bridge. Differential measurements of currents due to temperature differences at the thermistors are accomplished. The thermistors are located in a cell where the gas phase is saturated with solvent vapor. The cell temperature is electronically controlled and maintained with an accuracy of $\pm 10^{-3}\ {}^{0}$C. One drop of the same pure solvent located on either thermistor represents a zero temperature difference or equilibrium of the measurement system.

The vapor pressure of the any solution containing solutes is lower than the vapor pressure of a pure solvent. Hence, replacing one drop of pure solvent with one drop of solution leads to a vapor pressure difference between the two droplets. This difference however is compensated as follows: Some vapor of the pure solvent that saturates the gas phase condenses on the droplet of the solution until the vapor pressures are balanced. The increasing vapor pressure of the solution droplet leads to an increase of temperature. Once equilibrium is reached a constant measurement value is achieved. This particular ΔT between the thermistors is always proportional to the number of particles or number of moles dissolved in the solution. Thus either concentrations or the molecular mass can be determined, in the later case however only if sample concentrations are known.

The measuring cell is placed in a thermostat consisting of an anodized aluminum block. The two thermistors immerse into a glass beaker enriched with vapor. The operating temperature can be selected in the range between 20 and 130^0C. The cell is sealed with a circular cell cover and Teflon gasket. The head of the osmometer has 6 directional channels where the syringes can be introduced to attach droplets to the thermistors. The syringes are introduced by slightly moving them downward into individual channels. The needles of the syringes are equipped with springs. Direct contact with the probes should be avoided. The syringe ports are numbered from 1 to 4 for the solutions, the 2 ports without numbers are to provide both thermistors with pure solvent drops.

The sample ports are aligned with the left thermistors. The head of the osmometer will also be thermostatted. To preheat the syringes it is recommended to set the head temperature 2^0C higher than in the measuring cell. This value of experience provides an excellent screening against outside temperature variation and a minimum influence of cold syringes on the temperature in the cell. The elements of the measuring cell as shown in the Figure 3.1.

3.2.2 Dropping Techniques

Basically there are two types of dropping techniques, one is exchange the sample droplet only and the other one is exchange the sample and the solvent also. We can choose the desired technique according to our needs. It is important to decide for one of the techniques and constantly apply it. Measurement of new solvent and new sample droplets results in shorter measurement times.

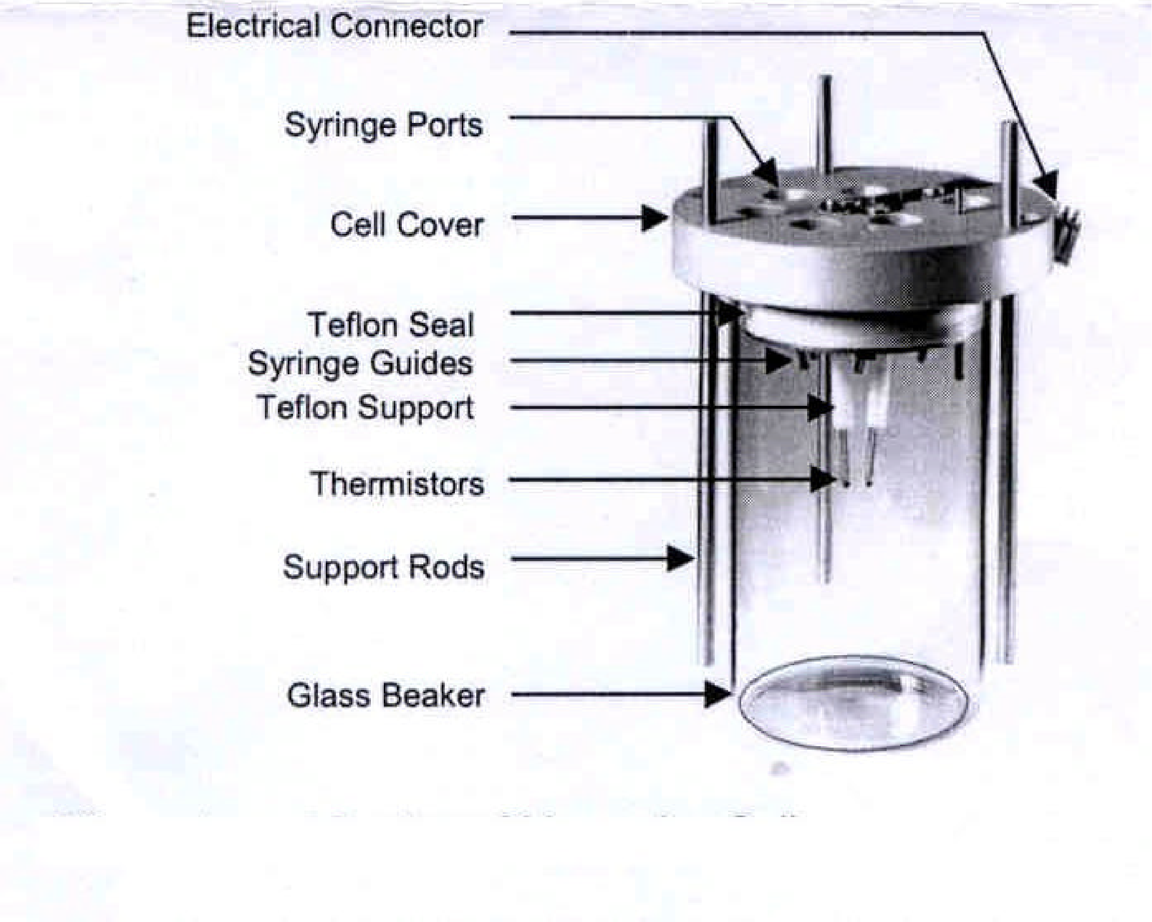


Figure 3.1. Elements and Design of measuring cell

3.2.3 Measuring new solvent and new sample droplets

To determine samples with different concentrations it is recommended to measure the samples in an order of increasing concentrations. To exchange both droplets in every measurement proceeds as follows:

Apply the sample droplet - The signal indicates a positive overload, shown as a 1 in Fig. 3.2. Apply the solvent droplet - The signal indicates a negative overload, shown as a 2 in Fig. 3.2.A constant measurement value is achieved when the thermal equilibrium is reached and the signal stops to increase see 3 in Fig. 3.2.The pattern of the signal may resemble graphs given in Fig. 3.2.

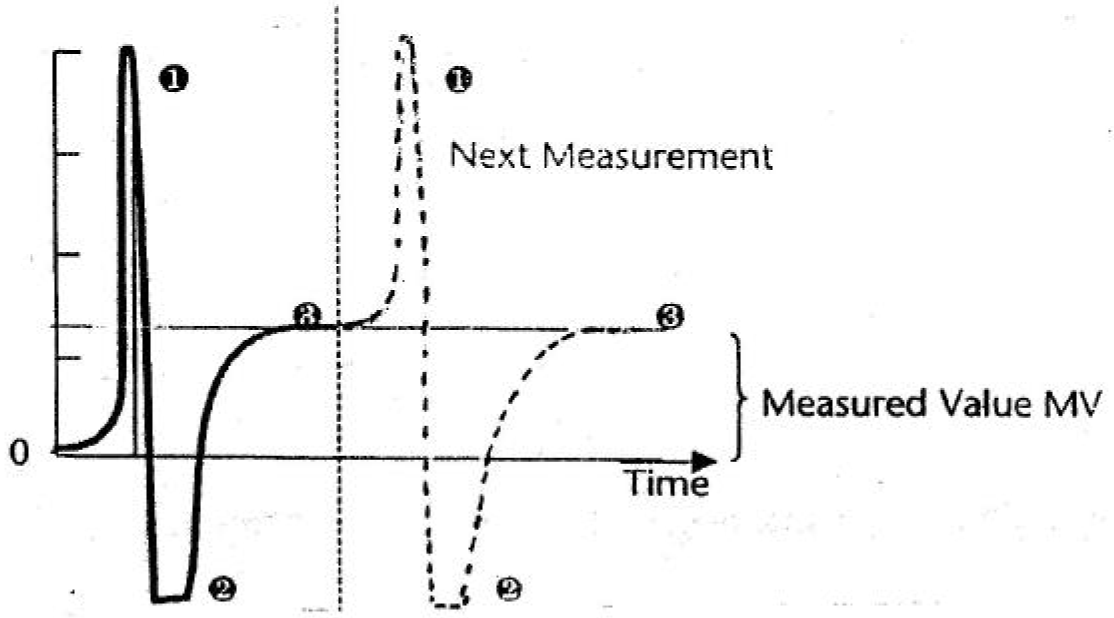


Figure 3.2. Schematic Osmogram for a two droplets exchange

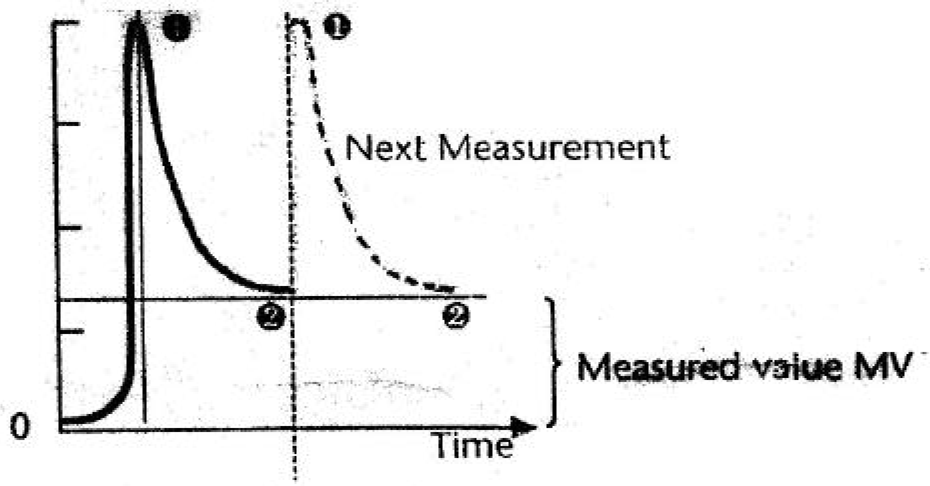


Figure 3.3. Schematic Osmogram for a single droplet exchange

3.2.4 Exchanging the sample droplet only

Apply a new sample droplet - The signal indicates a positive overload, see 1 in Fig. 3.3.A constant measurement value will be reached when the signal decreases until thermal equilibrium is reached, see 2 in Fig. 3.3.The pattern of the signal may resemble graphs given in Fig. 3.3.

3.2.5 Required Stabilization Time

Stabilization time is defined as the time interval required for the vapor pressure stabilization at the selected cell and head temperatures. Stabilization time begins when the present temperatures are roughly reached and the respective values in the display stop flashing.

3.2.6 Determination of water activity

In a solution, the chemical potential of solvent μ_1, is related to its activity by,

$$\mu_1 - \mu_1^0 = RT \ln a_w \qquad (3.1)$$

Where superscript, ^{0} represents pure solvent.

Expressing the chemical potential of solvent in terms of osmotic pressure following equation,

$$\mu_1 - \mu_1^0 = -\Pi V_m \qquad (3.2)$$

Combining the last two equations, we obtain following relation between solvent activity and osmotic pressure

$$\Pi V_m = -RT \ln a_w \qquad (3.3)$$

$$\ln a_w = \frac{-\ \mathbf{V_m}\Pi}{RT}$$

$$\ln a_w = \frac{-\ \mathbf{V_m}\rho\Pi}{\rho RT}$$

$$\mathbf{\ln a_W} = \frac{\mathbf{M \times MV}}{1000 \times \mathrm{Kcali}} \qquad (3.4)$$

Where, a_w is activity of water, M is molecular weight of water, MV is measured value,
Kcali is Calibration constant and ρ=Density

Measuring osmolality of solution using Vapor pressure osmometer, we can calculate water activity using equation (3.4)

3.2.7 Determination of the total osmolality of physical fluids

When determining the total osmolality of physical fluids, the measurement values are always proportional to the number of osmotically active particles within the measured fluid. For calibration the vapor pressure osmometer one solution of a standard with a known osmolality has been measured by the slope of the regression curve defined by the origin of the graph and the value K_{calib} unit is kg/mOsmol. A commonly used standard is an aqueous solution of NaCl with 400 mOsmol/kg.

$$K_{calibrated} = MV/c \qquad (3.5)$$

The osmolality of an unknown sample can be calculated with

$$C\ (mOsmolal/kg) = MV/\ K_{calib} \qquad (3.6)$$

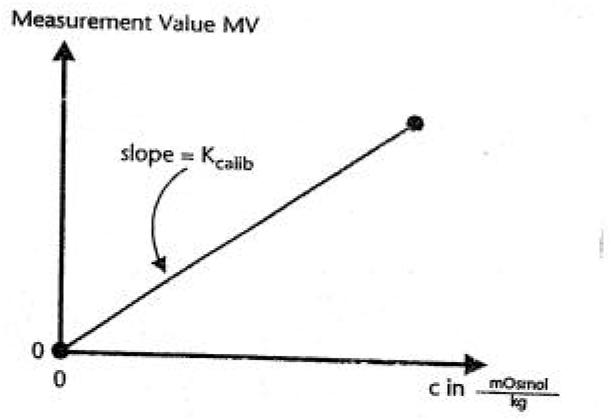


Figure3.4. Calibration Graph for the vapor pressure osmometer

3.3 Importance of water activity

Using thermodynamic properties like activity or chemical potential of polymer molecules in solution, one can obtain various properties of polymer in solution, like adsorbed amount, interfacial configuration etc. using a proper model. Osmometry is a powerful method for the measurement of above thermodynamic properties. Some applications of activity are discussed below.

3.3.1 Measurement of Interaction Parameter

Flory interaction parameter gives the interaction energy between the polymer and the solvent in which it is dissolved. This parameter is important in adsorption studies as it decides whether the given polymer prefers bulk than the interface. The relation between Flory interaction parameter and activity of solvent is given by,

$$\ln a_w = \ln\varphi_1 + (1-1/r_2)(1-\varphi_1) + \chi(1-\varphi_1)^2 \qquad (3.7)$$

Where, a_w is the activity of the solvent, φ_1 is the volume fraction of the solvent, r_2 is the number of segment of polymer defined as the molar volume of polymer divided by the molar volume of solvent and χ is the Flory interaction parameter.

From the above relation between second virial coefficient, the interaction parameter (χ) between the polymer and solvent can be found out. For example, for the study of polystyrene- cyclohexane system, polystyrene-carbon tetra chloride systems, osmometry can be used as a powerful tool to measure the interaction parameter.

In systems, where there is hydrogen bond interaction between polymer and solvent the above equation is not valid. An example is polyethylene oxide-water system. In that case one more term, a hydrogen bonding term, is to be added to the interaction parameter.

3.3.2 Adsorption Studies

Determination of activity can be used in adsorption studies. When a polymer gets adsorbed from the solution, its concentration in the solvent will reduce till the chemical potential of that component in both phases becomes equal. At the same time the activity of the solvent will increase as the polymer goes towards the interface. Therefore difference in activities of solvent before and after adsorption can be related to the amount of polymer adsorbed provided the difference is large.

3.3.3 Aggregation and micellisation

When a polymer is dissolved in a solvent, activity of latter is reduced. This reduction is linear with respect to concentration of polymer till polymer aggregation occurs. At that point, the slope of the plot of activity verses concentration will show an abrupt change. This change can be related to phase separation and aggregation of the polymer.

3.3.4 Degree of dissociation of polyelectrolytes

For strong polyelectrolytes, like sodium polystyrene sulphonate, which dissociate completely in solution, the osmotic pressure is related to polymer concentration by the following equation,

$$\pi/c = RT\,(1+rz)/\,M_n \tag{3.8}$$

Where r is the chain length and Z is the valency of the ionogenic group on the repeat unit. Weak polyelectrolytes, such as, poly acrylic acid do not dissociate completely. For this, the above equation needs to be modified to the following form.

$$\pi/c = RT\,(1+r\alpha z)/\,M_n, \tag{3.9}$$

Where α is the degree of dissociation. So equation (3.9) can be used to determine the degree of dissociation of weak polyelectrolytes.

3.3.5 Free energy of dilution of polyelectrolytes

Free energy of dilution, $\Delta G(m \text{ to } m_1)$ is defined as the change of free energy accompanying the dilution of which contains one monomole of the solute from monomolality m to some reference monomolality m_o. Free energy of dilution of a hypothetical uncharged polyelectrolyte solution can be obtained from the osmometric data as given below

$$\Delta G_D(m_1 \rightarrow m_2) = RT \ln \frac{m_0}{m} + RT \int_{m_0}^{m} (1 - \phi) \; d \ln m \qquad (3.10)$$

Where ϕ is the osmometric coefficient.

From the free energy of dilution, enthalpy and entropy of dilution can be calculated using suitable relations.

3.3.6 Counter-ion condensation on polyelectrolytes

Complete dissociation of a polyelectrolyte in to poly ions and counter ions is not seen in most of the polyelectrolytes. This is because of counter-ion condensation on the poly ion to reduce its charge density to a particular value. The extend of counter –ion condensation is given by a factor called osmotic coefficient, ϕ. Osmotic coefficient can be measured using vapour pressure osmometry. The temperature difference between the solution and the pure solvent, ΔT in osmometer is related to osmotic coefficient by the following relation.

$$\Delta T = k\, v\, \phi\, m \qquad (3.10)$$

Where v is the number of particle each molecule gives in solution and m is the molality of the solution. The constant k can be measured a solution with known osmotic coefficient.

3.4 Isothermal titration calorimeter

3.4.1 Principle of microcalorimetry

Calorimetry is the science of heat. The rate of heat evolution in the reaction vessel (rate of heat change, "thermal power") is $P = dQ/dt$ and is measured in units of watt (W). Part of the heat is exchanged with the surroundings, and part of it is contained in the reaction vessel. The sum of both is equal to rate of the heat change

$$P = dQ/dt = \Phi + C\, dT_{sample}/dt \qquad (3.11)$$

Where F is the heat flow (rate of heat exchange) between the reaction vessel and the surroundings. The term CdT/dt represents the rate of heat accumulated in the reaction vessel. C is the heat capacity of the sample and reaction vessel system (including part of the measuring sensors), and dT_{sample}/dt is the rate of change of the temperature of the reaction vessel. The heat flow, F, exchanged with the surrounding is directly proportional to the temperature difference between the reaction vessel and the surrounding

$$F = k \cdot (T_{sample} - T_{sur}) \tag{3.12}$$

k is the heat exchange coefficient between reaction vessel and the surrounding. By combining the two equations above, the rate of heat change, P, in the sample is related to the temperatures in a calorimetric system as given by equation (3.13)

$$P = k \cdot (T_{sample} - T_{sur}) + C \cdot dT_{sample}/dt \tag{3.13}$$

The ratio between the heat capacity and the heat exchange coefficient is the time constant of the calorimeter

$$t = C / k \tag{3.14}$$

By integrating equation (3.11) the heat quantity evolved in the reaction vessel, Q, can be determined.

$$Q = \int P = \int_{\text{start}}^{\text{end}} \phi . dt + C . \Delta T \tag{3.15}$$

3.4.2 Isothermal Titration Calorimetry

With ITC one measures directly the energetics (via heat effects) associated with reactions or processes occurring at constant temperature. Experiments are performed by titration of a reactant into a sample solution containing the other reactant(s) necessary for reaction. After each addition, the heat released or absorbed as a result of the reaction is monitored by the isothermal titration calorimeter. Thermodynamic analysis of the observed heat effects then permits quantitative characterization of the energetic processes associated with binding reaction. Isothermal microcalorimetry is a thermodynamic technique for monitoring any chemical reaction initiated by the addition of binding component, and has become the method of choice for characterizing biomolecular interactions. When substance bind, heat is either generated or observed. Measurement of this heat allows the very accurate determination of binding constants, reaction stoichiometry, enthalpy and entropy. ITC is routinely used to study all types of binding reactions including antigen-antibody, protein-ligand, protein-protein, DNA-drug and receptor-target, amongst others. Isothermal calorimetry is characterized by the incorporation of a peltier cooler and variable-rate heater in the reaction vessel configuration. The peltier cooler cools the vessel at a constant rate and the heater is pulsed as needed to maintain the vessel and its contents at a constant temperature. When exothermic reaction occurs, heat is produced and a lower heater pulse rate is required to balance the cooling effect of the peltier device. Conversely, for an endothermic reaction, a higher pulse rate is required to balance the energy effects of the reactions and the peltier cooler. The amount of heat produced by a reaction is determined by observing the time that the heater has to remain on to balance the peltier cooler and comparing this time to heater requirements during base-line conditions.

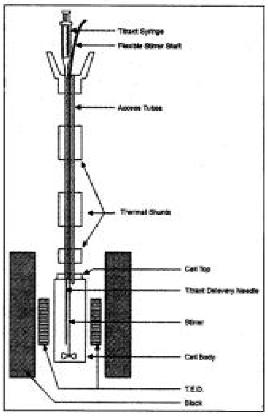


Figure 3.5. Diagram of ITC cell

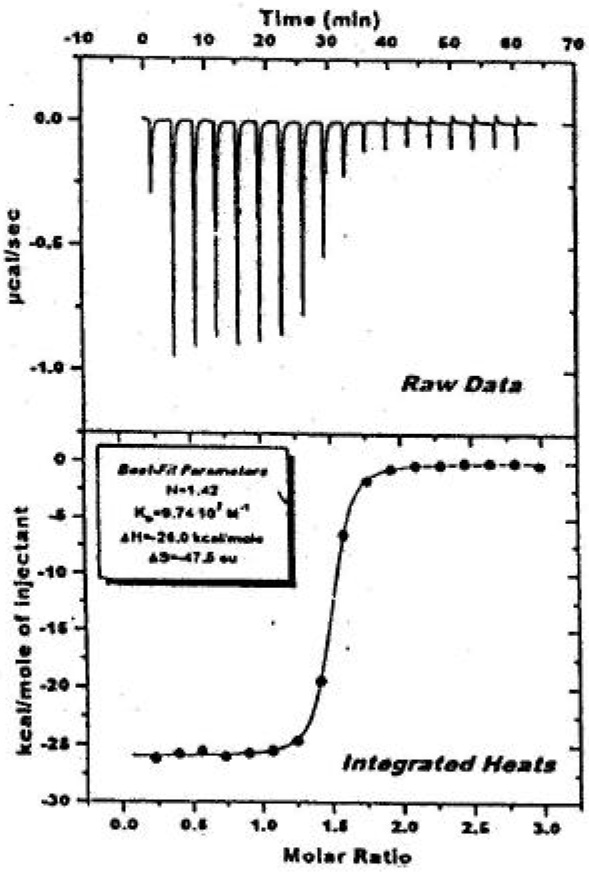


Figure 3.6. Representative data from an ITC experiment

3.4.3 Fundamental principle of ITC operation

Detection of heat effects in this isothermal calorimeter is accomplished by use of semiconductor thermopiles interposed between the titration cells and a heat sink (a large metal mass in thermal equilibrium with a thermostatted water bath). Two titration cells reside in the calorimeter assembly; one acts as the reference and the other as the sample titration cell. When the ITC experiment is being performed, the reference cell contains water only and the sample cell contains water plus the reactant to which the injected material will be titrated. Prior to beginning the experiment, the instrument's injection mechanism is filled with titrant, the titration cells are filled with the material to be titrated, and the calorimeter is equilibrated to the desired temperature such that all components of the instrument (i.e., titration cells, heat sink, and thermostatted water bath) have come to thermal equilibrium relative to each other. Identical injections of reactant are then introduced into both mechanically stirred titration cells by a dual-injection mechanism. The contents of the reference cell exhibit heat effects arising from injection and dilution of the reactant being titrated. The contents of the sample cell exhibit these same heat effects in addition to that associated with the reaction under study. Dual-injection isothermal titration calorimeters compensate in real time for both the heat effects arising from dilution of the injected reactant into the sample and for any mechanical heat effects arising from injection, yielding the heat of reaction of interest directly. The titration cell compartments are constructed to permit heat flow between the titration cells and the heat sink only through the thermopile thermal detectors. The output of the thermopiles, an electrical potential, is directly proportional to the temperature difference across the faces of the thermopiles. This temperature difference, in turn, is proportional to the thermal power being exchanged between the titration cell and heat sink. In the absence of power compensation, the time integral of this rate of heat transfer is the total heat of reaction induced in the respective titration cells as a result of injection.

3.4.4 Analysis of ITC data

In ITC, a syringe containing a 'ligand' solution is titrated into a cell containing a solution of 'macromolecule' at constant temperature (Figure 3.5). As the two materials interact, heat is released or absorbed in direct proportion to the amount of binding that occurs. As the macromolecule in the cell becomes saturated with added ligand, the heat signal diminishes until only background heat of dilution is observed. The area underneath each peak (Figure 3.6, top panel) is equal to the total released for that addition. When this integrated heat is plotted against the molar ratio of ligand added to macromolecule in the cell, a complete binding isotherm for the interaction is obtained (Figure3.6, bottom panel). The function of many biological systems is modulated by ligand binding (e.g., binding of hormones or toxins to their target receptors, allosteric or feedback control of enzymes or other functional proteins, signal peptide membrane interactions, and protein nucleic acid interactions). Characterization of the energetics of such processes may be accomplished by ITC experiments. Upon binding of a ligand to macromolecule (e.g., protein) or macromolecular assembly (e.g., multi subunit protein or membrane systems), heat will released or absorbed accompanying the binding event (the enthalpy of ligand binding). The heat effects associated with each addition ligand represent the experimentally observed response in an ITC experiment. For each injection, the heat released or absorbed is given by

$$q = V\Delta H\Delta[L_B] \qquad (3.16)$$

Where q is the heat associated with the change in bound ligand concentration, $\Delta[L_B]$ is the change in bound ligand concentration, ΔH is the enthalpy of binding (mol ligand)$^{-1}$, and V is the reaction volume

Because q is directly proportional to the increase in ligand bound resulting from each injection, its magnitude decreases as the fractional saturation of the system is titrated stepwise to completion. The total cumulative heat released or absorbed is directly proportional to the total amount of bound ligand as

$$Q = V\Delta H\sum\Delta[L_B] = V\Delta H[L_B] \qquad (3.17)$$

Where Q is the cumulative heat and $[L_B]$ is the concentration of bound ligand. Evaluation of calorimetric titration data as either individual or cumulative heat requires consideration of the heat evolved or absorbed as a function of total ligand added, or the total ligand concentration. Therefore, in the analysis of experimental data, the binding equations must be expressed in terms of individual or cumulative heat released or absorbed as a function of total ligand concentration because these are the quantities experimentally known.

The most widely used theoretical framework for the analysis of binding data in biology is the so-called Multiple Sets of Independent Binding Sites model. As expressed in equation (3.6), the heat associated with the binding reaction is directly proportional to the concentration of bound ligand, $[L_B]$. For a system exhibiting multiple sets of independent binding sites, the concentration of ligand bound to each set is given by

$$[L_{B,i}] = [M]\frac{n_i K_i [L]}{1 + K_i [L]} \tag{3.18}$$

Where $[L_{B,i}]$ is the concentration of ligand bound to binding sites of set i, [M] is the total concentration of macromolecule available for binding ligand, K_i is the intrinsic site association constant for binding sites of set i, n_i is the number of binding sites of set i on each macromolecule M, and [L] is the concentration of free ligand.

The cumulative amount of heat released or absorbed as a result of ligand binding is given by the sum of heats corresponding to each set as

$$\begin{aligned} Q &= V\sum_i \Delta H_i [L_{B,i}] \\ &= V[M]\sum_i \frac{n_i \Delta H_i K_i [L]}{1 + K_i [L]} \end{aligned} \tag{3.19}$$

Where H_i is the enthalpy of binding to binding sites of set i. This equation can be expressed in terms of the total ligand concentration by way of mass conservation expression

$$[L_T] = [L_B] + [L] \tag{3.20}$$

Where $[L_T]$, $[L_B]$, and [L] represent the total, bound, and free ligand concentrations, respectively). However, the independent variable in ITC experiments is the total ligand concentration, $[L_T]$. By recognizing that $[L_B] = Q/V\Delta H$, a closed form expression is obtained for the cumulative heat, Q, in terms of the total ligand concentration. The energetics of a system obeying this model for ligand binding may therefore be considered interms of $[L_T]$, [M], n, K, and ΔH for known V.

$$Q = V[M]\frac{n\Delta H K[L]}{1 + K[L]} \tag{3.21}$$

$$Q^2 \left(\frac{K}{V\Delta H}\right) + Q(-1 - [M]nK - K[L_T]) + ([M]V\Delta H nK[L_T]) = 0 \tag{3.22}$$

$$Q = \frac{(1 + [M]nK + K[L_T]) - [(1 + [M]nk + K[L_T])^2 - 4[M]nK^2[L_T]]^{1/2}}{\frac{2K}{V\Delta H}} \tag{3.23}$$

in general, a numerical approach is needed to express Q in terms of [L_T]. Estimation of the model parameters characteristics of this binding model (n, K, and ΔH) then requires fitting to either the cumulative heat, Q, (equation(3.23)) or to the individual heat, q.

3.4.5 Some design feature

Isothermal microcalorimeters form a heterogeneous group of instruments and many different designs have been described. Regardless of the calorimetric principle used, most microcalorimeters are designed as twin or differential instruments. The ‘reaction vessel’, which is used for the investigated process, and the ‘reference vessel’, which is charged with an inert material, should preferably be nearly identical, in particular with respect to heat capacity and thermal conductance. In some cases microcalorimetric reaction vessels are taken out from the calorimeter at cleaning and charging operations (‘insertion vessels’), alternatively vessels are permanently mounted in the heat sensitive zone of the calorimeter.

Measurements can be conducted as batch experiments, with or without agitation (stirring) of the contents, or as continuous or stopped flow experiments. For example in living materials, and slow degradation and relaxation processes in materials and products of technical importance are often measured using simple sealed ampoules as reaction vessels. Injection techniques are usually employed when liquid or gaseous reactants are used to initiate a batch process. Such methods are particularly well suited to automation, for example in titration experiments. Several microcalorimetric designs have been reported where processes are initiated by bringing reagents together in a flow-mixing vessel or in a stirred perfusion vessel. The mixing of a reagent with a heterogeneous system (*e.g.* a suspension of solid particles, which tend to sediment) can be difficult to achieve without causing large heat effects. In such cases rotating or rocking calorimeters using bi-component vessels can be the best choice. Electrodes and other analytical sensors can be positioned in the reaction vessels and light can be introduced by use of light guides.

3.4.6 Direct and indirect determination of enthalpy changes

Recent developments in isothermal microcalorimetry open several areas for direct calorimetric measurements where earlier indirect methods had to be used. Enthalpy values for well-defined chemical processes can be derived from values for equilibrium constants determined as function of temperature ['Van't Hoff enthalpies', equation (3.24)]. Energy-material balances of living systems are often estimated by ‘indirect calorimetry’, measuring that values for heat production are derived from analytical values for substances consumed and produced during metabolism. Microcalorimetric techniques are now available by which thermal power values can be determined accurately for small samples of living cells and tissues, under well-defined physiological conditions.

3.4.7.Measurement of enthalpy of Dissolution:

Results from calorimetric measurements of enthalpy of dissolution of pure substances (gases, liquids and solids) are essential for our understanding of the thermodynamics of process in solution. For aqueous systems, in particular, values for their temperature derivatives, i.e. corresponding heat capacity values, are of major importance.

Table 3.1 Some basic thermodynamic relationships (Ingemar Wadso, 1997)

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \qquad \text{(Van't Hoff Equation)} \tag{3.24}$$

$$\Delta G^0 = -RT \ln K \tag{3.25}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3.26}$$

$$\Delta C_p^0 = \frac{d\Delta H^0}{dT} \tag{3.27}$$

$$\Delta_{trans} H^\infty = \Delta_{sol} H^\infty (2) - \Delta_{sol} H^\infty (1) \tag{3.28}$$

$$\Delta_{solv} H^\infty = \Delta_{sol} H^\infty - \Delta_{vap} H^0 \tag{3.29}$$

$$C_{p,2}^\infty = \Delta_{sol} C_p^\infty + C_p^* \tag{3.30}$$

Detailed study of solute-solvent interaction should made by determination of enthalpies of dissolution, $\Delta_{sol}H$, preferably at different temperatures leading to corresponding heat capacity values. In microcalorimetric dissolution experiments the concentrations of the solutes are often low enough to regard the solutions as infinitely dilute. The difference between dissolution enthalpies for a compound in different solvents will give the enthalpy of transfer for the compound between the solvents, eqn. (3.28). Similarly, the difference between $\Delta_{sol}H^{\infty}$ and the enthalpy of vaporization $\Delta_{sol}H^{0}$ (the ideal gas phase value), will give the enthalpy change for the transfer of the compound gas phase and solution, often called the enthalpy of solvation, $\Delta_{solv}H^{\infty}$, equation (3.29). The function $\Delta_{trans}H^{\infty}$ and $\Delta_{sol}H^{\infty}$ and corresponding ΔC_p^{∞} values reflect changes in solute-solvent interactions, which are free from contributions from the interactions between the solute molecules in solution or in their pure form. The same applies to the partial molar heat capacity of solutes at infinite dilution, $\Delta C_{p,2}^{\infty}$, which can be derived from equation (3.30). The development of microcalorimetric dissolution techniques has been important, in particular for investigations of biochemical model systems and the hydrophobic effect.

3.4.8 Measurement of Solvent activity

The chemical potential μ of a substance is defined as

$$\mu = (\frac{\partial G}{\partial n})_{p,T} \tag{3.31}$$

Gibbs energy increases as n increased. For a pure substance the chemical potential is simply the molar Gibbs energy and at constant pressure and composition the Gibbs-Helmholtz equation becomes

$$(\frac{\partial \mu}{\partial T})_{p,x} = \frac{\mu - h}{T} \tag{3.32}$$

Where h is partial molar enthalpy. The above equation is divide with T^2 and simplified to

$$(\frac{\partial}{\partial T}(\frac{\mu}{T}))_{p,x} = -\frac{h - h_0}{T^2} \tag{3.33}$$

Where h_0 is standard molar enthalpy and integrate the above equation between two different temperatures will gives

$$\left.\frac{\mu}{T}\right|_{T^*}^{T} = -\int_{T^*}^{T} \frac{h - h_0}{T^2} dT \tag{3.34}$$

For liquid mixtures the activity is defined by

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{3.35}$$

For each substance i. by combining above two equations we find,

$$\ln \frac{a}{a^*} = -\int_{T^*}^{T_1} \frac{h - h^*}{RT^2} dT \tag{3.36}$$

Here h and h^* are partial molar enthalpies and these values can be measured using the microcalorimeter by doing the dilution experiments.

Chapter-4

Literature review

Polyelectrolytes are widely used in many fields for various applications. They are used in food, pharmaceutical, paper and cosmetic industries etc. Due to various applications the study of thermodynamic proprieties of polyelectrolyte solution becomes more importance.

4.1 Theoretical developments in polyelectrolyte solutions

Polyelectrolyte solutions play an important role in biological systems (e.g., DNA and proteins) as well as in practical applications. The widely used theories are Poission-Boltzman theory with its modification and Mannning's limiting law combined with counter ion-condensation scheme, where polyions are modeled as the rigid cylindrical or line –like molecules. Recently, theories were published where a polyion is more reasonably considered as a flexible charged hard sphere chain. Blum *et al.* used the WOZ integral equation theory to describe the polymerization of the monomer ions; however, no numerical results were presented (Blum *et al.*, 1996). Jiang *et al.* adopted a statical association scheme to account for the contribution of chain formation to the excess Helmholtz energy (Jiang *et al.*, 1996). Their results are consistent with MD data.

For the real polyelectrolyte solution, the short-range non-coulombic interaction between polyion and counterions should be taken into account. Nagvekar and Danner (1989) suggested excess Gibss free energy model, which is explained in chapter 2 in detail.

Hao and Harvey provided (Hao *et al.*, 1992) a lattice theory where an additional Helmholtz energy term responsible for the counterion binding is introduced as an extension of Manning's condensation formulization. Dolar and Bester used (Dolar *et al.*, 1995) a square-well potential to characterize the non-coulombic force and combined it with PB theory to predict the relative activity coefficient. Jiang *et al.* further treated the short-range non-coulombic interactions as stickiness between counterions and monomers of polyions, which are described by the integral-equation theory of sticky electrolytes;

however, numerical integration is needed in the final expression. Using this approach Jun Cai *et al.* obtain expression for the thermodynamic properties of polyelectrolyte solution that can be used more easily for practical purposes (Cai *et al.*, 2000).

4.2 Experimental studies of polyelectrolyte solution

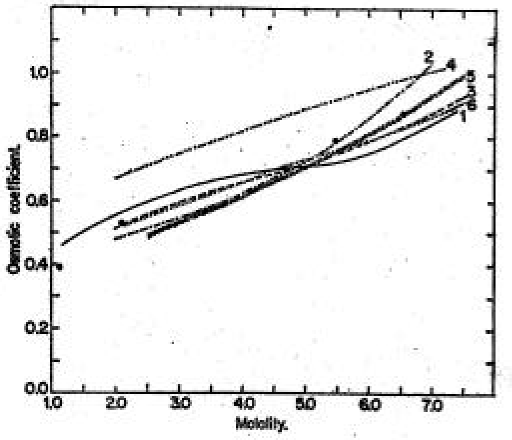
Various experimental techniques have been used for the study of osmotic properties of polyelectrolyte solution. These techniques include freezing point depression, boiling point elevation, dynamic and static vapor pressure measurement, osmotic pressure measurement and the isopiestic method.

The isopiestic method have been long established as a simple but reliable method of measuring vapor pressure of the solvent activity of a solution of nonvolatile solute. A detailed example of a well designed isopiestic apparatus and experimental procedure was described by Scatchard *et al.* (Scatchard *et al.*, 1938). The precision of their experiments was rather high and also the time for equilibrium was rather short. Unfortunately, high expense of the equipment was severely prohibited further development of this method. Thiessen and Wilson (1987) solved this problem partly by using a 3-legged glass apparatus and a constant temperature bath. Based on their work Ochs *et al.* developed (Ochs *et al.*, 1988) a 9-legged manifold apparatus and measured the solvent activities of divalent electrolyte solution and aqueous PEG solution. But it was difficult to achieve the equilibrium using this method. Lin *et al.* went (Lin *et al.*, (1990) one step ahead to make the sample cell to rotate around an axis inclined 45 to enhance stirring during the whole equilibrium process. In addition they applied constant temperature bath assembly by placing two tanks in series to reduce the temperature fluctuation not more than 0.01.

The VPO measurement is used for the study of dilute solutions. Reddy and Marinsky used (M. Reddy and J. A. Marinsky.,1970) the Mechrolab VPO commercial model of the thermoelectric osmometer of Bradt, Huff and Mcbain for the study of osmotic properties of polyelectrolyte such as osmotic coefficient. Boyd *et al.* has used (Boyd *et al.*, 1967) a vapor pressure osmometer to determine osmotic coefficient of aqueous solution of p-ethylbenzenesulfonic acid and its alkali metal salts.

Use of Mechrolab VPO was restricted to HPSS (M.W.40, 000) at concentration no grater than 1.5 m higher concentration values could not be employed because of the sizable viscosity of such samples. Osmotic study with this instrument of the higher molecular weight HPSS above a concentration value 0.9 m was unpractical for the same reason.

Bonner and Overton studied (O.D.Bonner and J.R.Overton, 1963) NaPSS using isopiestic method. Chu and Marinsky (1967) used both methods for the investigation of properties of NaPSS and HPSS. Narso Ise *et al.* determined (Narso Ise *et al.*, 1968) osmotic coefficient of NaPSS and HPSS using isopiestic method. Unfortunately not single result match each other. Reddy and Marinsky studied (M. Reddy and J. A. Marinsky.,1970) same system and compared their results with previous one. They explained some causes of discrepancies of results. They show that most affecting factor are purity of sample and degree of sulfonation. They claimed that their data is most acceptable because of higher purity of sample and precision of measurement. Following figure (4.1) comparison of data for NaPSS solution.



NaPSS with different molecular weights or cross-linkages (curve 1 mol wt 40,000 and 500,000 this study, curve 2 mol wt 10,000 ref 23, curve 3 mol wt 70,000 ref 23, curve 4 mol wt 400,000 ref 23, curve 5 Dowex 50 X-1 ref 23, curve 6 < 0.5% cross-linked (wt % DVB) ref 2, and ● 0.4% cross-linked (wt % DVB) ref 24.

Figure(4.1). Comparison of the concentration dependence of molal osmotic coefficient for NaPSS at high concentration (M. Reddy and J. A. Marinsky.,1970)

4.3 Isothermal titration calorimetry

The term microcalorimetry is commonly used for the calorimetry designed for use in microwatt range, under essentially isothermal conditions. The word isothermal is in this connection normally not used in a strict sense, but merely an indication that temperature of the calorimeter is constant or nearly so within narrow tolerances.

Isothermal microcalorimeteric techniques have been much improved during past decades, and several type of the instruments are commercially available. Applications areas includes ligand binding studies, dissolution and sorption measurements, estimation of the stability of chemical substances and technical products, and measurements of metabolic reactions in living cellular systems.

Hideyuki *et al.* studied (Hideyuki *et al.*, 1988) poly(acrylic acid)-water system using microcalorimetry. They measured heat of dilution of the poly(acrylic acid)-water system and poly(acrylic acid)-ethyl alcohol at 298.15°K with specially constructed automatic microcalorimeter. They found that heat of dilution of water system is endothermic while ethyl alcohol system is exothermic. They calculated interaction parameter. The dependence of the interaction parameter on the concentration was checked. They found that interaction parameter in dilute aqueous solution decrease with increase in the molecular weight of polymer by plotting the interaction parameter vs logarithmic of molecular weight.

Masaki Maeda *et al.* calculated (Masaki Maeda *et al.*, 1990) heat interaction parameter of aqueous hydroxypropylcellulose and gelatin solution using flow microcalorimeter. The heat of dilution of the HPC-water system moves from exothermic to endothermic with increase in the HPC concentration and heat interaction parameter is about -0.91. However the heat of dilution of the gelatin-water system is exothermic and heat interaction parameter is -1.00.They found that interaction between gelatin and water depends linearly on the gelatin concentration, but HPC-water system it depends considerably on the HPC concentration.

Chapter-5

Experimental Details

In this chapter results of the experiments carried on the vapor pressure osmometer are reported. Sodium polystyrenesulfonate (NaPSS) is very important macromolecular compounds in both industry and research. Activity of water in NaPSS solution and osmotic coefficient are measured with vapor pressure osmometer and isothermal titration calorimetry.

5.1 Materials Specifications :

Sodium polystyrene sulfonate (NaPSS) of molecular weight 70,000 was purchased from M/s Sigma Aldrich Company, USA. Semi permeable membrane (cut off m.wt. 12,000) was purchased from M/s Sigma Aldrich Company, USA for dialysis purposes. Cation exchange resin (Amberlite 200) and Anion exchange resin (Amberlite IRA 400C) was purchased from M/s Sigma Aldrich, USA for purification purposes and it is regenerated before use.

5.2 Purification of NaPSS:

The purchased sample may be contains low molecular weight impurities. So we have purified the sample by Yamanaka's (1990) procedure. According to this procedure Sodium polystyrene sulfonate (NaPSS) was first dialyzed in activated semi permeable membrane at least 48 hours. The outside water was changed time to time with the fresh distilled water. Then the NaPSS solution was passed through anion exchange resin (Amberlite IRA 400C, one-fourth times weight equivalent of NaPSS) and cation exchange resin (Amberlite 200, five times weight equivalent of polyions) column for several times to convert acid form. Then it was neutralized immediately with sodium hydroxide solution. Then the solution was evaporated to dryness to get solid NaPSS at 105-110 ^{o}C as the salt form is stable up to 130 ^{o}C (Butler *et al.*, 1957).

5.3 Determination of degree of sulfonation

For the determination of degree of sulfonation the purified sample was converted in to acid form by passing through Cation exchange resin column (Amberlite 200, five times weight equivalent of polyions) for several times and then titrated against standard alkali solutions. The acid titration gives the acid functionality and the total concentration of the NaPSS solution was measured by UV-VIS spectrophotometer. Then by taking ratio of the two concentrations gives the degree of sulfonation. The degree of sulfonation is found to be 82-83% for NaPSS sample.

5.4. Vapor Pressure Osmometer

5.4.1 Experimental procedure

Fill 2 syringes with pure solvent and place one in the red and the other in the yellow port. It is important to remove any air bubbles from the syringes prior to measurement. If the piston slips down by gravity it is recommended to empty the syringe and to press the Teflon head on a plain surface to improve its sealing properties. Fill the 4 syringes with the sample solutions. To avoid longer times for thermal equilibration, place all syringes in the desired ports as soon as possible. The syringe springs make sure that a defined distance from the thermistors is maintained. It is important that all ports are equipped with syringes, no matter if required for measurement. To attach droplet on a thermistor, push the syringes slightly down and thus move the needle towards the thermistor. By slightly pushing the piston downwards, droplets can be attached to the probes. It is important to produce droplets with identical sizes in this step. Always rinse the thermistor 3 to 5 times with every sample before a final droplet is attached.

5.4.2 Calibration of the Vapor pressure osmometer

The vapor pressure instrument is calibrated by Mannitol solution as the osmotic coefficient of this solution is almost one even for 1M concentration. The instrument is calibrated for different temperature and then signal/molal concentration vs molal concentration is plotted in figure (5.10). Then the line is extrapolated to zero concentration and the intersection point will be the instrument constant for that particular temperature. We have measured the instrument constant at 30^{o}C, 40^{o}C, 50^{o}C and 60^{o}C for aqueous medium.

5.4.3 Results and discussion

The activity of water in aqueous solutions of NaPSS was measured with vapor pressure osmometer at 40^{0}C, 50 ^{0}C and 60 ^{0}C. First I measured the real osmolality (π/RTρ) of the solution, then using the equation (3.4) the activity of water was calculated. Figure (5.2) shows that activity of water in NaPSS solution increases with temperature.

From activity osmotic coefficient is calculated. They are compared with literature data in Figure (5.3). We have also plotted the reported osmotic coefficient data in the same graph. Our data is perfectly matching with the Chu and Marinsky (1967) data. Chu and Marinsky reported that the higher osmotic coefficient data for Ise and Okubo (1968) is due to the presence of impurities in their sample. Takahashi *et al.* (1970) reported the lower osmotic coefficient of NaPSS, which may be due to the presence of lower charge density of the backbone chain.

The osmotic data is reproduced for same concentrations and temperatures. The deviation of both data is given in Table (5.1), (5.2) and (5.3). the data is reproducible within accuracy less than 0.1%.

In figure (5.11) and (5.12), the activity and osmotic coefficient are compared with the predicted values by an excess Gibbs free energy model. The value matches with the predicted values.

5.5 Isothermal Titration calorimetry

5.5.1 Dilution Experiments

In these dilution experiments there is no any binding or chemical reaction, just we are diluting the sample solution by adding the pure solvent to get the partial molar enthalpies. From these partial quantities we can calculate the activity of the solvent using the equation (3.36). Before doing the experiment the calorimeter temperature is turned to required temperature and allowed to equilibrate. To do this dilution experiments load the sample cell and reference cell with pure distilled water. After system has equilibrated the

250μl syringe is filled with solution of required concentration and allowed for re-equilibrate and then start the experiment by adding 10μl solution in each injection. Resultant peaks will gives the heat of dilution from which partial molar enthalpies are calculated and hence the activity. The same experiment is repeated for different concentrations of NaPSS at different temperatures.

5.5.2 Result and discussion

From these experimental heat of dilution data the activity of water is calculated using equation (3.26) and these obtained values are compared with vapor pressure osmometry data. Figure 5.4. Shows temperature dependence of osmotic coefficient. The heat peak generated for each injection gives the heat of dilution value for the diluting the sample from initial concentration to final concentration. For each experiment number of injection is 20, hence that accuracy of data is more. The activity of water obtained by VPO and ITC at 50 °C shows 0.031 % deviation and at 60°C it is 0.0175 %. Hence the both data obtained are in good agreement with each other. The osmotic coefficient is showing 10% deviation. The ITC can be used for the study of thermodynamic properties of polyelectrolyte solutions like osmotic coefficient and activity of solvent. ITC gives heat in nanoWatt. ITC gives correct temperature dependence. The causes of this deviation of data from VPO may be the errors in extrapolating the heat of dilution data at zero concentration. The experimental values are compared with the excess Gibbs free energy model given by Nagvekar.

5.5.3 Comparison with the an excess Gibbs free energy model

An excess Gibbs free energy model given by Nagvekar is combination of Manning model and NRTL local composition model. The values of osmotic coefficient and activity are predicted using this model.

The model parameters $\xi = 2.83$ for NaPSS (G.S. Manning, 1969)

$\tau_{1m} = -4.549$ (Chen *et al.*, 1982)

$\tau_{pm} = 0.010559$ (Cai *et al.*, 2000)

Model predicts value, which shows good agreement with the experimental values.

The experimental values obtained by VPO and ITC are shows good agreement with the predicted values by the model, which is shown figure (5.11) and (5.12).

Table5.1. Regeneration of Osmotic coefficient data by VPO at 40°C

M	A	B	% Deviation
0.1	0.2164667	0.19368081	0.117
0.25	0.2435321	0.22892025	0.0638
0.5	0.2979621	0.27778215	0.0726
1	0.3476814	0.3352005	0.0372

Table 5.2.Regeneration of osmotic coefficient data by VPO at 50°C

M	A	B	%Deviation
0.1	0.196706	0.185119	0.0622
0.25	0.228256	0.219835	0.38306
0.5	0.270356	0.267898	0.00917
1	0.342046	0.328336	0.04175

Table 5.3.Regeneration of osmotic coefficient data by VPO at 60°C.

M	A	B	%Deviation
0.1	0.174835	0.182656	0.04283
0.25	0.208844	0.212238	0.01599
0.5	0.250753	0.261568	0.04134
1	0.299936	0.320057	0.06286

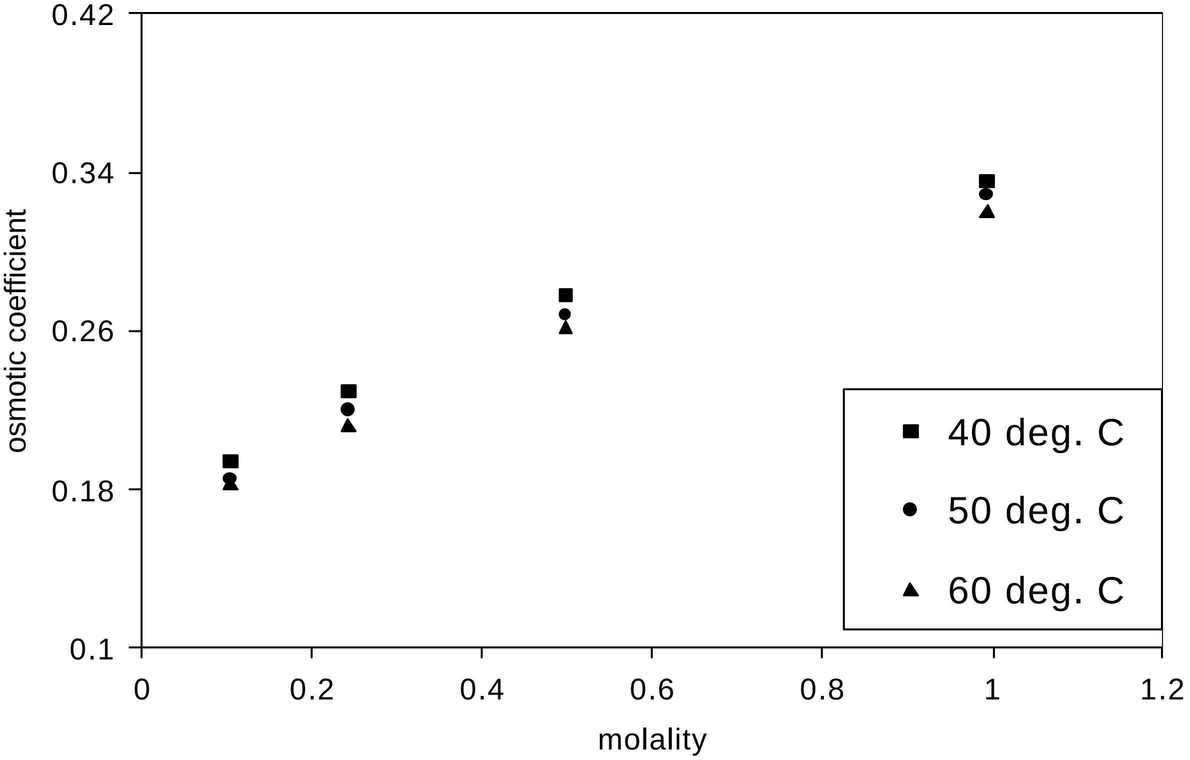


Figure 5.1: Comparision of osmotic coefficient by VPO at different temperature

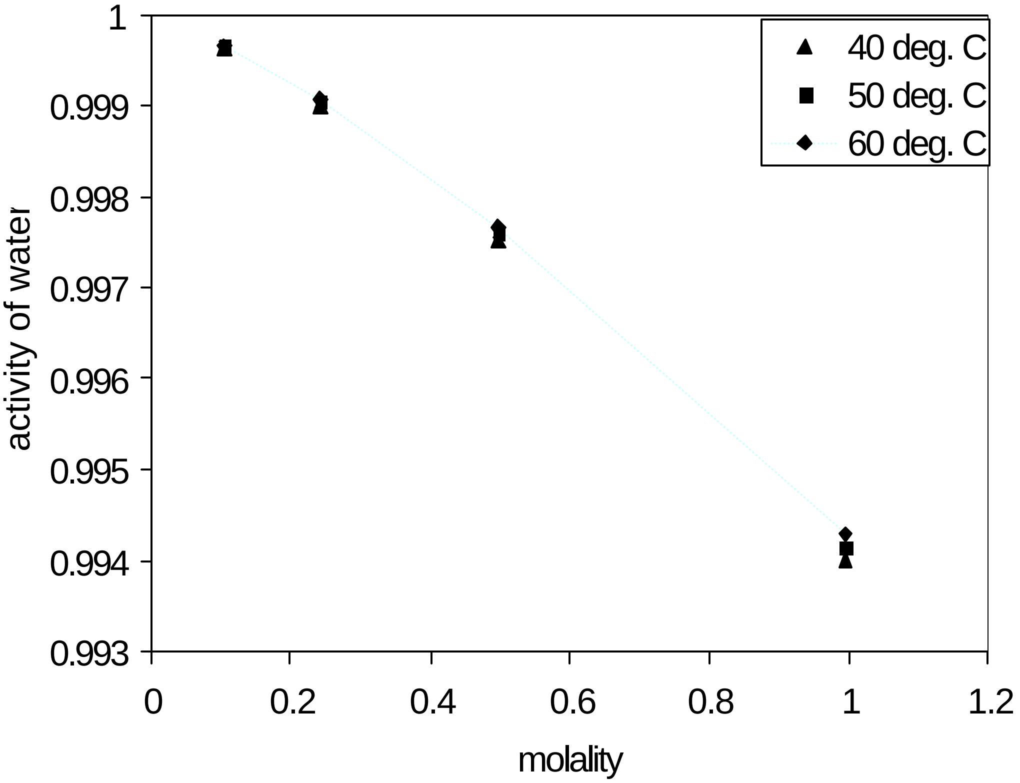


Figure 5.2: Comparision of activity of water by VPO at different temperatures

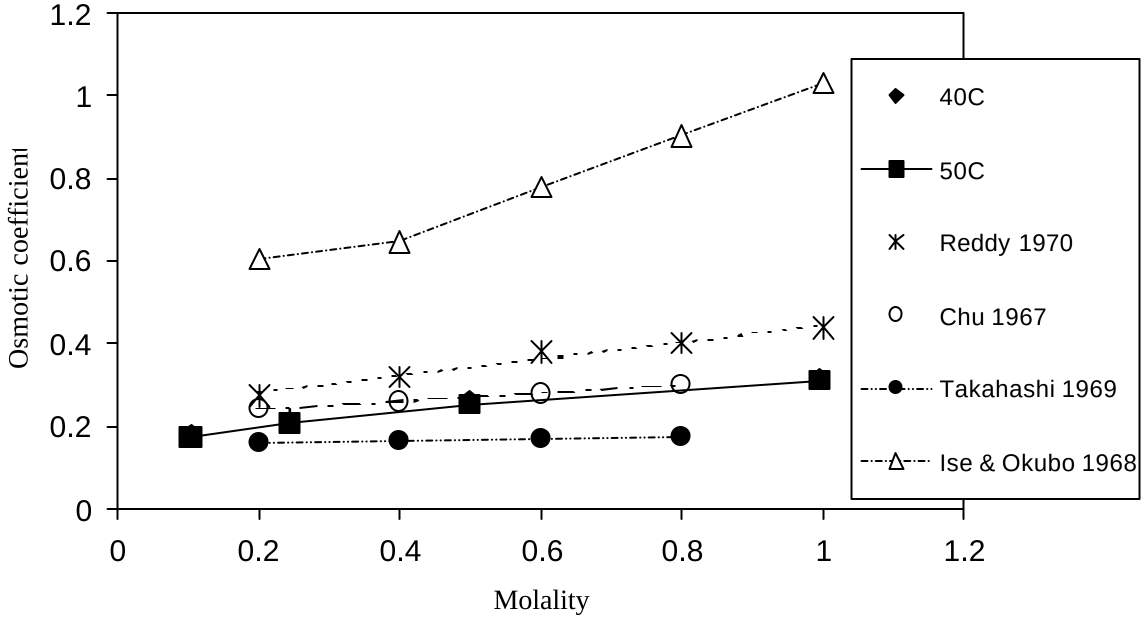


Figure 5.3:Comparision Osmotic coefficient by VPO with literature values

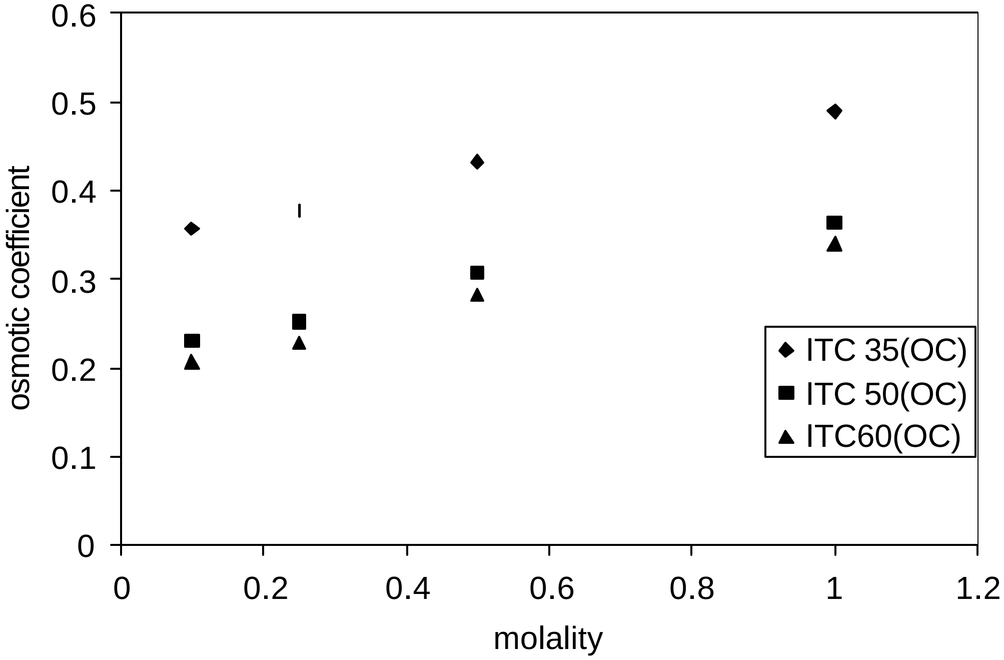


Figure 5.4: osmotic coefficient determined by ITC at different temperatures

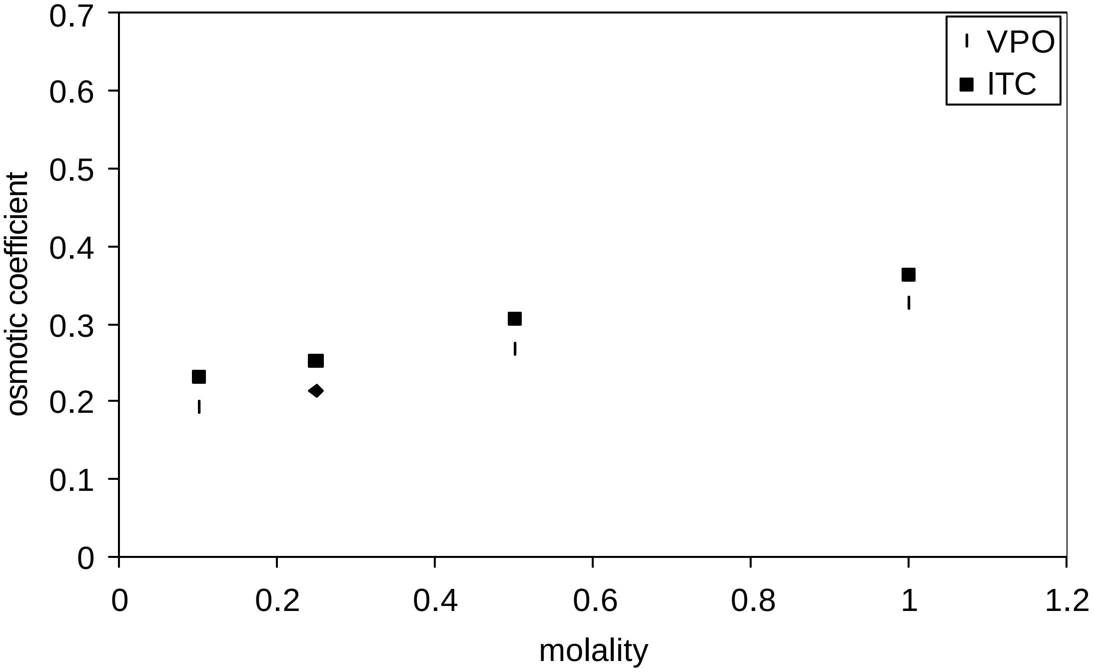


Figure 5.5:Comparision of the osmotic coefficient by VPO and ITC at 50 C

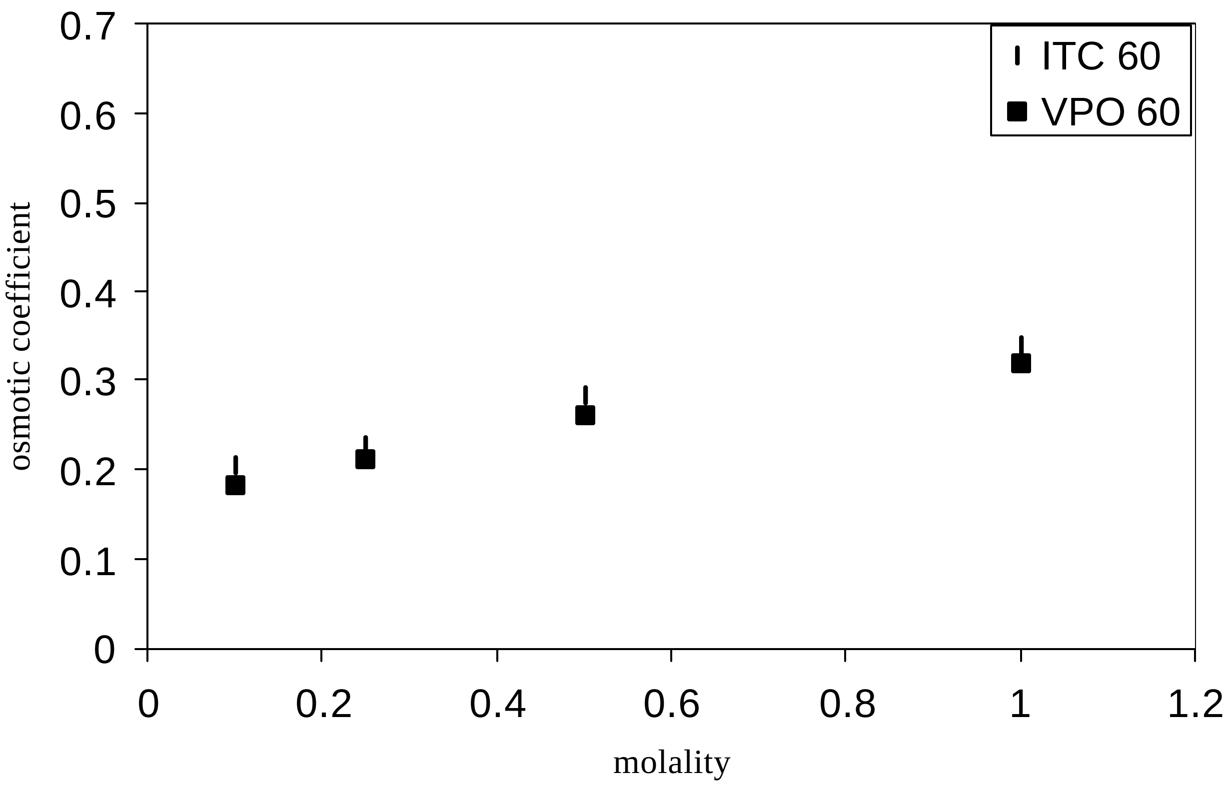


Figure 5.6: Comparision of the osmotic coefficient by ITC and VPO at 60 C

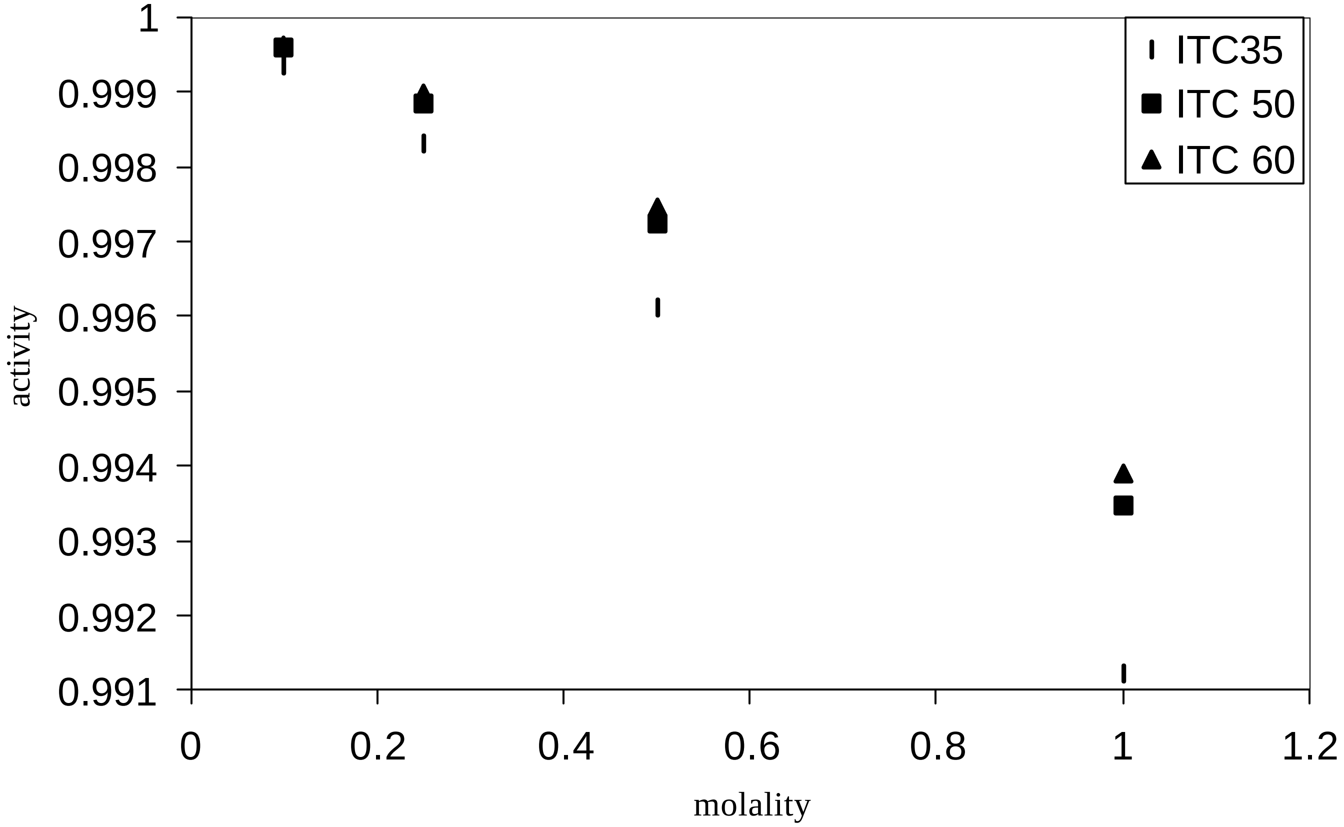


Figure 5.7: Activity determined by ITC at different tempeartu res

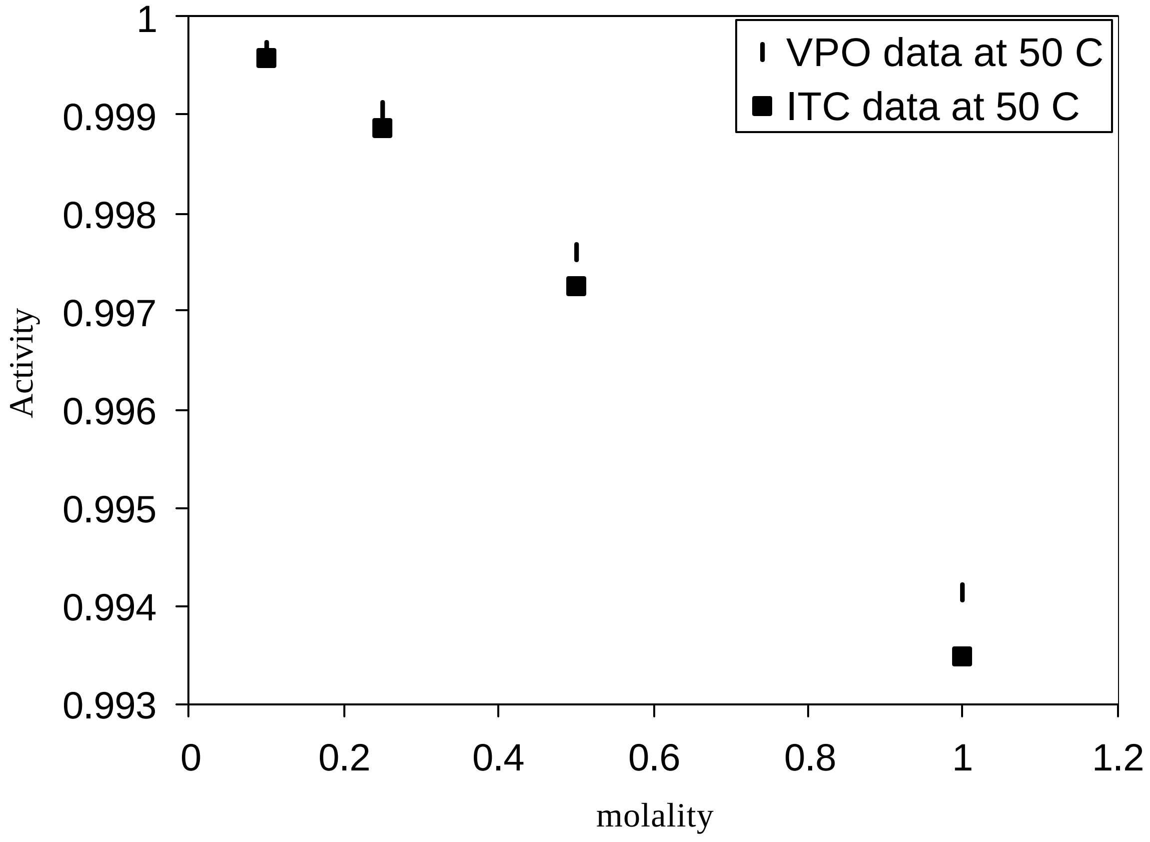


Figure.5.8. Comparision of activity by VPO and ITC at 50 C.

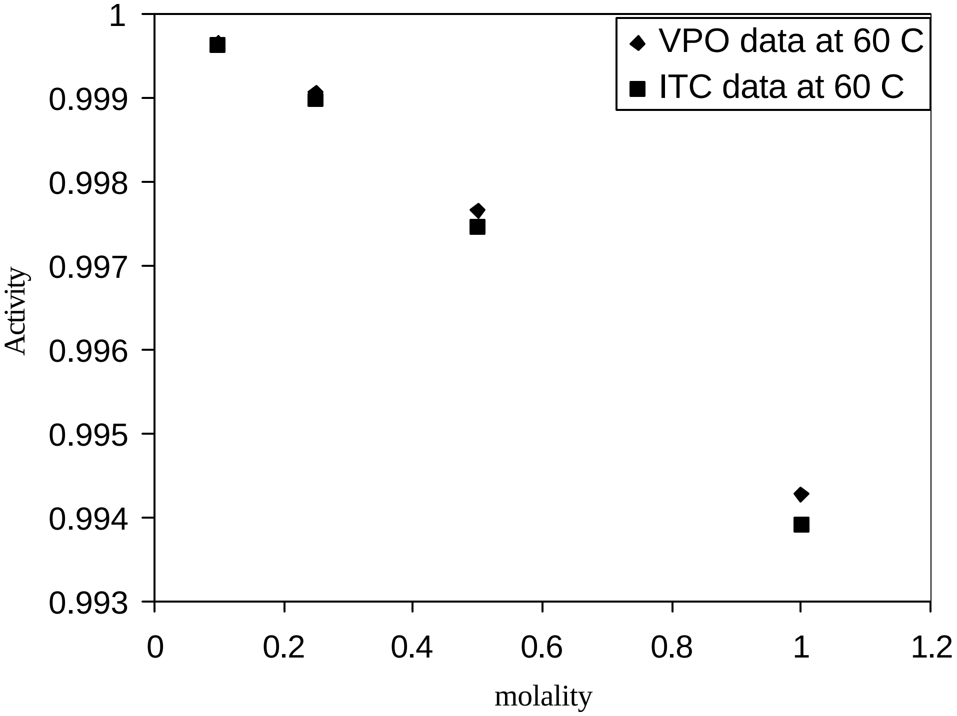


Figure.5.9:Comparision of activity by VPO and ITC at 60 C.

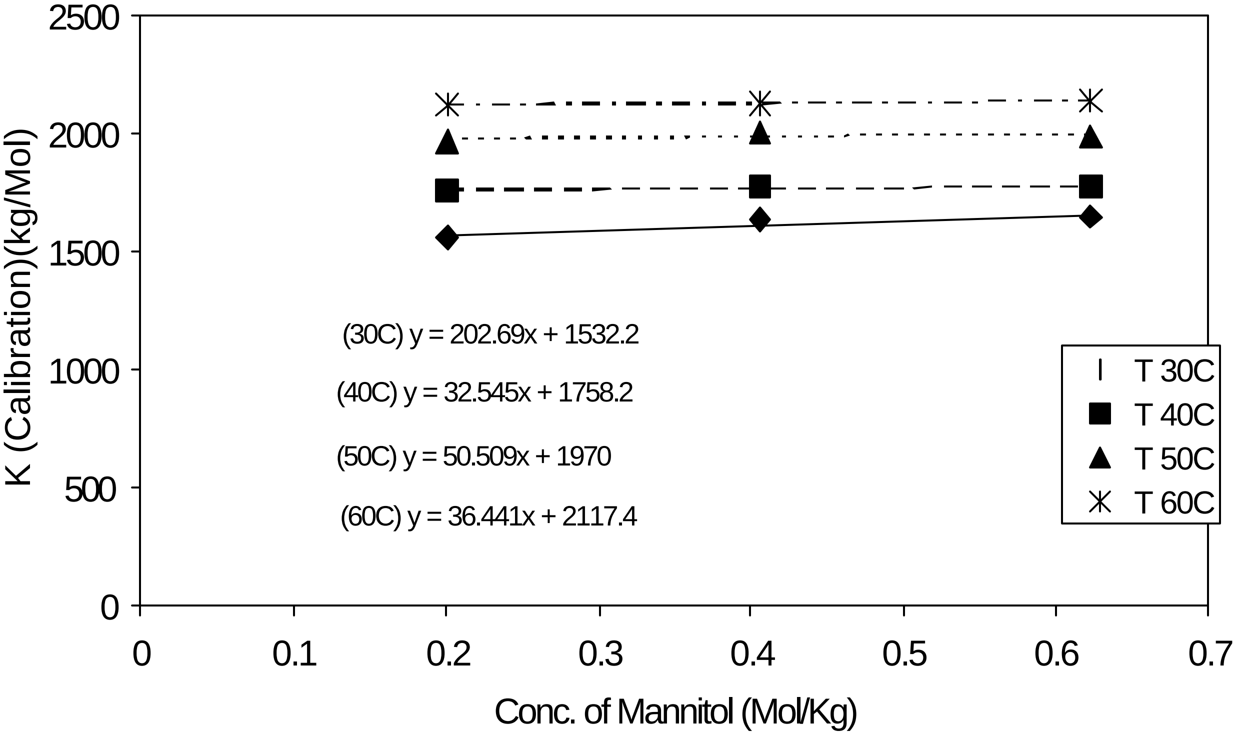


Figure 5.10:Determination of calibration const. by Mannitol

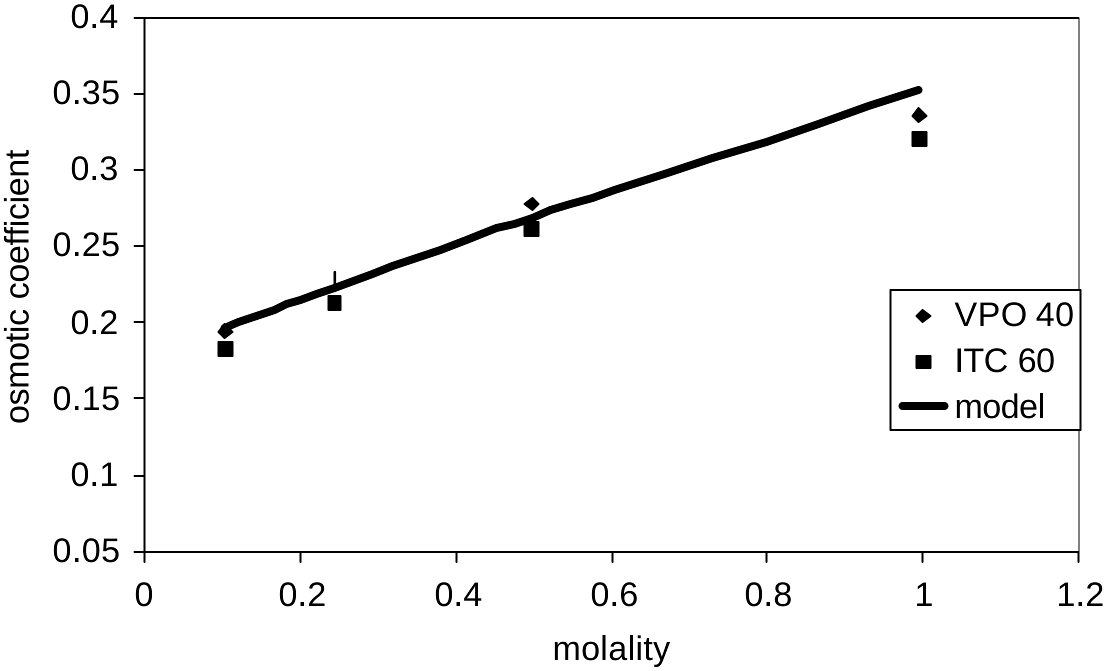


Figure 5.11:Graph of comparision of osmotic coefficient By VPO&ITC with Nagvekar's model

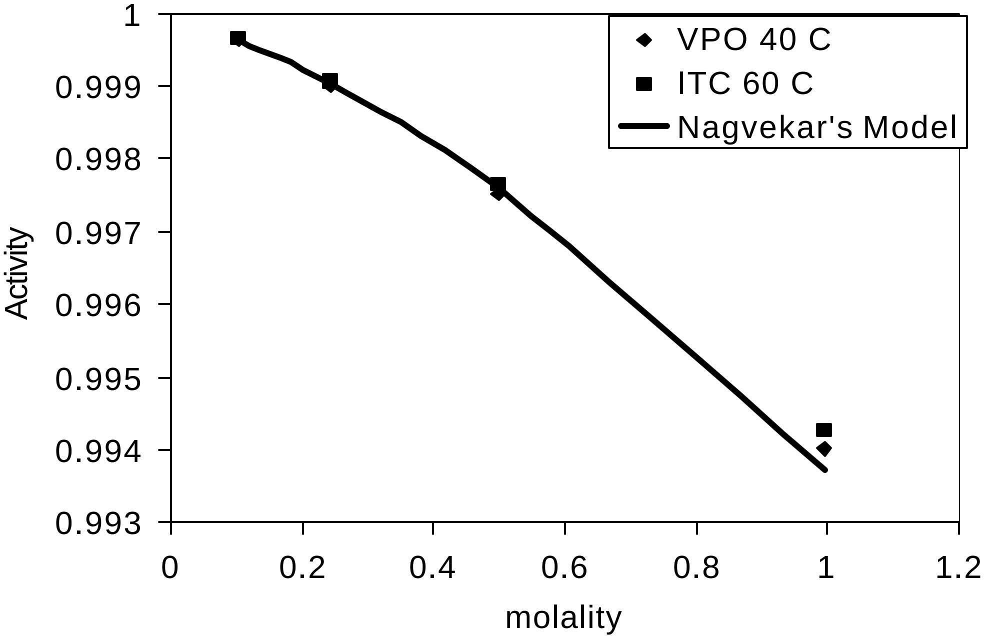


Figure 5.12:Comparision of Actvity of water by VPO&ITC with Nagvekar's model

Chapter 6

Conclusion and Future scope

6.1 Conclusion

In this study the thermodynamics of polyelectrolyte solutions are studied. Thermodynamics properties like activity and osmotic coefficient are determined for aqueous NaPSS solution using VPO and ITC at different temperatures. VPO is most widely used method of determination of osmotic properties of polyelectrolyte solutions. The results obtained by VPO are in good agreement with available literature data. VPO can be used temperature range between 37°C to 67°C using water as solvent.

ITC is the calorimetry of small samples, specifically microgram samples with micro level heats measurements. With help of ITC, it is possible to measure very small heat flows down to nanoWatt regions. Using this data we get more accuracy, in the measurements. We get correct temperature dependence form ITC.ITC results compared with VPO results. The ITC results are well agreed with the VPO results. The results are well matches with literature values. Hence ITC and VPO are suitable tools to study thermodynamics of polyelectrolyte solutions. ITC can be used for study of temperature effect from 0°C to 110 °C. The results obtained by VPO and ITC are good agreements with predicted values by excess Gibbs free energy model.

6.2 Future scope

In this study the aqueous NaPSS solution thermodynamic are studied using VPO and ITC without any added salt. In future the same system can be studied with addition of simple univalent, divalent salts. The study also can be done for different molecular weights of NaPSS. Also for the prediction of values excess Gibbs free energy model is used for which parameters are determined from available experimental data, in future these parameter can be obtained by another alternative method.

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Appendix

A1 Determination of partial molar enthalpy from heat of dilution

Consider the dilution process

n_1 solvent + solution($n_{1'}$ solvent+n_2 solute)$\rightarrow$ solution(($n_1 + n_{1'}$) solvent + n_2 solute)

The enthalpy change for this process is enthalpy of dilution, which is given by

$$\Delta H_{dil} = n_2 \phi L(\text{final}) - n_2 \phi L(\text{initial}) \qquad \text{(A1)}$$

Where ϕL is relative apparent molar enthalpy given by

$$\phi L = \phi H - \phi H^0$$

Here apparent molar enthalpy ϕH is given by

$$\phi H = \frac{H - n_1 H_1^*}{n_2} \qquad \text{(A2)}$$

Where, H_1^* is the enthalpy of solvent and H is total enthalpy of the solution mixture containing n_1 moles of solvent and n_2 moles of solute.

If the resulting solution is infinitely dilute,

$$\phi L(\text{final}) = 0$$
$$\Delta H_{dil} = -n_2 \phi L(\text{initial})$$
$$\phi L(\text{solution} = j) = \phi L(\text{solution} = i) + \Delta H_{dil}\,(\text{dilution} = i \rightarrow j)$$

The partial molar enthalpy is obtained by following relation at constant n_1.

$$L = n_2 \phi L$$

$$\frac{\partial L}{\partial n_2} = \phi L + n_2 \frac{\partial \phi L}{\partial n_2}$$

Hence the equivalent form is

$$h = \frac{\partial L}{\partial n_2} = \phi L + m \frac{\partial \phi L}{\partial m} \qquad \text{(A3)}$$

In this study, the heat of dilution is measured using ITC, then partial molar enthalpy is determined from which we get activity of solvent.

For the heat of dilution data at 50°C the heat of dilution is plotted vs molality as shown in following figure to get ϕL

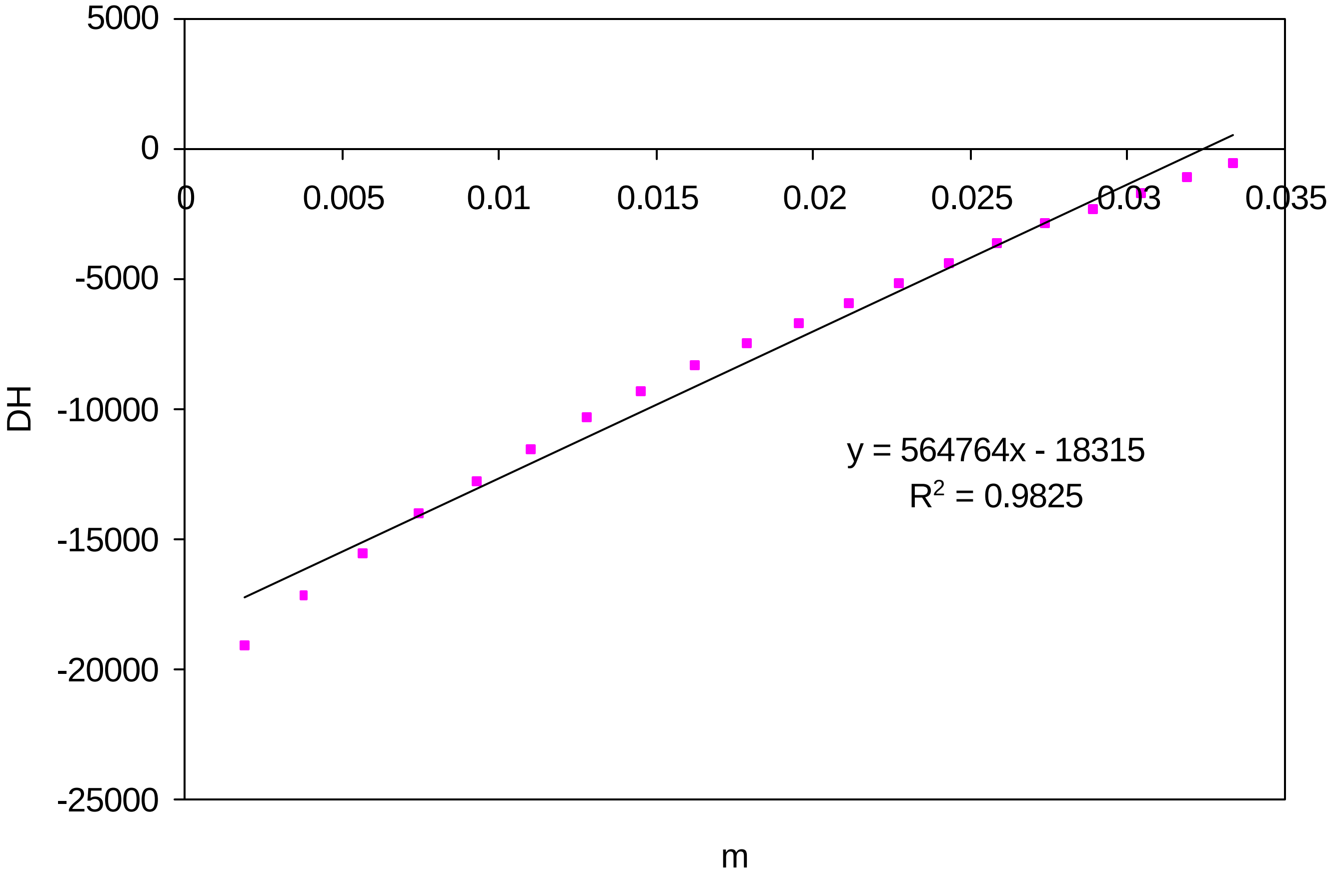

Figure A1. Heat of dilution is plotted vs molality

From the extrapolating we get initial ϕL . Plotting ϕL vs m we get following Figure (A2).

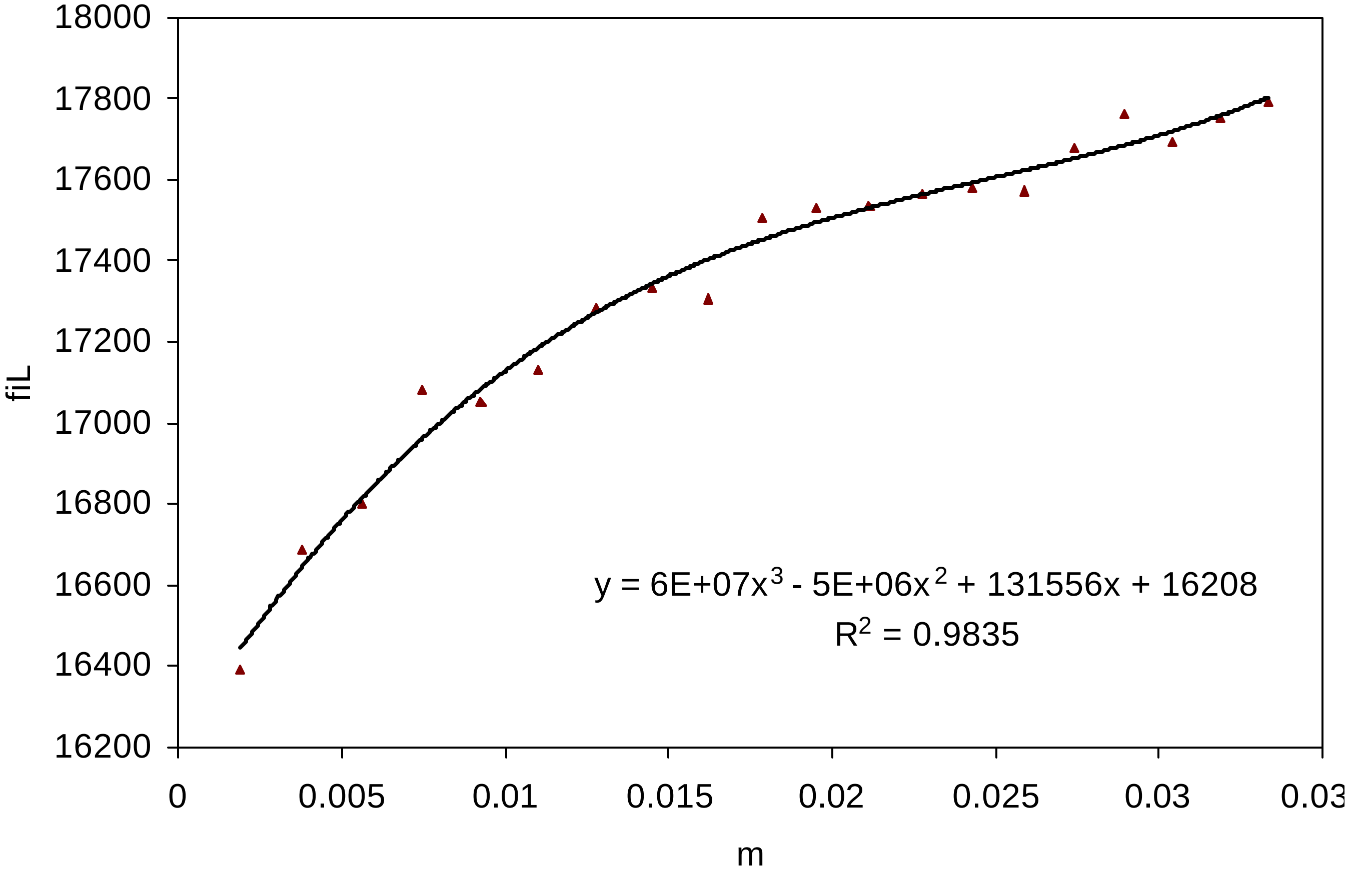

Figure A2. The graph of fiL vs molality.

Using slop of this graph partial molar enthalpy is found out using equation (A3).

A2 ITC and VPO

Isothermal Titration Calorimetry (ITC) is an analytical technique for studying different types of reactions involving covalent and/or non-covalent molecular changes. Heat is a universal property of all reactions, and it is either generated or absorbed in every chemical process. Using the CSC-ITC, it is possible to measure enthalpy, entropy of binding, as well as the binding constant. The manufacturer of this equipment is Calorimetry Sciences Corp.

The CSC-ITC system is an ultrasensitive Isothermal Titration Calorimeter that uses a cell feedback network to differentially measure heat produced or absorbed between a sample and reference cell. Cell design, including the adiabatic environment, cell have an effective volume of approximately 1.3 ml and are fabricated from Hastaloy, which has excellent chemical resistance properties. The injection device is a linear drive liquid delivery system incorporating a precision microliter syringe. The sample and reference cells are fixed in place to assure the highest level of sensitivity and reproducibility possible. The CSC-ITC system operates isothermally within a temperature range of 0 ^{0}C to 110 ^{0}C using an internal Peltier mechanism and therefore does not require external heating or cooling devices. Specifications of VP-ITC are shown in the Table-I.

Knauer Scientific Instruments is a company that develops, manufactures and markets analytical and preparative appliances. Vapor Pressure Osmometer K-7000, which is used in this study is purchased from Knauer Company.Table-II will give the list of troubles, which we will face while working with the vapor pressure osmometer, and also given the advice to overcome the specified problem. Specifications of Vapor Pressure Osmometer K-7000 are shown in the Table-III.

Table I: Specifications of CSC-Isothermal Titration Microcalorimetry

Minimum detectable heat:	0.1 µcal
Baseline stability	± 0.02 µcal /sec.
Operating Temperature Range	0 ^{0}C to 110 ^{0}C
Injection interval	90 seconds
Precision buret	25-250 µl (Delivery determined by syringe size and stepper motor speed.)
Cell volume	1.3 ml (Hastelloy)
Volume increment	1-25 µl
Stirring rate	0 to 500 rpm
Bath stability	± 0.0005 ^{0}C (Determined at 25 ^{0}C)
Delivery precision	± 0.01 µl (Applies for any size syringe or volume delivered.)
Minimum Response Time	5 seconds
Power Requirements	95-125 Volts, 50-60 Hz
Weight	80 lbs
Dimensions	22.5 L. x 17.8 H. x 15W.

Table II: Trouble Shooting Tips in Osmometer

Problem	Probable cause and advice
Needles of the syringes always pass the thermistor.	Thermistors need to be adjusted. The distance between both probes should be 0.9 cm. Also adjust the directional pipes for the needles.
Drops always fall down and cannot be permanently attached to the thermistor.	Rinse the thermistors with acetone followed by a surface active reagent and water.
Zero line not adjustable.	Defective thermistors, please press the test button.
Base line drift.	Temperature equilibrium not at reached, wait some time before continuing.
Syringe bleed.	Remove the piston and press it with the teflon end on a table to reset the seal to the glass cylinder.
Measurement values are not reproducible.	Temperature equilibrium not at reached, wait some time before continuing. Drop size is not consistent, the smaller the droplet the larger the measurement value. Equilibrium time too long, use a higher temperature or a different solvent.
No constant measurement value.	Volatile sample, cannot be measured.
Measured value: Increase followed by an immediate decrease.	Decomposition of the solvent, please exchange
Measurement graphs have different shape.	Dropping technique is not consistent.

Table III: Data sheet for the Vapor Pressure Osmometer K-7000

Features	Determination of the average molecular mass of polymers in aqueous and organic solutions Determination of the total osmolality of physical fluids External data evaluation with EuroOsmo 7000 software package
Molecular mass range	Aqueous: ≤ 10,000 g/mol Organic : 40 - 40,000 g/mol
Concentration range	0.01 - 15 molal
Lower detection limit	3.3×10^{-5} mol/kg in toluene 1.7×10^{-4} mol/kg in water
Temperature consistency	$\pm1\times10^{-3}$ ^{0}C
Cell temperature range	20 - 130 ^{0}C
ΔT Head thermostat	Max. 6 ^{0}C
Warm up times	40 ^{0}C : 0.5 hr. 60 ^{0}C : 1.0 hr. 100 ^{0}C : 1.5 hr. 130 ^{0}C : 2.0 hr.
Syringes	1ml. Glass cylinder with Teflon-headed steel piston
Min. cell solvent volume	20 ml
Gain	1 - 256
Voltage range	85 - 264V/47- 440 Hz. 60 VA
PC connection	RS 232
Recorder output	1V
Dimensions	60 × 182 × 340 mm
Weight	5.4 kg